ANNUAL REPORT 2018

理论有机化学与功能分子

教育部重点实验室

工作年报

Key Laboratory of Theoretical Organic Chemistry and Functional Molecule, Ministry of Education

理论有机化学与功能分子
教育部重点实验室工作年报
(2018年)

通讯地址：湖南科技大学理论有机化学与功能分子教育部重点实验室，411201

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目 录

一、实验室概况

湖南科技大学理论有机化学与功能分子省部共建教育部重点实验室，于2008年11月经教育部批准立项建设（教育部科技函 [2008]153号），并以湖南科技大学化学湖南省重点学科和化学（一级学科）、应用化学、化学工艺等硕士点为主要依托进行建设，于2013年7月通过教育部验收。

实验室主要以《国家中长期科学和技术发展规划纲要》为指导，面向《国家优先发展与重点支持领域》中的环保、新材料与药物等重大战略需求，聚焦环境治理、功能分子材料、药物创制与开发及其分子构效关系的研究，将合成的功能分子材料及药物重点用于环境治理，助推湖南医药产业升级。坚持理论与应用相结合，注重学科交叉，立足地方，瞄准学科前沿，形成四个稳定并具特色的研究方向：分子构效关系，资源环境功能分子材料，光电功能分子材料，生物活性分子与药物。注重微观与宏观相结合、理论与实践相结合，在提升知识创新能力和学术水平的同时，为地方经济建设服务。

通过 9 年来的建设与发展，实验室已形成一支结构比较合理、团结协作、具有多学科研究背景的学术队伍。现有研究人员 68 人，教授 31 人，副教授 20 人，具有博士学位者 66 人，博士生导师 8 人，硕士生导师 52 人，国务院政府特殊津贴专家 2 人，教育部新世纪人才 1 人，湖南省“杰出青年基金”获得者 1 人，湖南省121人才工程 6 人，湖湘英才 2 人，全国煤炭行业教学名师 1 人，湖南省青年骨干教师 12 人，湖南省普通高校学科带头人 2 人。湘潭市高层次人才 15 人，具有海外科研工作经历者 20 人。

9 年来实验室新增科研项目 259 项，其中国家级项目 81 项（国家自科基金项目 79 项、国际合作重点项目1项、国家科技支持计划子课题 1 项）、省部

级项目 80 项、横向项目 47 项，累积科研经费累计 9800 余万元。在***Angew. Chem. Int. Ed., Biomaterials, Biosens. Bioelectron., Anal. Chem., Chem. Comm., J. Phys. Chem. B, Org. Lett., J. Org. Chem.***等期刊上共发表论文 824 篇，其中被 SCI 、EI 、ISTP 等收录的论文 565 篇，出版专著 4 部、教材 6 部。获发明专利 129 项（授权），省部级科研奖励 27 项。获湖南省高校科技创新团队 1 个，获批精细聚合物可控制备及功能应用湖南省重点实验室 1 个。

实验室面积达 5000 平方米，拥有核磁共振波谱仪 (500M Hz)、液质联用仪、X-射线单晶衍射仪、扫描电镜、微量热仪、原子力显微镜、倒置荧光显微镜、酶标仪、X-粉末衍射仪、圆二色光谱仪、气质联用仪、液相色谱仪等一批先进大型仪器，总值达 6000 余万元。

在实验室的大力支撑下，获批矿业工程博士点和博士后科研流动站。实验室依托化学一级硕士学位授权点、应用化学和化学工艺二级硕士学位授权点进行研究生招生与培养，9 年来共招收硕士研究生 443 人，344 人获得硕士学位。同时还与瑞典查尔姆斯理工大学、美国得克萨斯大学圣安东尼奥分校、厦门大学、中南大学、湘潭大学等联合培养研究生， 共招收博士生 10 人，获博士学位 1 人，与中南大学联合博士生 1 人。实验室共有 8 个相关本科专业：化学、无机非金属材料化学、材料化学、应用化学、化工工艺、环境工程、制药工程、能源化工程等，其中化学为国家第一类特色专业，材料化学为省级特色专业。拥有有机化学省级优秀教学团队 1 个，省级精品课程 3 门（有机化学、物理化学和量子化学）。形成了“夯实基础，接触前沿，以培养创新能力为目标”的人才培模式，确保人才培养质量，获省级教学成果奖 2 项。

1．实验室各研究单元的构成

理论化学与功能分子教育部重点实验室由分子构效关系，生物活性分子与药物，资源环境功能分子材料，光电功能分子材料等 4 个研究单元构成，重点实验室学术带头人和学术骨干名单见下表。

实验室学术带头人和学术骨干一览表

研究方向	姓名	出生年月	获最高学位时间	专业技术职务
分子构效关系	曹晨忠	1957	2004.07(博士)	教授/博士导师
	易平贵	1961	2000.03(博士)	教授/博士导师
	曾荣今	1963	2006.12(硕士)	教授/硕士导师
	周再春	1974	2007.07(博士)	教授/硕士导师
	袁华	1976	2007.07(博士)	教授/硕士导师
资源环境功能分子材料	刘立华	1969	2006.07(博士)	教授/硕士导师
	冯涛	1957	1999.07(博士)	教授/博士导师
	戴财胜	1964	2000.07(博士)	教授/硕士导师
	曾坚贤	1970	2008.07(博士)	教授/硕士导师
	周虎	1981	2009.07 (博士)	教授/硕士导师
光电功能分子材料	黄昊文	1969	2004.08(博士)	教授/硕士导师
	田俐	1973	2009.07 (博士)	教授/硕士导师
	易清风	1963	2001.07(博士)	教授/硕士导师
	龙云飞	1969	2007.12(博士)	教授/硕士导师
	陈建	1980	2009.06 (博士)	教授/硕士导师
生物活性分子与药物	唐子龙	1967	2004.08(博士)	教授/硕士导师
	谢文林	1967	2003.06(博士)	教授/硕士导师
	李筱芳	1972	2003.06(博士)	教授/硕士导师
	周智华	1973	2007.06(博士)	教授/硕士导师
	于贤勇	1975	2005.07(博士)	教授/硕士导师

2. 实验室主任及管理人员

实验室主任：唐子龙

实验室副主任：黄昊文

学术秘书：周再春

室务会成员：曹晨忠，易平贵，唐子龙，曾荣今，易清风，周智华，黄昊文，周再春

3．实验室学术委员会组成人员

学术委员会主任：郭庆祥

学术委员会副主任：易平贵

学术委员会委员(按姓氏拼音排序)：

曹晨忠，方维海，郭庆祥，胡常伟，黄培强，刘又年，潘远江，唐子龙，吴海龙，吴水珠，肖文精，杨楚罗，杨松，易平贵，易清风，杨新玲，朱晓晴。

4．实验室2018年取得成绩

4.1 获得的科研项目

新增各类科研项目 35 项，其中国家自科基金课题 12 项、省部级课题 12 项、横向课题 9 项；累计经费 712 万元，学校配套经费 302.2 万元，合计 1020.2 万元。

序号	项目编号	项目、课题名称	项目来源	项目起讫时间	科研经费（万元）	负责人
1	21776067	温度和pH双重敏感型聚氨酯膜的制备及其可控分离特性与机理	国家自然科学基金项目	2018.01-2021.12	64 (+31.8)	周虎
2	51778226	磁性共轭微孔聚合物的设计、合成与优化及在铟回收中的应用	国家自然科学基金项目	2018.01-2021.12	60 (+31)	刘清泉
3	51773057	新型双相兼具自抗炎与自可控降解骨修复复合支架材料的研究	国家自然科学基金项目	2018.01-2021.12	56 (+30.2)	周智华
4	51773056	具有基因载体功能的光开关近红外荧光聚合物纳米材料设计合成与生物成像研究	国家自然科学基金项目	2018.01-2021.12	58 (+30.6)	陈建
5	51775183	可控分层降解超疏水海洋防污减阻复合涂层的制备及性能研究	国家自然科学基金项目	2018.01-2021.12	58 (+30.6)	欧宝立
6	21703062	三芳基硼单发光组分比率型温度探针的设计合成及细胞内温度测量的初步研究	国家自然科学基金项目	2018.01-2020.12	19 (+16.6)	刘玄
7	51703059	树枝状D-A型环金属铱(III)配合物的分子构筑及其近红外电致发光性能研究	国家自然科学基金项目	2018.01-2020.12	24 (+18.6)	于俊婷
8	21703061	铜催化C-H键活化与自由基介导构筑C-C键的反应研究	国家自然科学基金项目	2018.01-2020.12	26 (+19.4)	肖晶
9	51703060	极性与二面角双可调型聚苯乙烯-轴手性联苯双膦配体的制备及其拆分氨基酸对映体性能研究	国家自然科学基金项目	2018.01-2020.12	24 (+18.6)	刘雄

10	81701837	光固化丝素蛋白/硅酸盐生物活性陶瓷复合骨水泥的制备、优化和性能研究	国家自然科学基金项目	2018.01-2020.12	20 (+17)	刘文娟
11	11704116	新型复合纳米材料的可控合成及光催化性能研究	国家自然科学基金项目	2018.01-2020.12	22 (+17.8)	柴一峰
12	11704115	碳酸铋/钇钡铜氧异质结界面上新奇磁性和超导电性的研究	国家自然科学基金项目	2018.01-2020.12	20 (+17)	朱中华
13	2018JJ4005	优质槟榔卤水的制备技术研究	湖南省自然科学基金省市联合项目	2018.01-2020.12	10 (+5)	曾荣今
14	2018JJ3145	四苯并环辛四烯胺类双核过渡金属配合物催化剂的设计合成及性能研究	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	彭丽芬
15	2018JJ3143	基于聚合物点的能量转移体系在碱性磷酸酶荧光比率检测中的应用	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	张培盛
16	2018JJ3146	荧光性能导向的芳香多羧酸稀土配合物的可控合成	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	张少伟
17	2018JJ3141	环己亚胺二酮类 D-A 共聚物的设计合成及光伏性能研究	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	曹佳民
18	2018JJ3142	基于电场调制的高深宽比硅纳米线的制备及其在光催化中的应用	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	张杰
19	2018JJ3160	双极传输 D-A 型近红外环金属铱(III)配合物的构筑及其电致发光性能研究	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	于俊婷
20	2018JJ2113	高性能储气脲基 MOFs 材料的合成与构效关系研究	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	郑柏树
21	2018JJ2125	基于石墨烯/纳米 TiO2 海洋防污减阻涂层的仿生构筑及性能研究	湖南省自然科学基金项目	2018.01-2020.12	5 (+2)	欧宝立
22	18A192	含钒-有机框架的可控合成及其选择性催化氧化烯烃研究	湖南教育厅重点项目	2018.01-2020.12	5 (+2)	于贤勇

23	18A204	NanoSIMS 微区氧同位素分析技术在细粒包体中的应用	湖南教育厅重点项目	2018.01-2020.12	5 (+2)	戴德求
24	18B220	聚苯胺包覆 CoP/硅纳米线异质结的制备及其光电催化性能研究	湖南教育厅优秀青年项目	2018.01-2020.12	4 (+2)	张杰
25	18B221	新型两亲 AIE 分子的合成及其在温敏材料中的应用研究	湖南教育厅优秀青年项目	2018.01-2020.12	4 (+2)	赵云辉
26	18K065	多色荧光探针的构建及环境水样中多种抗生素同时快速检测研究	湖南教育厅创新平台开放基金项目	2018.01-2021.12	6	龙云飞
27	D118A2	N-取代-2-(2-羟基苄基)氨基乙酰胺类化合物及其制备和用途	湖南华腾制药有限公司	2018.01-2035.12	5	唐子龙
28	D118A8	新一代头孢抗生素药物中间体头孢卡品酯技术开发	湖南开元医药科技有限公司	2018.11-2020.11	20	谢文林
29	D118B3	湘潭市贯彻落实湖南省《水污染防治行动计划》实施方案（2016-2020）效果	湘潭市环境保护局	2018.10-2018.12	2	伍泽广
30	D11866	一种含螺吲哚-2-酮衍生物及其制备方法和作为抗癌药物的应用	江西开元生物医药科技有限公司	2018.08-2031.12	7	谢文林
31	D11872	安乡县地下水资源保护区划技术支持 2 期	北京南科大蓝色科技有限公司	2018.08-2019.07	16	易平贵
32	D11899	湘潭市环境保护“十三五”发展规划中期评估编制	湘潭市环保局	2018.07-2018.08	9	伍泽广
33	D11868	一种污泥脱水调理剂及其深度脱水方法	珠海科创环境资源有限公司	2018.05-2018.12	25	戴财胜
34	D118A9	湘潭市湘江保护和治理第二个三年(2016-2018)行动计划实施方案评估	湘潭市环境保护局	2018.12-2019.03	3	伍泽广
35	D118B4	替卡格雷的合成工艺开发	药雅科技（上海）有限公司	2018.07-2021.06	100	于贤勇

注：括号内为学校配套经费。

4.2发表论文

2018 年本实验室共发表SCI收录论文 108 篇。

4.3 专利授权

2018 年本实验室共获 25 项发明专利授权。

序号	专利名称	专利号	专利类型	授权时间	第一完成人
1	一种基于聚集诱导发光的氟离子检测探针及其制备方法和应用	ZL201610969539.7	发明专利	2018-12-14	赵云辉
2	一种检测肝细胞中一氧化氮的水溶性荧光探针及其应用	ZL201610870952.8	发明专利	2018-11-30	张培盛
3	一种镍双咔咯-碳纳米管超分子复合材料及其制备和应用	ZL201510947144.2	发明专利	2018-11-20	邓克勤
4	2-芳基-3-酰胺基-1,3-苯并恶嗪类化合物及其制备和用途	ZL201510947212.5	发明专利	2018-11-06	唐子龙
5	一种渗透有三聚氰胺的空心碳球的高温热解产物及其制备方法	ZL201611041067.5	发明专利	2018-10-26	易清风
6	一种基于荧光硅纳米粒子的比率型温度传感器、制备方法及应用	ZL201610376996.5	发明专利	2018-10-09	陈建
7	一种可比率检测次氯酸的聚合物荧光传感器及应用	ZL201610834650.5	发明专利	2018-09-14	陈建
8	一种碳纳米粒子检测四氢呋喃中水分含量的方法	ZL201610036849.3	发明专利	2018-09-14	陈建
9	一种亚铁离子/空气电池及其制备方法	ZL201710000579.5	发明专利	2018-09-04	易清风
10	一种长波型的苯硫醚荧光探针及其制备方法和应用	ZL201710027321.4	发明专利	2018-08-28	曾荣今
11	一种包裹型单层氧化石墨烯/碳纳米管复合物及其制备方法	ZL201510926115.8	发明专利	2018-08-17	邓克勤
12	一种室温条件下制备金属卟啉-石墨烯纳米复合材料的方法	ZL201610041189.8	发明专利	2018-07-06	曾荣今

13	一种两性离子型智能响应水凝胶的制备方法	ZL201610522024.2	发明专利	2018-06-22	周虎
14	具有两类 pH 响应基团的环境敏感型水凝胶的制备方法	ZL201610523069.1	实用新型	2018-06-08	周虎
15	一种锂离子电池正极材料 $LiCoBO_3$ 的制备方法	ZL201610260023.5	实用新型	2018-06-01	唐安平
16	一种基于聚集诱导发光的温敏荧光材料及其制备方法和应用	ZL201611112262.2	发明专利	2018-06-01	赵云辉
17	一种可检测次氯酸和铜离子的聚合物纳米粒子、制备方法及应用	ZL201610689409.8	发明专利	2018-05-15	张培盛
18	具有杀菌活性的 1-(芳氨基乙基)-2-芳基-3,1-苯并恶嗪类化合物及其制备和用途	Zl201510947231.8	发明专利	2018-05-04	唐子龙
19	一种固体聚硅硫酸铁混凝剂的制备方法	ZL201510882014.5	发明专利	2018-04-13	朱国成
20	一种异喹啉化合物及其合成方法	ZL201610049500.3	发明专利	2018-04-06	赵云辉
21	一种两性离子型聚氨酯水凝胶的制备方法	ZL201610522349.0	发明专利	2018-04-03	周虎
22	一种光致变色链转移剂的制备方法和应用	ZL201610593785.7	发明专利	2018-03-30	陈建
23	一种以 Fe(III)为氧化剂的肼燃料电池及其制造方法	ZL201510813044.0	发明专利	2018-03-16	易清风
24	一种具有次氯酸快速检测功能的荧光探针、制备方法及应用	ZL201610071721.0	发明专利	2018-01-09	张培盛
25	马来酸酐直接接枝聚丙乙交酯制备高分子量 MPLGA 的技术	ZL201510812709.6	发明专利	2018-01-05	周智华

4.4 学科建设与人才培养

2018年本实验室共招收 59 名硕士研究生，35 名研究生获得硕士学学位。

4.5 获奖情况

2018 获省部级以上科研成果奖 3 项。

序号	项目名称	完成人	单位	获奖时间	获奖名称、等级	发证机关
1	电路板精密制造用功能衬板的关键技术创新与产业化	周虎、曾坚贤、蹇建、刘玄、曾令玮、罗小阳、许建雄、杨柳、唐甲林	湖南科技大学	2018.02	湖南省科技进步二等奖	湖南省人民政府
2	高效絮凝剂合成方法及其污染控制的构效关系研究	朱国成、郑怀礼、马江雅、任伯帜、张鹏	湖南科技大学	2018.02	湖南省自然科学三等奖	湖南省人民政府
3	高浓度工业废水系列处理及其资源化综合利用	解付兵、石顺存、刘宜德、金建安、曹向东，邹灵峰、朱湘怀	湖南科技大学	2018.02	湖南省科技进步三等奖	湖南省人民政府

二、学术交流情况

2018 年主办的学术会议

学术会议名称	**时间**	**参加总人数**
第一届国际理论与计算化学概念学术研讨会	2018.12.08-2018.12.12	135
第五届全国储能科学与技术大会	2018.10.26-2018.10.28	600
第七届湖南省高分子与科学技术研讨会	2018.12.01-2018.12.02	80
2018 年功能分子高层论坛	2018.04.26-2018.04.28	50

2018 年实验室人员参加国内外学术会议统计情况

参会人	**时间**	**地点**	**会议名称**	**主办单位**
唐子龙	2018-12-22	长沙	2018 年湖南省化学化工学术研讨会	湖南省化学化工学会
唐子龙	2018-12-08	长沙	第一届国际理论与计算化学概念学术研讨会	中国化学会
唐子龙	2018-10-18	南京	第十四届全国生物无机化学学术会议	中国化学会
唐子龙	2018-08-15	南宁	中国化工学会农药专业委员会第十八届年会	中国化工学会农药专业委员会
黄昊文	2018-06-14	西安	中国化学会第 13 届全国分析化学年会	中国化学会
李筱芳	2018-10-18	青岛	第九届亚洲纳米科学和纳米技术会议	中国科学院国家纳米科学中心
李筱芳	2018-08-23	镇江	中国化学会第五届卟啉与酞菁学术研讨会	中国化学会
万义超	2018-10-18	南京	第十四届全国生物无机化学学术会议	中国化学会
万义超	2018-08-24	郑州	第 11 届世界华人药物化学研讨会	中国药学会
汪靖伦	2018-10-26	武汉	第五届全国储能科学与技术大会	中国化工学会
汪靖伦	2018-08-13	天津	2018 南开绿色化学论坛	南开大学
张培盛	2018-12-01	湘潭	第七届湖南省高分子科学与技术研讨会	湖南省化学化工学会
张培盛	2018-09-16	昆明	第一届全国光功能材料青年学者研讨会	中国化学会
张培盛	2018-04-06	广州	International Conference on Organic and Polymer Synthesis	South China University of Technology
张培盛	2018-09-26	西安	第一届华人聚集诱导发光学术研讨会	陕西师范大学
陈建	2018-09-26	西安	第一届华人聚集诱导发光学术研讨会	陕西师范大学
陈建	2018-11-09	武汉	2018 年稳态/瞬态光谱技术和应用研讨会	天美(中国)科学仪器有限公司
陈建	2018-08-02	上海	2018 先进材料研究国际研讨会	东华大学

陈建	2018-04-06	广州	有机和高分子合成国际研讨会	华南理工大学
李毅	2018-10-18	南京	第十四届全国生物无机化学学术会议	中国化学会
李毅	2018-05-05	杭州	中国化学会第 31 届学术年会	中国化学会
张少伟	2018-11-08	福州	中国化学会第十五届固态化学与无机合成学术会议	中国化学会
张少伟	2018-10-12	南京	中国化学会第七届多酸化学学术研讨会	中国化学会
于俊婷	2018-10-26	青岛	全国第十一届有机固体电子过程暨华人有机光电功能材料学术讨论会	中国化学会
曹佳民	2018-05-05	杭州	中国化学会第 31 届学术年会	中国化学会
曹佳民	2018-04-15	深圳	Nano-, Meso-, and Microstructured Materials	ACS publications

2018 年来访人员学术报告情况

姓名	**职称**	**单位**	**报告题目**	**时间**
陈小强	教授	南京工业大学	功能荧光染料的构筑及应用	2018.11.24
杨楚罗	教授	武汉大学	热活化延迟荧光材料的设计	2018.11.24
何卫民	教授	湖南科技学院	基于一物多用策略的清洁能源有机合成	2018.11.13
邓国军	教授	湘潭大学	吲哚直接选择性功能化反应研究	2018.10.23
雷鸣	教授	北京化工大学	加氢脱氢二三事--有机过渡金属催化理论研究的几点体会	2018.12.9
帅志刚	教授	清华大学	有机光电材料中的电子激发态与载流子输运理论研究	2018.12.9
谭斌	教授	南方科技大学	轴手性化学：不对称合成与应用	2018.9.26
杨国强	教授	中国科学院大学	荧光探针的分子设计及其在生物体系中的应用	2018.5.19
郑宜君	博士	德国 INM-莱布尼兹新材料研究所	Thiophene Supermolecular Nanosheet: Synthesis, Self-assembly and Application	2018.5.2
杨新玲	教授	中国农业大学	昆虫神经肽创制昆虫生长调节剂	2018.4.27
尹双凤	教授	湖南大学	以甲烷、环己烷、苯和炔烃为主要研究对象，在不断实践过程中发明常压转化工艺和高效催化剂	2018.4.27

杨光富	教授	华中科技大学	绿色农药的分子设计与新品种创制	2018.4.27
潘景轩	教授	中山大学	Neddylation blockade diminishes hepatic metastasis by dampening cancer stem-like cells and angiogenesis in uveal melanoma	2018.4.27
黎占亭	教授	复旦大学	超分子有机框架(SOF)-探索催化和输送功能	2018.4.27
巢晖	教授	中山大学	金属配合物的细胞器靶向抗肿瘤研究	2018.4.27
张文	教授	浙江工业大学	有机小分子药物化学	2018.4.27
徐晖	教授	西北农林科技大学	植物源先导化合物的新农药研发	2018.4.27
傅尧	教授	中国科学技术大学	生物质选择性催化脱氧制取燃料和化学品	2018.4.3
崔家喜	教授	电子科技大学	基于动态聚二甲基硅氧烷（PDMS）材料的仿生应用	2018.1.19
石枫	教授	江苏师范大学	含有吲哚母核的合成子在催化不对称反应中的应用	2018.1.12
邓晋	副研究员	中国科技大学	三氟甲磺酸金属盐促进C-O键选择性断裂	2018.1.3

三、开放基金评审

2018年理论有机化学与功能分子教育部重点实验室开放基金

编号	姓名	题　　目	经费/万元	申报人所在单位
1	陈绪旺	拉米夫定前药化合物的设计、合成及释药研究	2	山东大学齐鲁医院
2	廖博	金纳米族星型纳米复合材料的可控合成及均孔膜构建	1	湖南科技大学
3	李毅	铱氮杂环卡宾配合物的合成及抗肿瘤活性研究	1	湖南科技大学
4	黄昊文	食品中肠毒素 B 的可视化快速检测方法研究	1	湖南科技大学
5	熊斌	高选择性比率型 H_2S 荧光探针的构建及生物成像研究	1.5	湖南大学
6	许新华	“均相催化，多相分离”型铜配合物的设计、合成及催化性能研究	1.5	湖南大学
7	柳爱平	氨基酰胺类化合物的合成及生物活性研究	2	国家农药创制工程技术研究中心

四、科普传播

2018.06.05-2018.06.07（3 天)和2018.10.10-2018.10.12（3 天)作为实验室科普固定开放日。开放日期间，开展了“走进化学科学”主题活动，来自湘潭市二中 100 多位中学生参加了本次活动，本次活动的目的是对中学生进行科普教育，提高他们对化学的兴趣；举办了第一届“化学+”趣味知识竞赛，共有 80 余位同学参加了此次比赛；发表科普文章 1 篇。

五、2018年发表的主要研究论文

理论有机化学与功能分子教育部重点实验室2018年所发论文目录

1. Maolin Yu, Peisheng Zhang, Baiju P. Krishnan, Hong Wang, Yong Gao, Shu Chen, Rongjin Zeng, Jiaxi Cui, Jian Chen. From A Molecular Toolbox to A Toolbox for Photoswitchable Fluorescent Polymeric Nanoparticles. ***Advanced Functional Materials*** 2018, 28, 1804759.
2. Changwang Pan, Lipiao Bao, Xianyong Yu, Hongyun Fang, Yunpeng Xie, Takeshi Akasaka, Xing Lu. Facile Access to Y_2C_{2n} (2n = 92-130) and Crystallographic Characterization of $Y_2C_2@C_1$(1660)-C108: A Giant Nanocapsule With A Linear Carbide Cluster. ***ACS Nano*** 2018, 12, 2065–2069.
3. Peisheng Zhang, Hong Wang, Yongxiang Hong, Maolin Yu, Rongjin Zeng, Yunfei Long, Jian Chen. Selective Visualization of Endogenous Hypochlorous Acid in Zebrafish During Lipopolysaccharide-induced Acute Liver injury Using A Polymer Micelles- Based Ratiometric Fluorescent Probe. ***Biosensors & Bioelectronics*** 2018, 99, 318-324
4. Wei hu, Zhiquan Zhang, Yongzhuo Xu, Jiamin Cao, Shungang Liu, Zilong Tang, Bin Zhao, Jian Zhang. An Axisymmetric Heptacyclic Lactam Unit for Efficient Polymer Solar Cells. ***Journal of Materials Chemistry C*** 2018, 6, 6911-6915.
5. Peisheng Zhang, Yong tian, Hui Liu, Junyu Ren, Hong Wang, Rongjin Zeng, Yunfei Long, Jian Chen. *In Vivo* Imaging of Hepatocellular Nitric Oxide Using A Hepatocyte-Targeting Fluorescent Sensor. ***Chemical Communication*** 2018, 54, 7231-7234.

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8. Yongxiang Hong, Peisheng Zhang, Hong Wang, Maolin Yu, Yong Gao, Jian Chen. Photoswitchable AIE Nanoprobe for Lysosomal Hydrogen Sulfide Detection and Reversible Dual-Color Imaging. ***Sensors and Actuators B-Chemical*** 2018, 340-347.
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11. Peisheng Zhang, Hong Wang, Di Zhang, Xuyao Zeng, Rongjin Zeng, Lehui Xiao, Hongwen Tao, Yunfei Long, Pinggui Yi, Jian Chen. Two-Photon Fluorescent Probe for Lysosome-Targetable Hypochlorous Acid Detection Within Living Cells. ***Sensors and Actuators B-Chemical*** 2018, 255, 2223-2231.
12. Keqin Deng, Xinyan Liu, Chunxiang Li, Haowen Huang. Sensitive Electrochemical Sensing Platform for Micrornas Detection Based on Shortened Multi-Walled Carbon Nanotubes with High-Loaded Thionin. ***Biosensors & Bioelectronics*** 2018, 117, 168-174.
13. Yuanjiao Pei, Ming Hu, Feihui Tu, Xueyong Tang, Wei Huang, Shu Chen, Zelin Li, Yue Xia. Ultra-Rapid Fabrication of Highly Surface-Roughened Nanoporous Gold Film from Ausn Alloy with Improved Performance For Nonenzymatic Glucose Sensing. ***Biosensors & Bioelectronics*** 2018, 117, 758–765.
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15. Chao Wu, Linghui Lu, Aizhong Peng, Guokai Jia, Cun Peng, Zhong Cao, Zilong Tang, Weimin He, Xinhua Xu. Ultrasound-Promoted Brønsted Acid Ionic Liquid-Catalyzed Hydrothiocyanation of Activated Alkynes Under Minimal Solvent Conditions. ***Green Chemistry*** 2018, 20, 3683-3688.
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From a Molecular Toolbox to a Toolbox for Photoswitchable Fluorescent Polymeric Nanoparticles

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Switchable organic fluorescent materials are attracting much interest in many fields including flexible display, information storage, anti-counterfeit, and bioimaging, due to their prominent properties and relatively low cost. Herein, a class of novel photoswitchable fluorescent polymeric nanoparticles (PFPNs) toolbox that shows switchable full-colored emission including white light is described. This nanoparticles toolbox consists of a series of reversibly photoswitchable and non-PFPNs with red, green, and blue fluorescence, and is built up from three primary fluorescent dyes and a photochromic diarylethene molecule, through a facile one-pot miniemulsion method. The as-prepared PFPNs display the merits of high fluorescence resonance energy transfer efficiency and fluorescence quantum yield, rapid responsiveness, prominent photoreversibility, and brilliant long-term fluorescence stability (≈6 weeks). They enable switchable emission between white light and any visible color on-demand in both solution and film states. Their potential in complex fluorescent encryption and photoswitchable white light-emitting diode is described and its great potential in anti-counterfeiting technology, data encryption, and the next generation of optoelectronic materials is foreseen.

1. Introduction

Organic fluorescent materials play an important role in many fields such as flexible display,[1–4] anti-counterfeit,[5–7] and bioimaging,[8–10] because they are cheap, environmentally friendly, and easy to fabricate on large scale.[11–13] The emission color is one of the most important parameters in the design of these fluorescent materials.[14] Unlike inorganic fluorescent materials such as semiconductor quantum dots[15,16] and metal nanoparticles[17,18] whose emission color can be tuned by their size, the emission color of organic fluorescent materials basically depends on their conjugated structures.[19–21] Shifting emission color normally requires a new design in molecular structure, which often implies tedious effort in organic synthesis.[22–26] The situation becomes even worse in the case that a combinational color, i.e., white light, is the target because it consists of more than two emission colors with a subtle ratio.[27–31] Although various organic fluorescent molecules have been designed and developed,[32] there remains a lot of issues that must be addressed prior to their practical application, for example, the lack of a photoswitching mechanism that allows the use of the materials in rewritable data storage and photoresponsive optoelectronic devices etc.,[33–37] and high fabrication cost of some molecules with specific emission colors (like white light).[38] Efficient, photoswitchable fluorescent material toolbox is still not built up yet.

Photoswitchable fluorescent polymeric nanoparticles (PFPNs) constitute a powerful way to expand the organic fluorescent material toolbox.[39–41] In these nanoparticles, more than one kind of dye molecules can be embedded together to tune the emission color.[42–45] The molecules are fixed in a polymer matrix, shielded from the environment or each other, for preventing undesirable aggregation-induced quenching or energy transfer.[46] As a result of the predictable emission colors of different compositions, the final emission spectrum can be tuned and even significantly expanded in the case that fluorescence

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ARTICLE

Facile Access to Y_2C_{2n} ($2n$ = 92−130) and Crystallographic Characterization of $Y_2C_2@C_1(1660)\text{-}C_{108}$: A Giant Nanocapsule with a Linear Carbide Cluster

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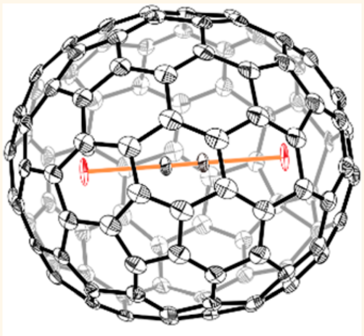
Supporting Information

ABSTRACT: A series of giant metallofullerenes Y_2C_{2n} ($2n$ = 92−130) have been successfully obtained through the treatment of the fraction enriched by 1,2-dichlorobenzene with $SnCl_4$. Subsequent chromatographic separation gives a pure sample with a composition of Y_2C_{110}. Crystallographic results reveal that this endohedral takes the carbide form, namely $Y_2C_2@C_1(1660)\text{-}C_{108}$, representing as the largest metallofullerene that has been characterized by crystallography to date. Despite the disorder of the metal cluster, the major Y_2C_2 adopts a previously predicted linear configuration, indicating that the compression of the internal cluster by the cage is almost negligible in this giant cage. Electrochemical studies suggest that $Y_2C_2@C_1(1660)\text{-}C_{108}$ is a good electron donor instead of an electron acceptor.



$Y_2C_2@C_1(1660)\text{-}C_{108}$

KEYWORDS: *fullerene, metallofullerene, carbide cluster, crystallography, nanocapsule*

Giant fullerenes, for example, those consisting of 100 or more carbon atoms ($C_{2n\geq100}$) possess a seemingly infinite regime that show close connections with carbon nanotubes (CNTs).[1−3] However, the enormous possible isomers of giant fullerenes make the identification of their structures challenging, and thus single crystal X-ray diffraction (XRD) crystallography stands as one of the most reliable solutions. Another obstacle impeding final acquisition of giant fullerenes is their poor solubility in common solvents, which is closely associated with their electronic structures.[4] Thus, electrochemical or chemical modifications have been applied to alter the electronic structures of giant fullerenes to make them more soluble. Though the electrochemical method appeared efficient for the enrichment of giant fullerenes like C_{2n} ($100 \leq 2n \leq 112$), their anionic form hindered further isolation of pure isomers.[5] Alternatively, chemical modification has led to the identification of several chlorinated fullerenes, such as $C_{100}(18)\text{-}Cl_{28/30}$,[2] $C_{102}(603)\text{-}Cl_{18/20}$,[6] $C_{104}(812)\text{-}Cl_{16/18/20/22}$,[6] $C_{106}(1155)\text{-}Cl_{24}$,[7] and $C_{108}(1771)\text{-}Cl_{12}$,[7] but the cages are distorted because of the severe exohedral modification and sometimes cage shrinkage also took place.

Meanwhile, endohedral metal-doping represents another effective way to alter the electronic structures of giant fullerenes by forming endohedral metallofullerenes (EMFs).[8−10] Many giant EMFs have been isolated and crystallographically characterized during recent years. Although the first two examples are both di-EMFs, namely, $Sm_2@D_{3d}(822)\text{-}C_{104}$[11] and $La_2@D_5(450)\text{-}C_{100}$,[3] it has been revealed that carbide cluster metallofullerenes (CCMFs) are also preferred because of the strong metal−cage interactions. Successful examples are $La_2C_2@D_5(450)\text{-}C_{100}$,[12] $La_2C_2@C_s(574)\text{-}C_{102}$,[13] and $La_2C_2@C_2(816)\text{-}C_{104}$.[13] In these compounds, the C_2-unit plays an essential role in stabilizing the giant cages by coordinating with the metal ions so as to compensate the repulsion between them. As a direct proof of the strong metal−carbon interactions, $La_2C_2@D_5(450)\text{-}C_{100}$ shows an anomalous axial compression as compared with $La_2@D_5(450)\text{-}C_{100}$, indicating that giant fullerenes can be viewed as capped short CNTs to

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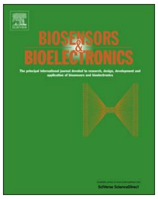

Selective visualization of endogenous hypochlorous acid in zebrafish during lipopolysaccharide-induced acute liver injury using a polymer micelles-based ratiometric fluorescent probe

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ABSTRACT

The development of effective method for monitoring of endogenous hypochlorous acid (HClO) in vivo is of great significance for early diagnosis of lipopolysaccharide (LPS) induced acute liver injury. Herein, we report a polymer micelles-based ratiometric fluorescent probe (**PM**) based on the combination of intramolecular charge transfer (ICT) mechanism and fluorescence resonance energy transfer (FRET) principle for selective visualization of endogenous HClO in vivo. Upon the reaction of **PM** with HClO, the electron-donating thiourea moiety is oxidized and transformed into imidazoline moiety (electron-withdrawing group), resulting in a dramatic blue shift (~100 nm) in the fluorescence emission. The as-prepared **PM** shows good water dispersibility (100% aqueous media), fast response (< 40 s), high sensitivity (a detection limit of 1.75 nM), and outstanding selectivity toward HClO over other ROS/RNS (50 equiv.). In addition, the vivo imaging experiments demonstrate that **PM** facilitates the visualization of endogenous HClO generation with LPS induced acute liver injury in zebrafish model.

1. Introduction

Acute liver injury is a common concern for both clinicians and patients (Stravitz et al., 2007). Taking too much inflammatory is one of the most common causes of acute liver injury (Hartmut, 2000; Lonsdale et al., 2010). Lipopolysaccharides (LPS), which are found in Gram-negative bacteria, have been identified as one of the most common inflammatory mediators that lead to acute liver injury (Gao et al., 2016; Yao et al., 2016). It has been well documented that endogenous hypochlorous acid (HClO) can be produced by myeloperoxidase enzyme-mediated peroxidation of chloride ions, and myeloperoxidase is overexpressed when LPS induced acute liver injury (Jaeschke et al., 2011; Li et al., 2005). Obviously, the design of effective tools which aim to monitor endogenous HClO level is helpful for early diagnosis of LPS induced acute liver injury.

In recent years, fluorescent probes have been proven to be effective tools for monitoring biologically relevant species in vivo due to their numerous advantages, such as high sensitivity, simple manipulation, excellent temporal-spatial resolution, real-time spatial imaging, etc. (Aron et al., 2015; J. Chen et al., 2015; W. Chen et al., 2015a; Cheng et al., 2012; Contreras-Gutierrez et al., 2013; Ding et al., 2013; Francesco et al., 2014; Guo et al., 2016; He et al., 2016; Hou et al., 2016; Hu et al., 2016; Karima et al., 2012; Li et al., 2014; Lin et al., 2015; Liu et al., 2014; Qing et al., 2016; Ramon-Marquez et al., 2016; Sauer et al., 2012; Sun et al., 2016; Tao et al., 2013; Xiao et al., 2017; Zhou et al., 2015). With the development of molecular fluorescence technology, a number of fluorescent probes for HClO detection in vivo have been reported (Jaeschke et al., 2011; Li et al., 2005, Zhu et al., 2016). However, most of them display one fluorescence emission signal, which are readily perturbed by some limitations, such as microenvironment, sensor concentration, photobleaching and excitation intensity, etc. By contrast, the ratiometric fluorescent probes with two distinct emission signals can greatly overcome the above limitations of one emission signal-based probes (Yu et al., 2013a, 2013b).

To date, several ratiometric fluorescent probes for imaging endogenous HClO in vivo have been developed (Huang et al., 2016; Xiao et al., 2015). Despite these efforts, to our best knowledge, in vivo imaging of endogenous HClO with the aid of small molecule probes is

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An axisymmetric heptacyclic lactam unit for efficient polymer solar cells†

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An axisymmetric heptacyclic lactam unit TD3 has been developed by replacing the thieno[3,2-*b*]thiophene core of a known acceptor unit TD1 with dithieno[3,2-*b*:2′,3′-*d*]thiophene. PThTD3 was obtained by copolymerizing TD3 with thiophene in good yield. PThTD3 showed red-shifted absorption, lower LUMO energy level, and better hole mobility relative to the analogue PThTD1. Inverted polymer solar cells based on PThTD3:PC$_{71}$BM exhibited a decent PCE of 7.25%, which is much higher than that of PThTD1. These results have demonstrated that axisymmetric lactam TD3 is a good building block for PSC applications.

Polymer solar cells (PSCs), usually employing conjugated polymers as electron donors, and fullerene derivatives as electron acceptors, have attracted much attention due to their unique advantages such as low cost, solution processing, lightweight, and flexibility.[1–7] Since 2015, the success of nonfullerene acceptor materials has revitalized PSCs and the power conversion efficiencies (PCEs) of single PSCs based on polymer donor material/nonfullerene acceptor material systems have exceeded 14%.[8–12] As a result, many efficient small-molecule or polymer acceptors have been developed.[13–23] Meanwhile, highly efficient polymer donor materials still need to be developed.[24]

In 2013, we synthesized a pentacyclic lactam acceptor unit thieno[2′,3′:5,6]pyrido[3,4-*g*]thieno[3,2-*c*]isoquinoline-5,11(4*H*,10*H*)-dione (TPTI) and its D–A copolymer PThTPTI exhibited a decent PCE of over 9%.[25,26] Based on this work, lactam acceptor units BDTP, TD1, TD2 and TITI were developed by replacing the benzene ring of TPTI with 2,2′-bithiophene, thieno[3,2-*b*]thiophene or naphthalene. Meanwhile, a heptacyclic lactam unit TTP was also produced by replacing the terminal thiophenes of TPTI with two thieno[3,2-*b*]thiophenes. Copolymers based on these acceptor units have exhibited PCEs over 10%.[27–31] In addition, these lactam acceptors are good building blocks for small-molecule donor and polymer acceptor materials, and have shown great potential in nonfullerene PSCs and tandem cells.[32–39]

It is noteworthy that these lactam acceptors reported by us all possess centrosymmetric chemical structures. Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) is a rigid and electron-donating unit and its copolymers possess high crystallinity and charge carrier mobilities.[40–42] Herein, we have designed and synthesized an axisymmetric heptacyclic lactam unit **TD3** *via* replacing the thieno[3,2-*b*]thiophene of TD1 with dithieno[3,2-*b*:2′,3′-*d*]thiophene. As shown in Fig. 1, **TD3** contains seven fused aromatic rings with five thiophenes and two pyridones. D–A copolymer **PThTD3** based on a thiophene donor unit and **TD3** was synthesized. The thermal, optical, and electrochemical properties, crystallinity, and hole mobility of **PThTD3** were studied. Compared with **PThTD1** based on centrosymmetric lactam acceptor TD1, **PThTD3** exhibited an narrower optical bandgap and higher hole mobility. Under illumination of AM 1.5G (100 mW cm^{-2}),

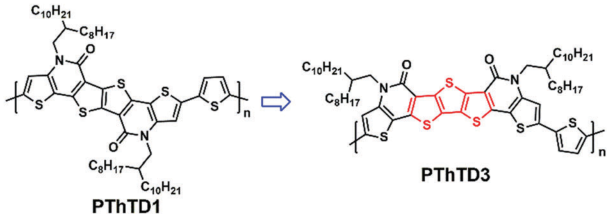

Fig. 1 The molecular structures of **PThTD1** and **PThTD3**.

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In vivo imaging of hepatocellular nitric oxide using a hepatocyte-targeting fluorescent sensor†

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Imaging of hepatocellular nitric oxide (NO) *in vivo* is of great importance for understanding its roles in liver diseases, but such an imaging approach is still lacking. Herein, a hepatocyte-targeting fluorescent NO sensor has been fabricated. This sensor exhibits good water solubility, excellent selectivity, and high sensitivity (∼1.62 nM). The cells and *in vivo* imaging experiments reveal that Gal-RhB facilitates the visualization of hepatocellular NO in both HepG2 cells and zebrafish. These results demonstrate that Gal-RhB may be a promising tool for studying the function of NO in NO-associated liver diseases.

Chronic liver inflammation can be involved in many health problems that affect the quality of life and disease progression. In chronic liver inflammation, a large sustained amount of endogenously produced nitric oxide (NO) from NO synthase (iNOS) can lead to the development of liver cancer.[1] Additionally, during prolonged ischemia, high levels of NO have cytotoxic effects leading to severe liver injury.[1] Obviously, *in vivo* imaging of hepatocellular NO is helpful to further understand the roles of NO in liver diseases, but such an imaging approach is still lacking.

Recently, small-molecule based fluorescent sensors have attracted wide attention due to their high sensitivity, simple manipulation, excellent temporal-spatial resolution, real-time spatial imaging, *etc.*[2–4] To date, a number of fluorescent sensors for NO imaging in living cells and *in vivo* have been reported.[5–7] Despite intensive efforts, most of the elegant NO sensors can specifically localize in mitochondria or lysosomes and do not allow for specific analysis at the level of individual organs (liver). Thus, the design of novel sensors that address hepatocyte-selective imaging of NO is extremely urgent.

It is well known that the asialoglycoprotein receptor (ASGP-R) is uniquely expressed on the surface of mammalian hepatocytes, and it can selectively recognize terminal galactose (Gal) and *N*-acetylgalactosamine (GalNAc), allowing for the selective internalization of them within the hepatocyte *via* receptor-mediated endocytosis.[8] Indeed, the introduction of a galactose moiety (as a targeting agent) to a fluorescent sensor can greatly enhance its selective internalization by hepatocytes derived from a certain tissue, achieving the targeting of hepatocytes for imaging application.[9] Inspired by this strategy, a variety of hepatocyte-targeting fluorescent sensors have been developed for metal ions, amino acids and enzymes, *etc.*[9] So far, however, a practical hepatocyte-targeting fluorescent sensor capable of imaging NO in live cells and *in vivo* is unavailable at present.

In this work, we report the first hepatocyte-targeting fluorescent NO sensor (**Gal-RhB**) (Scheme 1). For the sensor, a galactose moiety is selected not only as the hepatocyte targeting agent, but also to improve the water solubility of fluorescent sensor. In the presence of NO, **Gal-RhB** exhibits a dramatic fluorescence increase with excellent selectivity and high sensitivity (∼1.62 nM). Moreover, the living cells and *in vivo* imaging experiments demonstrate that **Gal-RhB** can selectively image hepatocellular NO.

In molecular design, the sensor (**Gal-RhB**) is composed of a galactose moiety, which serves as a hepatocyte-targeting ligand,[9] and an *o*-phenylenediamine-linked rhodamine moiety is selectively cleaved by NO and gives rise to a strong, red fluorescence signal, as illustrated in Scheme 1. The presumed hepatocyte-targeting sensor (**Gal-RhB**) was synthesized *via* the synthetic routes outlined in Scheme S1 (ESI†). To verify the liver targeting role of the galactose unit in **Gal-RhB**, a structural analogue **5** without galactose was also prepared. All of the compounds were well characterized by ^{1}H NMR, IR and HRMS (Fig. S1–S6, ESI†).

To unequivocally establish that **Gal-RhB** is a highly specific sensor for NO, the spectroscopic properties of **Gal-RhB** were initially analyzed in simulated physiological conditions (10 mM PBS buffer, pH 7.0, 37 °C), and the results are shown in Fig. S7 (ESI†). As expected, the sensor **Gal-RhB** itself displays no absorption at 555 nm, and no emission at 580 nm can be recorded

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Extension of antiaromatic norcorrole by cycloaddition†

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Piotr J. Chmielewski*[b]

The antiaromatic ring of norcorrole, a contracted tetrapyrrolic porphyrinoid, was subjected to [2+3] dipolar cycloaddition of iminonitriles. The paratropic character of the resulting chiral chlorins was retained. The chlorins were easily dehydrogenated in the presence of air, yielding pyrazole-fused norcorroles with markedly enhanced paratropicity.

In planar molecules containing a fully π-conjugated ring or ring system, aromaticity is normally associated with the presence of conjugation pathways satisfying Hückel's $4n$+2 electron count. In contrast to the energetically stabilizing aromatic conjugation,[1,2] considerable destabilization[3] is usually observed in systems containing $4n$ π-electron circuits, which are accordingly termed antiaromatic.[4–11] Antiaromaticity typically leads to distinct structural, optical, magnetic, and redox properties, which are of both fundamental and practical interest, with relevance in the field of organic electronics.[12–18] In particular, because of their narrow HOMO–LUMO energy gaps and balanced electron-donating and accepting abilities, antiaromatic systems often show molecular conductivity superior to that of comparable aromatic or non-aromatic materials.[16–19]

Porphyrinoids are a group of conjugated macrocycles comprising both aromatic systems (*e.g.* porphyrins and corroles) as well as antiaromatic ones. Norocorrole (**1a**, Fig. 1), a prominent example of porphyrinoid antiaromaticity, is a contracted tetrapyrrole consisting of two arylmethine-bridged bipyrroles, and containing 16 π-electrons in the formal delocalization path.[20–25]

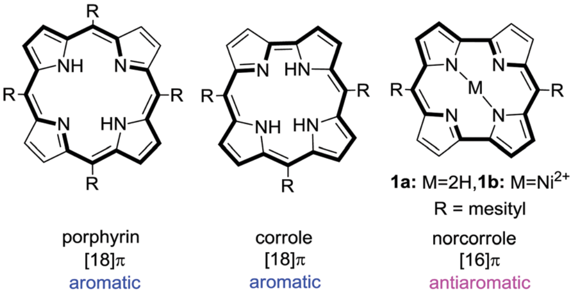

Fig. 1 Delocalization paths in aromatic and antiaromatic tetrapyrroles.

The readily obtainable *meso*-dimesityl-norcorrolatonickel(II) **1b**[21] is stable under ambient conditions, but it can be subjected to various chemical modifications under mild conditions. To date, exploration of synthetic norcorrole chemistry encompassed substitution,[23,26–30] hydrogenation,[31,32] dimerization,[26,31,33] and insertion[30,34] reactions, which produced a range of intriguing systems, many of which displayed either enhanced or diminished antiaromaticity with respect to that of **1b**. Redox-induced antiaromatic/aromatic transitions have been also observed,[22,29] as well as single-molecule conductivity of norcorrolatonickel(II) which is about order of magnitude higher than that of the aromatic porphyrinatonickel(II).[35]

To further elucidate the unusual reactivity of this promising system and to extend the scope of possible derivatives of fine-tuneable properties, we turned our interest to cycloaddition reactions of **1b** (Scheme 1). Dipolar [2+3] cycloadditions leading to pyrazole, triazole, or oxazole annulations have been frequently used in organic synthesis[36–45] including modification of aromatic porphyrinoids acting as dipolarophiles.[46–50] Here we present for the first time a cycloaddition-based route to an extended antiaromatic macrocyclic system.

Reaction of **1b** with aryl-substituted hydrazonyl bromides in the presence of triethylamine (TEA) brought about formation of 1,3-cycloaddition products **2a–c** which are readily dehydrogenated in the presence of air, yielding **3a–c** as the major and final products. The products were separated by chromatography,

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† Electronic supplementary information (ESI) available: Synthetic and separation details, spectroscopic characterization of the compounds, electrochemistry, calculation details, calculated structures (PDB format). CCDC 1817605. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc00447a

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Nickel-catalyzed cross-coupling of aldehydes with aryl halides *via* hydrazone intermediates†

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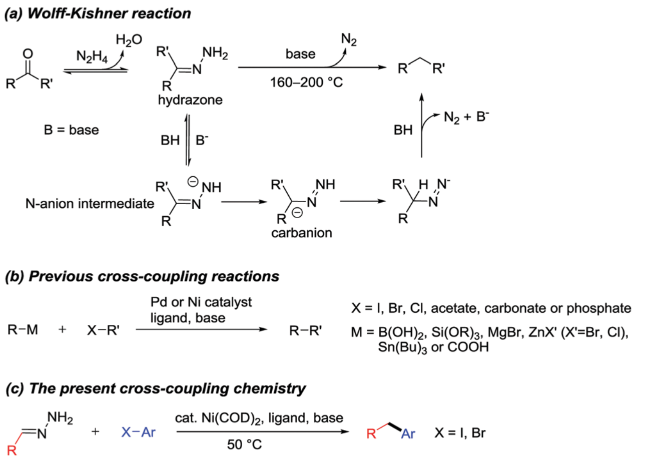
Traditional cross-couplings require stoichiometric organometallic reagents. A novel nickel-catalyzed cross-coupling reaction between aldehydes and aryl halides *via* hydrazone intermediates has been developed, merging the Wolff–Kishner reduction and the classical cross-coupling reactions. Aromatic aldehydes, aryl iodides and aryl bromides are especially effective in this new cross-coupling chemistry.

The Wolff–Kishner reaction, discovered by Kishner in 1911[1] and Wolff in 1912,[2] is a synthetically effective method to reduce carbonyls into methylene derivatives through the decomposition of the formed hydrazone intermediates.[3] It is widely accepted that the reaction (Scheme 1a) begins with the reversible formation of hydrazone and, then, the deprotonation gives an *N*-anionic intermediate.[4] The subsequent transformation of this intermediate to the carbanion is the rate-determining step, which is followed by rapid proton-transfer, evolution of nitrogen gas and protonation of the new carbanion to finally deliver the reduced product.[4] However, Wolff's and Kishner's original protocols are inconvenient because the prepared hydrazones need to be mixed with hot solid KOH and porous platinized plates,[1] or heated within a sealed tube at 160–200 °C.[2] Thus, different modifications for this reaction were developed to replace these harsh conditions, of which a milestone was attained by Huang who operated the reaction by employing highly safer and cheaper hydrazine hydrate ($N_2H_4 \cdot H_2O$) as well as high-boiling-point solvents.[5] This protocol is also problematic since a temperature of about 190 °C is required to achieve a satisfactory reaction rate.[5] In this regard, Cram, Myers, Caglioti and Henbest further improved the reaction by lowering the temperature to room temperature,[4,6] 66 °C[7] and 100 °C,[8] respectively.



Scheme 1 Conceptual design for cross-coupling between hydrazone and aryl halides.

However, under such temperatures, these methods necessitate intractable isolation of generally unstable hydrazones ahead of their reduction,[4,7] or suffer from low yield (≤60%) of the target products,[8] or need laborious preparation of 1,2-bis(*tert*-butyldimethylsilyl)-hydrazine.[6] Therefore, continuous efforts to make the Wolff–Kishner reaction more practical by simultaneously lowering the reaction temperature, simplifying the operation procedure and achieving high yields are still highly desirable.

Besides the Wolff–Kishner reduction, another essential tool in modern synthetic chemistry is the various transition-metal catalyzed cross-coupling reactions (Scheme 1b) between different electrophiles,[9] or between nucleophiles and electrophiles such as the Suzuki coupling,[10,11] the Kumada coupling,[10] the Stille coupling,[10,11] the Hiyama coupling,[10,11] the Negishi coupling,[10,11] the Sonogashira coupling[11] and decarboxylative coupling.[12] The "carbanion equivalents" are $R{-}B(OH)_2$,[10,11] $-Si(OR)_3$,[10,11] –MgBr,[10] –ZnCl,[10,11] $-Sn(Bu)_3$,[10,11]–COOH,[12] *etc.*, while the electrophiles are generally Ar–I,[10,11] –Br,[10,11] or –Cl.[10,11] We postulated that the hydrazones involved in the well-known Wolff–Kishner reaction might be intercepted as the carbanion equivalents in the classical

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Photoswitchable AIE nanoprobe for lysosomal hydrogen sulfide detection and reversible dual-color imaging

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ABSTRACT

Current lysosomal H_2S-responsive fluorescent probes usually possess notorious aggregation caused quenching (ACQ) phenomenon and suffer from the inevitable background fluorescence signals. To circumvent this problem, we here combined H_2S recognizing aggregation-induced emission (AIE) group with photochromic spiropyran moiety to rational design novel photoswitchable AIE nanoprobe (DNBS-DCM-SP) for lysosomal H_2S detection with high spatiotemporal resolution. In the presence of H_2S, the electron-withdrawing DNBS moiety will deviate from DNBS-DCM-SP via a H_2S-induced O—S bond cleavage, induced a sensitive turn-on fluorescence response at about 592 nm. The prepared nanoprobe displays good sensitivity (~5.0 nM), and high specificity (especial against other thiols). In additon, the fluorescence of the H_2S-activated AIE nanoprobe (DCM-SP) can be reversibly switched by selective fluorescence resonance energy transfer (FRET) from the AIE fluorophore (DCM) to ring-opened state of spiropyran via alternating UV/visible light irradiation. Moreover, the feasibility of the prepared photoswitchable AIE nanoprobe is also demonstrated by mapping the production of endogenous H_2S in living cells as well as reversible dual-color fluorescence imaging.

1. Introduction

Lysosomes, as important acidic membrane-enclosed cytoplasmic organelles (pH 4.5–5.5), are involved in many physiological processes such as metabolism, intracellular transport and apoptosis [1,2]. Hydrogen sulfide (H_2S), derived endogenously from L-cysteine in lysosomes, spontaneously produced by the enzymes Cystathionine β-Synthase (CBS) and γ-Cystathionase (CSE), and can disturb the lysosomal membrane and induce cell apoptosis by virtue of activating calpain proteases [3–5]. Despite of the tremendous advances, the roles of H_2S in lysosomes are still not fully understood. Thus, the exploitation of practical strategies for selectively detecting of lysosomal H_2S levels with high anti-background interference ability is of great importance.

Recently, the non-invasive fluorescent probes gain wide attention since they possess the advantages of simple operation, high sensitivity and selectivity, real-time and in-situ temporal and spatial imaging [6–23]. So far, several rational designed fluorescent probes have been created for monitoring lysosomal H_2S [24–29]. Nevertheless, the existing of notorious aggregation caused quenching (ACQ) phenomenon and small Stokes shift caused "self-absorption" effect further restricted the utilization of the above reported traditional organic probes [30,31]. To address these problems, the recently developed aggregation-induced emission (AIE) based fluorescent probes with large Stokes shift characteristic, which are intriguingly discovered by Tang et al., have been proposed [32–38]. However, most of them are still suffered from the inevitable background fluorescence signals and the lack of high spatiotemporal resolution.

Photoswitchable fluorescent systems, generally composed of photochromes (spiropyran, azobenzene and diarylethene, etc.) and fluorophores via fluorescence resonance energy transfer (FRET) strategy, have been increasingly developed and served as smart probes for bioimaging due to the reversibly switchable dual-color or on-off fluorescence feature upon alternating UV/visible light irradiation [39–51]. This distinctive nature endows them to effectively preclude false positive/negative signals from background fluorescence, as well as achieve (ultra) high spatiotemporal resolution bioimaging.

In view of the unique excellent features of AIE fluorogen and photoswitchable fluorescent systems, it is extremely urgent to construct a H_2S fluorescent probe capable of both AIE and photoswitchable reversible dual-color characteristic. This photoswitchable AIE-based H_2S

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NiCo-doped C-N nano-composites for cathodic catalysts of Zn-air batteries in neutral media

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ABSTRACT

One of the major challenges towards the development of the conventional alkaline Zn-air battery is its spontaneous discharge caused by the unstability of the anode Zn in concentrated alkaline electrolyte. Utilization of a neutral electrolyte as the alternative to alkaline electrolyte is likely to be a promising strategy to overcome this issue because of much high stability of anode Zn in neutral solution. To realize the normal operation of the neutral Zn-air battery however, a crucial issue is how to ensure that the cathodic catalyst can efficiently electro-catalyze oxygen reduction reaction (ORR) in neutral solution. Herein, we report a facile preparation of Ni/Co-doped C-N nano-composite catalysts (NiCo/C-N) from direct pyrolysis of Ni/Co salt, polyaniline (PANI), carbon nanotube (CNT) and dicyandiamide. Among the as-synthesized catalysts, Ni_1Co_3/CN-3 presents high and stable ORR current density of 5.27 mA cm^{-2} in 0.5 mol L^{-1} KNO_3 solution at 2000 rpm. Electron transfer number of ORR on Ni_1Co_3/CN-3 catalyst is 3.78, showing a nearly completed reduction of O_2 to H_2O. A neutral Zn-air battery with the prepared NiCo/C-N composite coated on carbon paper as the air electrode catalyst and metal Zn as the anode was constructed in 0.5 mol L^{-1} KNO_3 solution. For the catalyst Ni_1Co_3/CN-3, the open circuit voltage of the neutral Zn-air battery is 1.16 V, and the maximum power density is 38.5 mW cm^{-2}. The galvanostatic discharge time is 345.7, 160.6, 18.1 and 1.3 h as the discharge current density keeps 10, 50, 100 and 150 mA cm^{-2} respectively. A stable voltage plateau arises at various discharge current densities. The neutral Zn-air battery can repeatedly discharge after the zinc anode has been replaced, indicating that the synthesized ORR catalyst is an excellent cathode material for the neutral Zn-air battery. This kind of neutral Zn-air battery has a wide application prospect as mobile power supply.

1. Introduction

The energy crisis and environmental pollution caused by excessive consumption of fossil energy are becoming serious, which may be a huge threat to the development of society [1]. New energy conversion devices play an important role in solving such problems, such as metal-air batteries [2–5] and fuel cells [6,7], which have the advantages of high energy density, portability and environment friendly. Zn-air battery is a very promising technology owing to the large capacity, high specific energy, easy fuel storage, low cost, non-flammable and non-explosive behaviors. It has huge market application prospect and attracts widespread attention [8–10]. Although Zn-air batteries have been well developed, synthesizing efficient catalysts of air cathode and improving the stability of the anodic zinc are the most noteworthy challenge [11,12]. To date, Pt or Pt-based catalysts have been considered to be the most efficient electrocatalysts for oxygen reduction reaction [13,14]. However, the low natural abundance and high cost of Pt are significantly limiting its application. Therefore, enormous research effort has been directed towards the development of non-Pt cathode catalysts with low cost and high performance for ORR over the past few decades. Research showed that electroactivity of this type of catalyst for ORR was greatly influenced by heteroatom-doped carbon materials, especially N-doped carbon materials, which can

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New insight into electropolymerization of melamine. I: Chloride promoted growth of polymelamine in different pH medium

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ABSTRACT

Electropolymerization of melamine, 1,3,5-triazine-2,4,6-triamine, has been investigated here in aqueous solutions in a very wide pH range, which formerly was believed to be confined only in an acidic medium. We report here for the first time the polymerization can take place in neutral and alkaline besides acidic solution in presence of Cl^- ions. The key effects of the acidity of solution, potential window and concentration of Cl^- ions and melamine monomer on the polymelamine (pMel) deposition have been further confirmed one by one, respectively. We proved that presence of Cl^- ions is the necessary condition rather than H^+. The electropolymerization of melamine is very sensitive to Cl^- (even in 1 mM), and in situ electrogeneration of active chlorine effectively promote the growth of pMel film in separate solutions with different pH. Based on the relevant reactions during the process of electropolymerization, a tentative mechanism is given here. With this knowledge, a better control of the electrochemical synthesis can be envisioned, thus making pMel film suitable for the construction of multifunctional platforms.

1. Introduction

Since the revolutionary discovery of conducting polymers [1,2], they have attracted intense attention owing to their specific properties for various applications in corrosion protection, electrocatalysis, energy storage, bio/chemical sensors and electronic devices [3–7]. Conducting polymer can be prepared using chemical [8,9], electrochemical [10,11], biocatalytic [12–14], photoinitiating [15,16] and plasma deposition [17–19] methods of polymerization. Among them, electropolymerization represents a perfect mean for the synthesis of conducting polymer films with controllable film thickness, permeation, and charge transport characteristics [20], which can be manipulated by adjusting the electrochemical parameters and composition of the corresponding monomer solution [21].

So far, the families such as polypyrrole, polyaniline, polythiophene and their derivatives are studied extensively [22], which lies in the fact that their monomer is easily oxidized, their film possess good redox properties and high electrical conductivities [23]. Recently, as a quite new electroactive polymer, polymelamine (pMel) was electrochemically synthesized from melamine [24,25], 1,3,5-triazine -2,4,6-triamine, a raw material used to produce resins possessing high stability [26]. The electropolymerization of melamine monomer was achieved by oxidation of the amino groups to give a pMel film of head-to-head coupling at the NH-NH bonds [27]. In view of its abundant nitrogen matrix and amine functional groups, electroactive pMel and composite film modified electrodes were recently applied to construct sensitive and selective electrochemical sensors for different targets, such as DNA, hydrogen peroxide, NADH, bisphenol A, neurotransmitters and pharmaceutical molecules [25,27–42]. However, as compared to volume of

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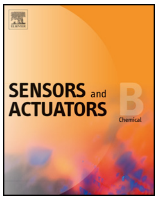

Research Paper

Two-photon fluorescent probe for lysosome-targetable hypochlorous acid detection within living cells

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ABSTRACT

The design of robust tools for hypochlorous acid (HClO) detection at subcellular level is highly desired for the better understanding of its biological function in cellular signaling pathways. Herein, we report the development of a two-photon fluorescent probe (TPFP) for lysosome-targetable HClO detection through the integration of a lysosome-targetable group (aminoethyl)morpholine, two-photon fluorophore 1,8-naphthalimide and HClO capturing phenyl-thiourea together. In the presence of HClO, the thiourea moiety is oxidized to urea and thereby restores the fluorescence of 1,8-naphthalimide(at 538 nm) due to the inhibition of photo-induced electron transfer (PET) effect. As is demonstrated in the spectroscopic characterizations, the probe **TPFP** exhibits excellent probing performance toward HClO, including short response time (<30 s), outstanding selectivity, high photostability and low detection limit (~5.7 nM). In addition, it is confirmed that **TPFP** displays promising cell-membrane permeability and high specificity toward HClO in lysosomes through the one-photon and two-photon intracellular fluorescent microscopic imaging experiments. As a consequence, this lysosome-targetable two-photon fluorescent probe provides a promising platform for HClO detection at subcellular level and would inspire the design of plummy tools for other analytes detection.

1. Introduction

Reactive oxygen species (ROS), such as HO$^\bullet$, H_2O_2, $HClO/ClO^-$, $^1O_2$, are a class of important oxygen-containing molecules which mediate redox modifications of a variety of biomolecules, and they have aroused considerable attention due to their significant roles in many physiological and pathological processes, for example, neuronal aging and anti-inflammation regulation [1–3]. Among various ROS, endogenous hypochlorous acid ($HClO/ClO^-$), which is produced mainly from chloride ions and hydrogen peroxide through a heme enzyme myeloperoxidase (MPO)-catalyzed reaction [4,5], acts as an extremely formidable oxidant in the innate immune systems and plays an important role in killing a wide range of pathogens [6]. However, the aberrant production or accumulation of $HClO/ClO^-$ not only is associated with various diseases including Alzheimer's disease, neuronal apoptosis and rheumatoid arthritis [5,7–11], but also can lead to downstream generation of reactive nitrogen species and other ROS, which will cause cell injury by nitration, chlorination or oxidation of biomolecules [12]. Thus, it is significant to maintain the concentration of $HClO/ClO^-$ at an appropriate level as well as to study its distribution in different organelles. Nevertheless, some characteristics of $HClO/ClO^-$, such as strong oxidization, short-lived time and relatively low concentration, lead to tremendous difficulty in monitoring $HClO/ClO^-$ at the subcellular level [13]. Consequently, it is urgent and challenging to build revolutionary tools for the detection of $HClO/ClO^-$ at subcellular level.

So far, several methods have been developed for $HClO/ClO^-$ detection including atmospheric pressure ionization mass spectrometry (API-MS) [14,15], liquid chromatography-mass spectrometry (LC–MS) [16], ultraviolet absorption spectrum [17] and ion chromatography [18,19]. Even though these methods can provide analytical results of a great sensitivity and selectivity, they are not suitable for *in situ* and real-time sensing in living biosystems (e.g.,

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Sensitive electrochemical sensing platform for microRNAs detection based on shortened multi-walled carbon nanotubes with high-loaded thionin

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ABSTRACT

The loading capacity of thionin (Thi) on shortened multi-walled carbon nanotubes (S-MWCNTs) and acidified multi-walled carbon nanotubes (A-MWCNTs) was compared. Two DNA probe fragments were designed for hybridization with microRNA-21 (miR-21), the microRNAs (miRNAs) model analyte. DNA probe 1 (P1) was assembled on Au nanoparticles (AuNPs) modified electrode. MiR-21 was captured by the pre-immobilized P1. A signal nanoprobe was synthesized by loading large amount of Thi on S-MWCNTs with covalently bonded probe 2 (P2). Owing to the large effective surface area of MWCNTs, fast electron shuttle of MWCNTs, high-loaded Thi on S-MWCNTs, and the increased conductivity from AuNPs, after signal probe hybridized with miR-21, it gave rise to a magnified current response on electrode. The increased electrochemical current enabled us to quantitatively detect miR-21. Expensive bioreagents and labeled target/detection DNA or miRNAs were avoided in this strategy. The operation complexity and assay cost were also reduced.

1. Introduction

Enzyme-free electrochemical biosensor based on the signal amplification of nanomaterials for the detection of microRNAs (miRNAs) has made great progress (Zhu et al., 2017; Dong et al., 2012; Wu et al., 2013). Zhu et al. used MoS_2 nanosheet functionalized with thionin (Thi) and gold nanoparticles to detect microRNA-21 (miR-21) with high sensitivity (Zhu et al., 2017). The magnetic nanoparticles loaded with DNA probes and Thi/Fc as signal indicators were used for simultaneous detection of microRNA-14 and microRNA-21 (Yuan et al., 2017). Although the detection limits reported by many of these works were not as low as that of the enzyme-based amplification strategies (Zhang et al., 2016; Kilic et al., 2012; Li et al., 2016). But, these methods have their merits such as simplicity, stability, high sensitivity, rapid response, and low cost.

Multiwalled carbon nanotubes (MWCNTs) have been widely employed in the construction of electrochemical biosensors (Li and Lee, 2017; Saeedfar et al., 2017). It was reported that the inner surface of MWCNTs was hardly utilized because ions or electrolytes were not easy to reach the inner pore surface (Song et al., 2010). Therefore, shortened MWCNTs or short MWCNTs were studied (Song et al., 2010; Lu et al., 2005; Centi et al., 2009). They exhibited more open ends and defects than long MWCNTs, which was favorable for allowing active species to reach their inner pore surface.

The self-assembly of DNA monolayers on electrodes is of great interest for developing DNA-based electrochemical sensor (Kaplan et al., 2017; Yuan et al., 2017; Tian et al., 2018). Despite great progress achieved in this field, the reproducibility of electrochemical signals and signal amplification via nano/microstructures is still a challenge. Furthermore, owing to the local aggregation, the uncontrollable interprobe distance and heterogeneity of preassembled DNA monolayers is unfavorable for the reproducibility of the signals (Josephs and Ye, 2012a, 2012b). Thus, many groups are still working on developing new protocols and strategies for assembling homogeneous DNA monolayer. It was reported that valid spaces between DNA probe could eliminate steric impedance and electrostatic repulsion (Pei et al., 2010; Peterson et al., 2001), and low probe density was helpful for electrochemical signal amplification. Therefore, a proposed insertion method, in which DNA probe was inserted into an alkane monolayer at lower surface density, has the above-mentioned advantages (Yang et al., 2014; Deng et al., 2017a). But, the probe assembling was still time-consuming. Then, it was found that a constant potential of + 0.4 V was applied for probe assembling, the optimized assembling time was just 500 s (Cui et al., 2015). To combine these two advantages, we proposed a

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Ultra-rapid fabrication of highly surface-roughened nanoporous gold film from AuSn alloy with improved performance for nonenzymatic glucose sensing

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ABSTRACT

Using one-step anodization strategy, a nanoporous gold film (HNPG) with large surface area was rapidly fabricated on $Au_{80}Sn_{20}$ (wt%) alloy in just 80 s. The formation of highly surface-roughened nanoporous structures results from a complex process of electrochemical dealloying of Sn component from AuSn alloy, anodic electrodissolution, disproportion and deposition of Au component, and spontaneous redox reaction between electrodissolved Sn^{2+} and $AuCl_4^-$ species at the applied anodic potential. As-prepared HNPG/AuSn shows enhanced electrochemical performance for glucose oxidation in alkaline electrolyte. At a low potential of 0.1 V (vs. SCE), it offers a short response time of 4 s, a wide linear detection range of 2 μM to 8.11 mM, an ultralow detection limit of 0.36 μM (S/N = 3), an ultrahigh sensitivity of 4374.6 $\mu A\,cm^{-2}\,mM^{-1}$, and satisfactory selectivity and reproducibility. Specifically, after 6 weeks, no obvious loss of glucose amperometric signal was observed on HNPG/AuSn. The facile preparation and excellent sensing performance of HNPG/AuSn electrode make sure that it is a promising candidate for advanced enzyme-free glucose sensors.

1. Introduction

Due to the remarkable catalytic/electrocatalytic activity, unique optical property, rapid electron transport, good chemical stability and biocompatibility, nanoporous gold (NPG) is the most popular materials among porous metals materials system and widely used in catalysis/electrocatalysis (Wittstock et al., 2010; Zhang and Ding, 2013), sensing (Zheng et al., 2013), surface enhanced Raman scattering (SERS) (Qi et al., 2013), etc. NPG with high surface area are attractive for electrochemical sensing application, e.g. nonenzymatic glucose sensing, because high surface area can effectively improve the detection sensitivity, anti-interference and anti-biofouling, even in the presence of excessive Cl^- ions (Patel et al., 2013; Jeong and Kim, 2014; Farghaly et al., 2016).

Templating, dealloying and electrochemical methods are the main strategies to fabricate NPG, among which electrochemical method is the most efficient and convenient one (Collinson, 2013; Zheng et al., 2013). For example, using an electrochemical co-alloying/dealloying strategy, NPG films can be obtained by multi-cyclic voltammetric scanning of Au in a mixed electrolyte of $ZnCl_2$/benzyl alcohol (Jia et al., 2007), $ZnCl_2$/dimethyl sulfoxide (Dong and Cao, 2009), $ZnCl_2$/ethylene glycol (Lu et al., 2015) or $ZnCl_2$/ionic liquids (Jiang et al., 2013) under an elevated temperature. Using an anodic oxidation method to form gold oxides with followed chemical/electrochemical reduction, NPG films can be prepared by applying relatively high anodic potentials on Au substrate in oxalate-containing solution (Nishio and Masuda, 2011; Xu et al., 2013), citric acid (Jeong and Kim, 2014) or other carboxylic acids solution (Nishio and Masuda, 2010), phosphate buffer solution (Zhao et al., 2006) or H_2SO_4 solution (Sukeri et al., 2015). Using square wave voltammetry technique, nanoporous structures can be fabricated on Au in NaOH (Huang et al., 2009) or H_2SO_4 (Zhong et al., 2015) solution accompanying with the evolution of gas bubbles as template. Above all,

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Bis(methoxypropyl) ether-promoted oxidation of aromatic alcohols into aromatic carboxylic acids and aromatic ketones with O_2 under metal- and base-free conditions†

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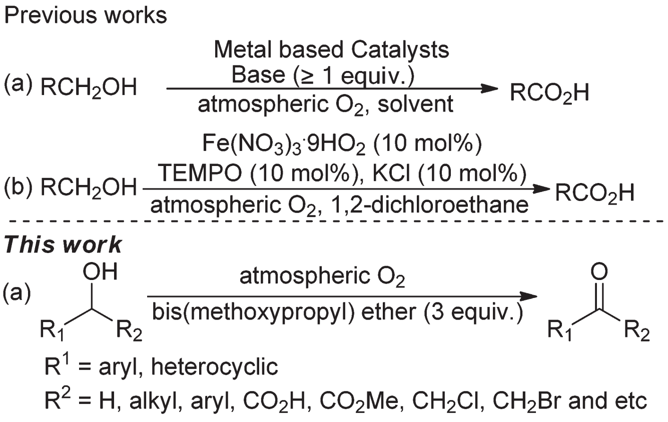
We describe an eco-friendly, practical and operationally simple procedure for the bis(methoxypropyl) ether-promoted oxidation of aromatic alcohols into aromatic carboxylic acids and aromatic ketones with atmospheric dioxygen as the sole oxidant. This chemical process is clean with high conversion and good selectivity, and an external initiator, catalyst, additive and base are not required. The virtue of this reaction is highlighted by its easily available and economical raw materials and excellent functional group tolerance (acid-, base- and oxidant-labile groups).

Introduction

The selective oxidation of alcohols into carboxylic acids and ketones is one of the most fundamental chemical processes in the chemical industry and a challenging task in the realm of green organic synthesis.[1] Generally, toxic and expensive (super)stoichiometric quantities of inorganic or organic oxidants[2] are employed to achieve this chemical transformation, which would lead to an environmental burden due to the generation of a large amount of chemical waste. Compared with traditional oxidants, molecular oxygen[3] is perfect for incorporation into organic molecules because of its low cost, natural abundance and eco-friendly advantages.[1a,4]

Many impressive achievements have been accomplished in base-promoted[5] noble metal–ligand complex (Ni,[6] Ag,[7] Pt,[8] Rh,[9] Ru,[10] and Pd[11]) and commercially unavailable supported-metal catalyst[12] catalyzed oxidation of alcohols with molecular oxygen (Scheme 1a). Although these improved protocols revealed remarkable characteristics, all the processes show the need for two-step operation procedures (oxidation and acidification), noble metal catalysts and (super)stoichiometric amounts of strong bases to facilitate the oxidation reaction, which not only leads to environmental pollution problems and high manufacturing cost but also hampers subsequent direct transformations. In 2016, Ma's group developed the oxidation of alcohols catalyzed by $Fe(NO_3)_3{\cdot}9H_2O$/TEMPO/KCl concertedly in 1,2-dichloroethane (Scheme 1b).[13] However, to our knowledge, there exists no example of metal- and base-free oxidation of alcohols into carbonyl compounds with atmospheric oxygen. With our continuing interest in green organic synthesis,[14] we herein present a practical and eco-friendly bis(methoxypropyl) ether-promoted oxidation of aromatic alcohols into aromatic carboxylic acids and aromatic ketones with atmospheric dioxygen as the sole oxidant under catalyst- and base-free conditions.



Scheme 1 Oxidation of aromatic alcohols with atmospheric oxygen.

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Ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions†

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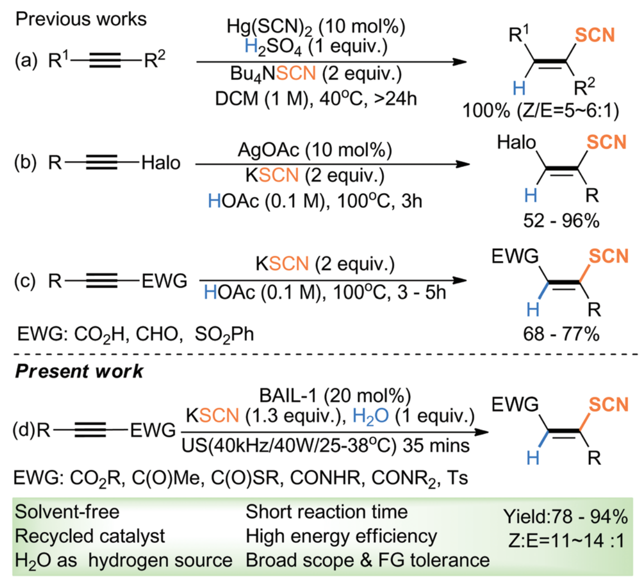
By using water as the hydrogen source, an eco-friendly and practical protocol for the synthesis of *Z*-vinyl thiocyanates through ultrasound-promoted Brønsted acid ionic liquid-catalyzed hydrothiocyanation of activated alkynes under minimal solvent conditions has been developed. This process effectively avoids the use of organic solvents, metal catalysts and harsh reaction conditions. This reaction shows attractive characteristics such as operational simplicity, broad substrate scope with good to excellent yields, ease of scale-up and high energy efficiency and recyclable and reusable catalysts.

Introduction

Sulphur-containing organic compounds are extremely valuable because of their abundance in numerous natural products, pharmaceuticals and agrochemicals.[1] Among them, organic thiocyanates not only display a variety of biological activities but also serve as versatile building blocks and synthetic intermediates in organic synthesis.[2] Over the past few decades, many impressive achievements have been made in the preparation of alkyl and aromatic thiocyanates.[2a,b,3] However, the construction of vinyl thiocyanates,[4] especially for thermodynamically unfavored *Z* isomers has rarely been achieved. A conventional method for the preparation of vinyl thiocyanates is the nucleophilic substitution of vinyl halides with thiocyanate salts.[5] However, the pre-installation of a halogen atom at an expected position remains a formidable challenge. In 1985, Cousseau first reported the synthesis of vinyl thiocyanates through Hg(II)-catalyzed thiocyanation of alkynes with Bu_4NSCN and H_2SO_4 in dichloromethane (Scheme 1a).[6] However, this strategy suffers from the usage of toxic metal catalysts, the limitations of the substrate scope, low atom economy and *Z*/*E* selectivity. Jiang and Wu reported silver-catalyzed thiocyanation of haloalkynes with KSCN at 100 °C in acetic acid to give *Z*-vinyl thiocyanates (Scheme 1b).[7] Maddi Sridhar Reddy treated electron-deficient alkynes with KSCN at 100 °C in acetic acid to form *Z*-vinyl thiocyanates.[8] Although these methods are representative of considerably advanced methods, both approaches employed a large amount of acetic acid as the reaction medium and a hydrogen source as well as a high temperature to facilitate the hydrothiocyanation, which requires an excess amount of an inorganic base to neutralize the acidic solution leading to not only environmental issues



Scheme 1 Synthesis of *Z*-vinyl thiocyanates.

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Switchable single fluorescent polymeric nanoparticles for stable white-light generation†

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The development of switchable white-light emitters is extremely challenging but urgently needed for various applications. We describe a class of switchable fluorescent polymeric nanoparticles (SFPNs) that can alternate their emission color among stable white, cyan, or pink. These SFPNs consist of a dye with cyan-light emission and a spiropyran (SP) derivative with photochromism. When the SP derivative is transferred to its merocyanine state, fluorescence resonance energy transfer (FRET) occurs from the cyan dye to the merocyanine one. In a rational design of transfer efficiency, a stable white-light emission is achieved. This white-light emission can be switched to the cyan-light one upon photoirradiation or pink-light one by solvent-induced swelling. Such multi-color fluorescent alternation is reversible and therefore allows for data encryption. Because of the facile synthesis, excellent long-term stability, fast photo-responsibility, high-contrast fluorescence, and outstanding switchability of these nanoparticles, we envision that they should have great potential in various applications such as high-resolution imaging, white luminescence, and data encryption.

1. Introduction

Fluorescent polymeric nanoparticles (FPNs) have been attracting more and more attention due to their potential in a wide range of applications, including encryption, data storage, imaging, illumination, *etc.*[1–5] They are normally made from conjugated polymers or polymer matrices embedding small dye molecules and providing fairish flexibility for processing.[6] In these nanoparticles, the fluorescent molecules are shielded from the environment or each other to prevent undesired aggregation.[7,8] When more than one kind of fluorophore molecules are embedded together in the nanoparticles, the emission color can be flexibly tuned by varying the dyes and their combinational ratios.[9–11] The emission spectrum is further extended if fluorescence resonance energy transfer (FRET) is designed to occur between embedded dyes.[12–14] In this case, the reversible chromatic molecules are used to switch the FRET process in these FPNs and interesting switching properties can be expected, which would significantly expand the application fields of the materials.[15–20] This strategy has been applied to prepare switchable FPNs (SFPNs) with different fluorescent colors, including pure RGB and even white light – a combination of at least two lights with different wavelengths.[6,21–24] However, the main purpose of this work was mainly focused on acquiring systems with dual emission, generally alternating between green light (energy donor) and red light (energy acceptor), to use them as new tools for live-cell imaging.[6,14,23,24] It is important to note that switchable white-light generation is a demanding target because any unexpected intermolecular FRET and aggregation-caused quenching (ACQ) would shift the emission color.[21,25–27] When a subtle design is required to get white-light emission in various material systems, such as small organic molecules, conjugated polymers, metal complexes, carbon dots, and quantum dots, SFPNs show an intrinsic advantage for this purpose through color combination due to their isolation effect and efficient FRET process.[28–35] In a system with a 1,2-dithienylethene derivative as the switchable acceptor, transient white-light emission was observed when the emission was turned from blue to yellow by the isomerization of the acceptor.[22] Similar isomerization was also applied to generate SFPNs with RGB. By rational combinations, these RGB nanoparticles can be used to generate switchable and stable white-light emission.[21] In this case, however, three kinds of nanoparticles are required in a single sample to tune the emission color, which hinders their applications in the fields where high resolution is essential.[36] To the best of our knowledge, single SFPNs that can generate stable white-light emission have not been developed yet. Herein, we describe our effort to prepare these types of SFPNs.

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Electron Transfer and Geometric Conversion of Co−NO Moiety in Saddled Porphyrins: Implications for Trigger Role of Tetrapyrrole Distortion

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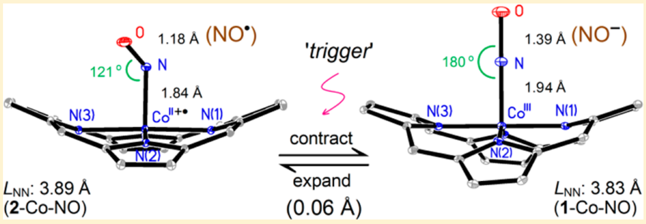
Supporting Information

ABSTRACT: The electrons of NO and Co are strongly delocalized in normal {Co-NO}^{8} species. In this work, {Co-NO}^{8} complexes are induced to convert from $(\mathrm{Co^{II}})^{+\bullet}$−NO$^{\bullet}$ to Co$^{\mathrm{III}}$−NO$^-$ by a core contraction of 0.06 Å in saddled cobalt(II) porphyrins. This intramolecular electron transfer mechanism indicates that nonplanarity of porphyrin is involved in driving conversion of the NO units from electrophilic NO$^{\bullet}$ as a bent geometry to nucleophilic NO$^-$ as a linear geometry. This implies that distortion acts as a trigger in enzymes containing tetrapyrrole. The electronic behaviors of the Co$^{\mathrm{II}}$ ions and Co−NO moieties were confirmed by X-ray crystallography, EPR spectroscopy, theoretical calculation, UV−vis and IR spectroscopy, and electrochemistry.



1. INTRODUCTION

Nitric oxide (NO)[1,2] is responsible for transmitting important signals and regulating cellular functions in the human body. Nitric oxide and nitroxyl anion (NO$^-$) are physiologically important heart modulators.[3,4] However, the biological effects of NO and NO$^-$ can differ significantly from each other. Pharmacological studies have shown that the effects of NO$^-$ are distinct from those of NO.[5] Moreover, the signaling pathway of NO$^-$ is different from those of NO.[6] Bioassay discrimination between NO and NO$^-$ is still problematic, and definitively resolving this issue is extremely difficult.[3,4,7]

The macrocyclic distortion is a conserved feature of particular proteins containing heme,[8,9] vitamin B$_{12}$,[10] or chlorophylls,[11,12] and nonplanarity is crucial in tetrapyrrole chemistry. The capture, generation, or conversion of NO and NO$^-$ can hardly work without nitric oxide synthase[13] or nitric oxide reductase[14] under normal physiological conditions. Most of two types of enzymes contain natural tetrapyrroles, e.g., heme cofactors, participating in each of these processes,[12,14] which indicates that distortion greatly influences functions of these enzymes and redox properties of nitrosyl ligands.

Distorted tetrapyrroles needed for a variety of biological functions can both stabilize the low-valent oxidation state of metal species and generate relevant high-valent complexes such as the iron(II)− and iron(IV,V)−oxo species in heme,[15] or the cobalt(I) and cobalt(III) complexes in vitamin B$_{12}$.[16] Recently, we showed that the core contraction derived from the ruffling or saddling deformations of porphyrin rings can induce structural conversions of coordinated Fe$^{\mathrm{III}}$,[17−19] Co$^{\mathrm{II}}$,[20,21] Cu$^{\mathrm{II}}$,[22] and Zn$^{\mathrm{II}}$.[23] For materials containing Fe$^{\mathrm{III}}$ and Co$^{\mathrm{II}}$ ions with unpaired electron(s), such a size contraction also increases the spin density in the d_{z^2} orbital and excites the d_{z^2} electron to generate π-cation radicals, without the need for any environmental changes.

Binding to small molecules, e.g., NO, is universal to all proteins containing heme or corrin.[24] In this work, we investigated whether an intramolecular electron transfer (ET), not the general electron delocalization, in {Co-NO}^{8} complex can occur in the presence of NO as noninnocent ligands.[25] This will provide a novel avenue for better understanding how the heme or corrin conformation affects the electronic structures of metal ions and the resulting intramolecular ET.[26] The conversion of cobalt ions and NO units in {Co-NO}^{8} complex can be proven or supported by the macrocycle core size, the bond parameters of the Co−NO moiety, the binding geometry of the axial NO, and orbital energy levels. Here, four 5,10-15,20-distrapped cobalt(II) porphyrins, **1**-Co to **4**-Co (Scheme 1), with successive saddled distortions, were synthesized and characterized to determine the conformational driving effect of this macrocyclic deformation on the axial NO.

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An unprecedented water stable acylamide-functionalized metal–organic framework for highly efficient CH_4/CO_2 gas storage/separation and acid–base cooperative catalytic activity†

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The high porosity, excellent water stability and optimized supramolecular host–guest interactions of MOFs are the three key factors for their potential practical applications in many important areas including gas storage/separation, catalysis and so on. In this study, we designed and constructed a highly porous (3, 36)-connected *txt*-type acylamide-functionalized metal–organic framework (HNUST-8) from a pyridine-based acylamide-linking diisophthalate and dicopper(II)-paddlewheel clusters. Interestingly, HNUST-8 possesses an exceptionally water-stable framework with a high BET surface area of about 2800 $m^2\ g^{-1}$. At 298 K, HNUST-8 exhibits a high excess CO_2 uptake of 19.7 mmol g^{-1} at 40 bar, an excellent total CH_4 storage capacity of 223 cm^3(STP) cm^{-3} with a large working capacity of 178 cm^3(STP) cm^{-3} at 80 bar, as well as highly efficient CO_2/CH_4 and CO_2/N_2 separation under dynamic conditions at 1 bar. Moreover, with the Lewis acidic open copper(II) sites and Lewis basic acylamide groups integrated into the framework, HNUST-8 demonstrates efficient catalytic activity as an acid–base cooperative catalyst in a tandem one-pot deacetalization–Knoevenagel condensation reaction.

1. Introduction

Metal–organic frameworks (MOFs), a unique class of crystalline materials constructed from metal ions or clusters and multidentate organic linkers, have garnered tremendous attention from academia and industry for the past two decades owing to their intrinsic porosity[1] and numerous potential applications in many important areas, *i.e.* gas storage[2]/separation,[3] heterogeneous catalysis,[4] luminescence,[5] proton conductivity,[6] *etc*. Owing to the modularity of both organic and inorganic moieties, a series of landmark MOF materials with ultra-high experimental BET surface area (exceeding 5000 $m^2\ g^{-1}$) have been successfully obtained under the concept of reticular chemistry so far.[7] However, the relatively low stability of many highly porous MOFs in water or other harsh conditions (such as aqueous acid/base and coordinating anions) has considerably limited their practical applications.[8] Therefore, how to design and construct highly porous MOFs with excellent hydrostability is of fundamental importance in MOF chemistry, and a great deal of effort has been made to achieve this goal:[8,9] (i) strengthening the metal–ligand coordination bonds by judicious selection of metal ions/clusters and organic linkers according to Pearson's hard/soft acid/base (HSAB) principle, (ii) designing hydrophobic surfaces or interfaces, (iii) narrowing the pores through interpenetration or catenation, and so on.

Besides high porosity and excellent hydrostability, it has been well demonstrated that the optimized interactions/affinities between guest molecules and frameworks is also crucial for realizing high-performance MOF materials toward the abovementioned applications.[10] Various approaches have been employed to effectively increase the host–guest interactions in MOFs, including incorporating high-density open metal sites (OMSs),[11] grafting functional polar groups onto framework backbones,[12] impregnating metal ions,[13] contraction of interior pores,[14] *etc*. It must be noted that, although a certain quantity of MOFs with high specific surface area, excel-

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† Electronic supplementary information (ESI) available: TGA, IR, ^1H NMR, gas sorption/separation and crystallographic data (CIF). CCDC 1581346. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8qi00662h

Synthesis of 2-(1-oxo-2,3-dihydro-1*H*-pyrrolizin-2-yl)-2-(aryl)acetonitrile derivatives *via* Michael addition of trimethylsilyl cyanide

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Several 2-aryl-2-(1-oxo-2,3-dihydro-1*H*-pyrrolizin-2-yl)acetonitrile derivatives were synthesised by Michael addition of (*E*)-2-arylidene-2,3-dihydro-1*H*-pyrrolizin-1-ones with trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride in moderate yields. The structures of all of the products were fully characterised by NMR, IR and high-resolution mass spectrometry, together with X-ray crystallographic analysis.

Keywords: pyrrolizin-1-one, Michael addition, trimethylsilyl cyanide, tetrabutylammonium fluoride

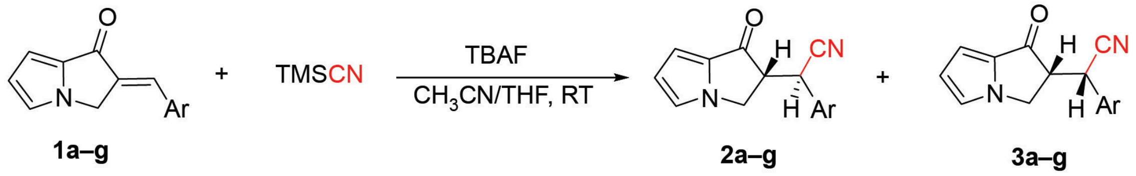
The pyrrolizinones are a frequently encountered structural motif in many pharmacologically relevant alkaloids.[1] Their derivatives show a broad spectrum of biological activities, including antitubulin,[2] analgesic,[3] antitumour,[4] neurokinin-1 (NK1) antagonist activity,[5] anti-inflammatory[6] and psychostimulant activity.[7]

Nitrile is a valuable functional group in medicinal coordination chemistry and organic synthesis.[8–9] It can be transformed easily into other important functional groups such as ester, aldehyde, carboxylic acid, ketone, amide, amine and tetrazole.[10] Trimethylsilyl cyanide (TMSCN) is a better cyanide source than others such as sodium cyanide (NaCN) and tetrabutylammonium cyanide (Bu_4NCN), with the advantages of it being readily available, easy to handle and possessing high activity.[11]

In continuation of our work on the synthesis of nitrile derivatives[12–14] and pyrrolizine derivatives,[15,16] in this paper we report the synthesis of 2-aryl-2-(1-oxo-2,3-dihydro-1*H*-pyrrolizin-2-yl)acetonitrile derivatives by the reaction of (*E*)-2-arylidene-2,3-dihydro-1*H*-pyrrolizin-1-ones with TMSCN in the presence of tetrabutylammonium fluoride (TBAF) *via* a Michael addition pathway (Scheme 1).

Results and discussion

The structures of all compounds **2** and **3** were established by different spectroscopic techniques (NMR, IR) and by high resolution mass spectrometry (HRMS). The HRMS spectrum of **2e** gave the molecular ion peak at *m/z* 251.1178. The IR spectrum of **2e** showed ν_{CN} at 2241 cm^{-1} and $\nu_{C=O}$ at 1692 cm^{-1}. The ^1H NMR



Ar: a, 4-BrC_6H_4; **b**, 4-ClC_6H_4; **c**, 4-FC_6H_4; **d**, 4-$CH_3SC_6H_4$; **e**, 4-$CH_3C_6H_4$; **f**, 3,4,5-$(OCH_3)_3C_6H_2$; **g**, 3,5-$(OCH_3)_2C_6H_3$

Scheme 1 Synthesis of 2-aryl-2-(1-oxo-2,3-dihydro-1*H*-pyrrolizin-2-yl)acetonitrile derivatives.

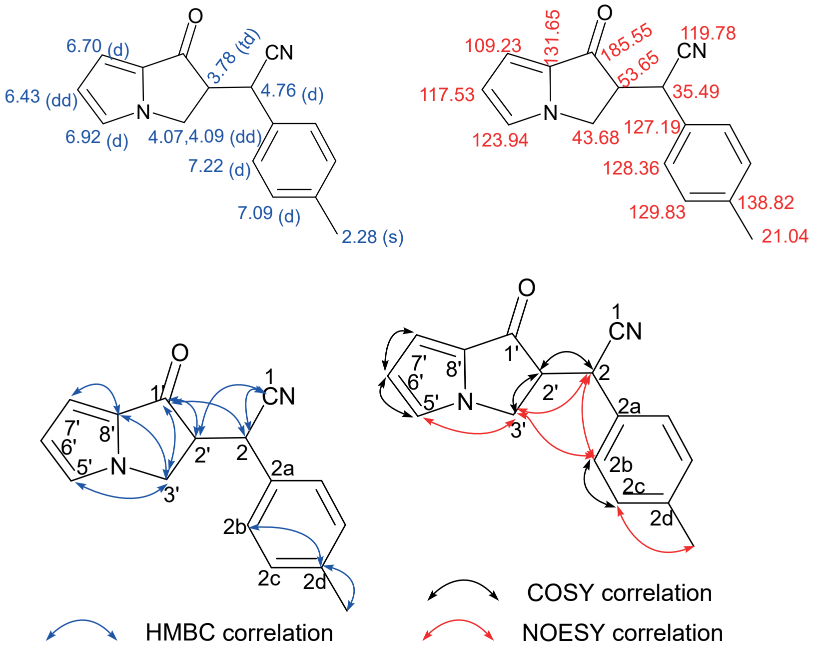


Fig. 1 2D-NMR correlations and ^1H and ^{13}C NMR chemical shifts of **2e**.

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Full Length Article

Room temperature Zinc-metallation of cationic porphyrin at graphene surface and enhanced photoelectrocatalytic activity

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ABSTRACT

A stable zincporphyrin functionalized graphene nanocomposite was prepared by using positively charged cationic porphyrin (5,10,15,20-tetra(4-propyl pyridinio) porphyrin, TPPyP) and successive reduced graphene oxide (rGO) with tuned negative charge. The nanocomposite preparation was accompanied first by distinct electrostatic interactions and π-π stacking between TPPyP and rGO, and followed by fast Zinc-metallation at room temperature. In contrast to free TPPyP with Zn^{2+}, the incorporation reaction is very slow at room temperature and heating or reflux conditions are required to increase the metallation rate. While at the surface of rGO nanosheet, the Zinc-metallation of TPPyP was greatly accelerated to 30 min at 25 °C in aqueous solution. The interaction process and composites formation were fully revealed by significant variations in UV–vis absorption spectra, X-ray photoelectron spectra (XPS) measurements, atomic force microscope (AFM) images, and fluorescence spectra. Furthermore, photoelectrochemical activity of resultant rGO/TPPyP-Zn nanocomposites was evaluated under visible-light irradiation, and enhancement of the photoelectrocatalytic reduction of CO_2 was achieved.

1. Introduction

Porphyrins and metalloporphyrins derivatives have been widely regarded as excellent light harvesting materials [1,2]. Their unique photophysical and electrochemical properties including various electron transfer and catalytic reactions are tunable by varying the meso-functional groups and central metal ions [3–5]. For example, there are iron porphyrin in heme for oxygen transport in the bloodstream of mammals and magnesium chlorin in chlorophyll as a light driven proton pump [6]. The crucial central metal in metalloporphyrins is closely related to their versatile functionalities such as photosynthesis, photodynamic therapy, photoelectrical devices and etc [7,8]. However, the metallation of free base porphyrin at room temperature is very slow, e.g. their complex rate is several orders of magnitude lower than open–chain ligand o-phenathroline with bivalent metal ions [9]. In order to avoid heating or reflux at high temperature, several attempts have been made to accelerate the formation of metalloporphyrins, such as enzymes-catalyzed metal ions insertion [10], cyclodextrin/porphyrin inclusion complex with Zn^{2+} ion [11], graphene/porphyrin supermolecular assembly with Cd^{2+} ion [12], surface chemical reaction at the solid-vacuum interface around room temperature [13,14]. Therefore, numerous artificial assemblies and sensors based on porphyrins have been designed under mild conditions.

Graphene, a monolayer of carbon atoms in 2-D honeycomb lattice, is regarded as one of the most promising catalyst support due to its huge specific surface area and remarkable electron transfer ability [15,16]. Especially, the organization of porphyrins onto graphene surface via covalent or noncovalent interaction has attracted significant interest recently [17]. It was found that the formation of porphyrin-graphene nanohybrids to yield donor-acceptor system could create synergistic effect and provide more efficient photoinduced electron transfer, which significantly enhances the photo/electro-catalytic activity [18,19]. Chen's group first prepared an organic soluble graphene hybrid material with excellent optical limiting property, in which porphyrin was covalently bonded to graphene oxide by the amide linkage [20]. Xu and Geng et al. reported the noncovalent functionalization of graphene with free-based porphyrins and metalloporphyrins [12,21]. Porphyrins were found to be noncovalently assembled onto the surface

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0169-4332/

JOURNAL OF CHEMICAL RESEARCH 2018 VOL. 42 DECEMBER, 631–635 **RESEARCH PAPER** 631

Synthesis of spiro[cyclopent-2/3-ene-1,2'-[1,3]thiazolo[3,2-*a*] pyrimidine] derivatives *via* 1,3-dipolar cycloaddition reaction of ethyl buta-2,3-dienoate

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The 1,3-dipolar cycloaddition reaction of ethyl (2*Z*)-5-aryl-2-(2-methoxy-2-oxoethylidene)-7-methyl-2,3-dihydro-5*H*-thiazolo[3,2-*a*] pyrimidine-6-carboxylate and ethyl buta-2,3-dienoate catalysed by triphenylphosphine afforded novel spiro[cyclopent-2-ene-1,2'-[1,3] thiazolo[3,2-*a*]pyrimidine] and spiro[cyclopent-3-ene-1,2'-[1,3]thiazolo[3,2-*a*]pyrimidine] derivatives in moderate yields. The structures of all the products were characterised thoroughly by NMR, IR and HRMS together with X-ray crystallographic analysis.

Keywords: 1,3-dipolar cycloaddition, thiazolo[3,2-*a*]pyrimidine, ethyl buta-2,3-dienoate, triphenylphosphine

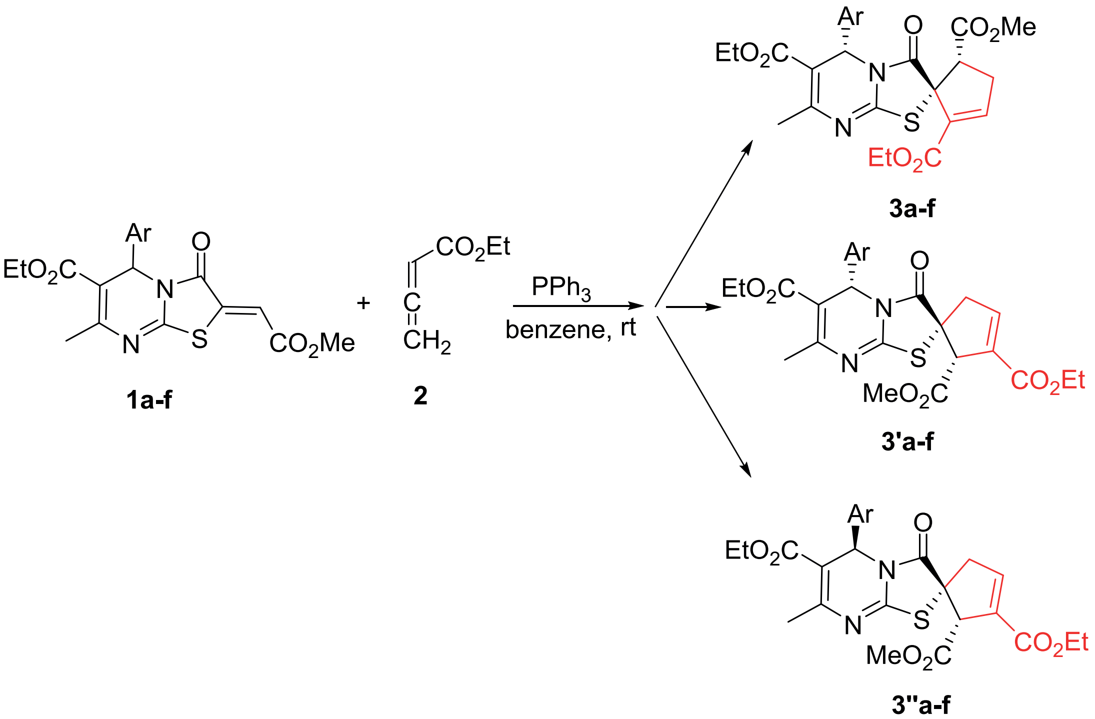
The thiazolo[3,2-*a*]pyrimidine nucleus is a key chemical building block for numerous pharmacological compounds that display a diverse range of biological activities such as anti-inflammatory,[1] antihypertensive,[2] anti-HIV,[3] antiviral,[4] antifungal,[5] antibacterial,[6] antitumour[7] and 5-HT2a receptor antagonistic activities.[8]

Spiroheterocycles are good targets for drug candidates and clinical pharmaceuticals,[9,10] and are important motifs in many biologically active natural products.[11] The 1,3-dipolar cycloaddition of exo-cyclic electron-deficient olefins with 1,3-dipoles generated from phosphines and but-2-ynoates or buta-2,3-dienoates is a feasible method to synthesis spiroheterocycle compounds.[12,13]

In continuation of our work[14–20] on the synthesis of heterocycles, we now report the synthesis of spiro[cyclopent-2-ene-1,2'-[1,3] thiazolo[3,2-*a*]pyrimidine] and spiro[cyclopent-3-ene-1,2'-[1,3] thiazolo[3,2-*a*]pyrimidine] derivatives by the 1,3-dipolar cycloaddition reactions of ethyl buta-2,3-dienoate with ethyl (2*Z*)-5-aryl-2-(2-methoxy-2-oxoethylidene)-7-methyl-2,3-dihydro-5*H*-thiazolo[3,2-*a*]pyrimidine-6-carboxylate (Scheme 1).

Results and discussion

The structures of all compounds **3, 3'** and **3''** were established by different spectroscopic techniques (NMR and IR) and HRMS. The high-resolution mass spectrum of **3e** gave the molecular ion peak at *m/z* 513.1690. The IR spectrum of **3e** showed $\nu_{C=O}$ at 1749, 1726 and 1709 cm^{-1}. The ^{1}H NMR spectrum of **3e** revealed: two triplets at δ 1.16 (*J* = 7.0 Hz) and δ 1.24 (*J* = 7.0 Hz) assigned for two $-CH_2\underline{CH_3}$ respectively; three singlets at δ 2.32, 2.51 and 3.20 assigned for $-Ph\underline{CH_3}$, 7'-CH_3 and $-CO_2\underline{CH_3}$; two doublet of doublets at δ 2.75 (*J* = 19.0, 8.0, 3.0 Hz) and 3.03 (*J* = 19.0, 9.0, 2.0 Hz) assigned for two H-4; a triplet at δ 3.92 (*J* = 9.0 Hz) assigned for H-5; a quartet at δ 4.06 (*J* = 7.0 Hz) assigned for $-\underline{CH_2}CH_3$; a multiplet at δ 4.16-4.23



Ar: a, C$_6$H$_5$; **b,** 4-ClC$_6$H$_4$; **c,** 4-FC$_6$H$_4$; **d,** 4-CH$_3$SC$_6$H$_4$; **e**, 4-CH$_3$C$_6$H$_4$; **f**, 4-BrC$_6$H$_4$

Scheme 1 Synthesis of spiro[cyclopent-2/3-ene-1,2'-[1,3]thiazolo[3,2-*a*]pyrimidine] derivatives.

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Synthesis of 4-aryl-3,4,5,6-tetrahydropyrimido[5,4-*g*]indolizine-2(1*H*)-thione

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A number of 4-aryl-3,4,5,6-tetrahydropyrimido[5,4-*g*]indolizine-2(1*H*)-thiones were synthesised by the reaction of (7*E*)-7-arylidene-6,7-dihydroindolizin-8(5*H*)-one and thiourea in the presence of potassium hydroxide in moderate yields. The structures of all the products were characterised thoroughly by NMR, IR and HRMS together with X-ray crystallographic analysis.

Keywords: indolizine, thiourea, tetrahydropyrimidine

Dihydropyrimidinone derivatives are important compounds that are found in natural products[1] and display a broad range of biological activities, for example, as calcium channel blockers,[2] antihypertensive agents,[3] mitotic kinesin inhibitors,[4] and α-1a-antagonists.[5] Therefore, the synthesis and study of pharmacological properties of compounds containing the dihydropyrimidinone skeleton have attracted the attention of researchers.[6]

The indolizine moiety is an important building block of many biological activities, for example, alkaloids such as (+)-monomorine,[7] kinganone,[8] polygonatines[9] and indolizidine 209D.[10] Currently, this kind of compound has been widely used in biological activities, such as anti-HIV,[11] hypoglycemic,[12] glycogen synthase kinase-3β inhibitors,[13] antitumour,[14] antimicrobial[15] and 5-hydroxytryptamine (5-HT3) receptor antagonists.[16]

In continuation of our work on the synthesis of heterocycle derivatives,[17–20] we now report the synthesis of 4-aryl-3,4,5,6-tetrahydropyrimido[5,4-*g*]indolizine-2(1*H*)-thione derivatives by the reaction of (*E*)-7-arylidene-6,7-dihydroindolizin-8(5*H*)-ones with thiourea in the presence of potassium hydroxide (Scheme 1).

Results and discussion

The structures of all compounds **2a–i** were established by different spectroscopic techniques (NMR and IR) and HRMS. The high-resolution mass spectrum of **2a** gave the molecular ion peak at *m/z* 328.0940. The IR spectrum of **2a** displayed $\nu_{C=S}$ at 1681 cm^{-1}. The ^{1}H NMR spectrum of **2a** revealed: two single signals at δ 8.96 ppm (3-NH) and at δ 9.89 (1-NH); two singlet signals at δ 2.46 ppm ($-SCH_3$) and at δ 4.91 ppm (4-CH); two multiplet signals at δ 1.97–2.03 ppm (5-CH_2) and at δ 2.31–2.36 ppm (5-CH_2); two multiplet signals at δ 3.77–3.82 ppm (6-CH_2) and at δ 3.87–3.92 ppm (6-CH_2); a doublet of doublet at δ 6.01 (dd, J = 3.5, 3.0 Hz, 1H) ppm (9-CH); and two doublets at δ 7.22 (d, J = 8.5 Hz, 2H) ppm (–ArH) and 7.26 (d, J = 8.5 Hz, 2H) ppm (–ArH).

The ^{13}C NMR spectrum of the product **2a** exhibited the presence of $-SCH_3$ carbon at δ 14.68. The signals at δ 24.44, 42.77 and 57.47 are assignable to the carbon of –C5, –C6 and –C4 respectively, The signals at δ 100.77, 105.22, and 107.57 are assignable to the carbon of –C13, –C10 and –C9 respectively, The signals at δ 122.28, 122.50 and 122.69 are assignable to the carbon of –C11, –C12 and –C8 respectively, the presence of –C=S carbon was at δ 173.56. The assignment of all ^{1}H and ^{13}C NMR signal of **2a** were based on 2D NMR (HSQC, HMBC, NOESY and COSY). Some important NOESY and COSY correlations are shown in Fig. 1. The NOESY spectrum of **2a** is shown in Fig. 2. Further, the structure of the product was confirmed by X-ray diffraction analysis of **2b** (Fig. 3).

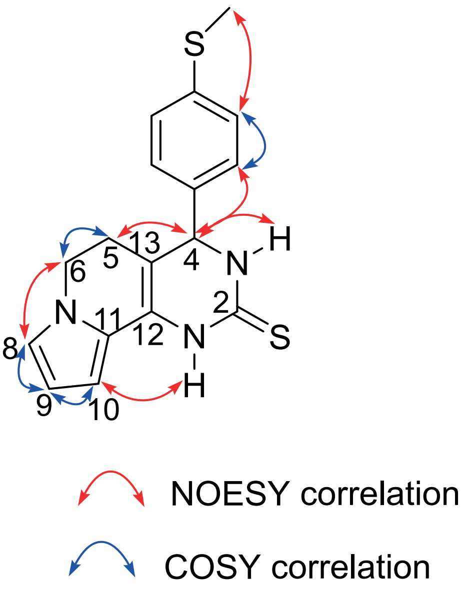
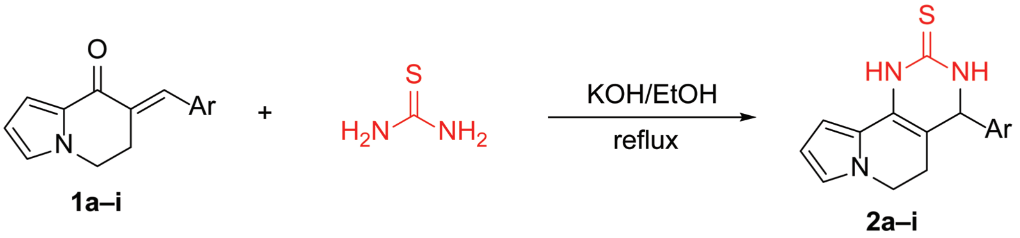


Fig. 1 NOESY and COSY correlations of **2a**.



Ar: a, 4-$SCH_3C_6H_4$; **b,** 4-ClC_6H_4; **c,** 4-BrC_6H_4; **d,** 3,4,5-$(CH_3O)_3C_6H_2$; **e**, 4-FC_6H_4; **f**, 4-$CH_3C_6H_4$; **g**, 2,4-$Cl_2C_6H_3$; **h**, 2-ClC_6H_4; **i**, C_6H_5

Scheme 1 Synthesis of pyrimido[5,4-*g*]indolizine-2(1*H*)-thione derivatives.

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Synthesis of dispiro[indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizine-2′,2″-[1,3] thiazolo[3,2-*a*]pyrimidine *via* cycloaddition reactions

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The 1,3-dipolar cycloaddition reaction of ethyl 5-aryl-2-(2-methoxy-2-oxoethylidene)-7-methyl-3-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*] pyrimidine-6-carboxylate and azomethine ylide, which was generated *in situ* by the reaction of 11*H*-indeno[1,2-*b*]quinoxalin-11-one and L-proline, afforded novel 6″ethyl 1′-methyl 5″aryl-7″methyl-3″oxo-5′,6′,7′,7a′-tetrahydro-1′*H*,3″*H*,5″*H*-dispiro[indeno[1,2-*b*]quinoxaline-11,3′-pyrrolizine-2′,2″-[1,3]thiazolo[3,2-*a*]pyrimidine-1′,6″-dicarboxylates in good yields. The structures of all the products were characterised thoroughly by NMR, IR and HRMS together with X-ray crystallographic analysis.

Keywords: 11*H*-indeno[1,2-*b*]quinoxalin-11-one, thiazolo[3,2-*a*]pyrimidine, spirohetercycle, 1,3-dipolar cycloaddition

1,3-Dipolar cycloaddition is one of the classic methods for the synthesis of five-membered heterocyclic rings.[1] Azomethine ylides, convenient building blocks for the preparation of pyrrolidine, are used extensively in organic synthesis.[2] Azomethine ylides are generally generated by a decarboxylative route from amino acids and isatin or acenaphthenequinone.[3–7] The use of azomethine ylides generated by the reaction of 11*H*-indeno[1,2-*b*]quinoxalin-11-one and amino acids in the synthesis of complicated heterocycle systems has been less explored.[8–10]

Indenoquinoxaline derivatives are an important classes of nitrogenous heterocycles that have been used in dyes and organic semiconductors.[11,12] They also exhibit pharmacological activities such as anti-HIV, anticancer, antiproliferative and cytotoxicity activity.[13–15]

Thiazolo[3,2-*a*]pyrimidine derivatives are an important group of nitrogen-containing heterocycles displaying a broad spectrum of biological activities. For example, as antagonist of 5HT2 serotonin receptors and dopamine D2 receptors,[16,17] antifungal properties,[18] anti-inflammatory properties[19] and CDC25 phosphatase inhibitor activity.[20]

In continuation of our work[21–25] on the synthesis of heterocycles, here we report the synthesis of dispiro[indeno[1,2-*b*] quinoxaline-11,3′-pyrrolizine-2′,2″-[1,3]thiazolo[3,2-*a*] pyrimidine derivatives by the 1,3-dipolar cycloaddition reactions of azomethine ylide, which was generated *in situ* by the reaction of 11*H*-indeno[1,2-*b*]quinoxalin-11-one and L-proline, with ethyl 5-aryl-2-(2-methoxy-2-oxoethylidene)-7-methyl-3-oxo-2,3-dihydro-5*H*-[1,3]thiazolo[3,2-*a*]pyrimidine-6-carboxylates (Scheme 1).

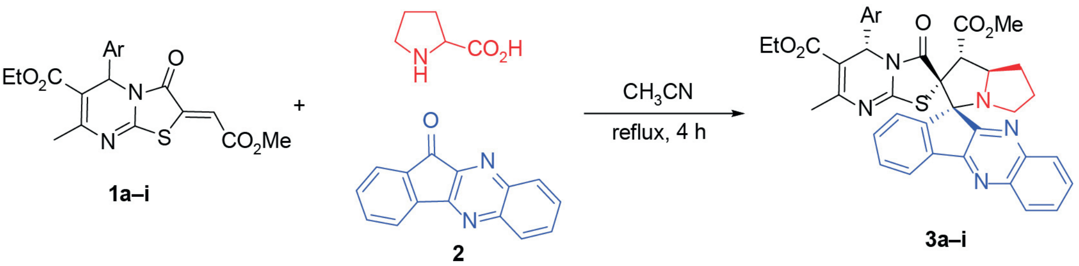
Results and discussion

The structures of all compounds **3** were established by spectroscopic techniques (NMR, IR and HRMS). The HRMS of **3a** gave the molecular ion peak at *m*/*z* 718.2156. The IR spectrum of **3a** displayed $\nu_{C=O}$ at 1744.9 and 1714.6 cm^{-1}. The ^{1}H NMR spectrum of **3a** revealed a triplet at δ 1.02 ppm (J = 7.0 Hz, $-CH_2\underline{CH_3}$), four singlets at δ 2.35, 2.37, 2.99 and 5.43 ppm, which were assigned to 7″–CH_3, –SCH_3, $-CO_2\underline{CH_3}$ and H5″, respectively, a quadruplet at δ 3.91 ppm (J = 7.0 Hz, $-\underline{CH_2}CH_3$). A doublet signal at δ 5.37 ppm (J = 9.0 Hz) was assigned to H1′. A triplet of doublet signals at δ 4.20 ppm (J = 9.0, 6.0 Hz) was assigned to H7a′. The four multiplets between δ 1.98 and 2.57 ppm were assigned to H5′, H6′ and H7. The presence of signals at δ 7.02–8.11 ppm corresponded to aromatic protons.

The ^{13}C NMR spectrum of the product **3a** exhibited the presence of –SCH_3 carbon at δ 22.39, –CH_3 carbon at δ 15.38, $-CH_2\underline{CH_3}$ at 13.90, $-\underline{CH_2}CH_3$ at 60.33, $-CO_2\underline{CH_3}$ at 51.77, C5″ at 54.16, C1′ at 54.44, C7a′ at 65.64, C6′ at 29.94, C7′ at 30.70 ppm. The signals at δ 75.06 and 79.43 ppm represent the spiro carbon of C2′and C3′. The three C=O signals at δ 165.09, 168.63 and 169.20 ppm were assigned to the carbons of $-CO_2Et$, C3″ and $-CO_2Me$ respectively. These assignments were based on 2D NMR (COSY, HSQC and HMBC). Some important HMBC correlations are shown in Fig. 1. Further, the structure of the product was confirmed by X-ray diffraction analysis of **3h** (Fig. 2).

Conclusion

We have developed a practical 1,3-dipolar cycloaddition reaction to synthesise dispiro[indeno[1,2-*b*]quinoxaline-11,3′-



Ar: a, 4-$CH_3SC_6H_4$; **b**, 4-BrC_6H_4; **c**, 2-ClC_6H_4; **d**, 4-FC_6H_4 **e**, 4-ClC_6H_4; **f**, 3,4,5-$(CH_3O)_3C_6H_2$; **g**, 4-$CH_3C_6H_4$; **h**, C_6H_5; **i**, 4-$CH_3OC_6H_4$;

Scheme 1 Synthesis of spiroindeno[1,2-*b*]quinoxaline derivatives.

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Synthesis of 6-aryl-6*H*-chromeno[4′,3′:4,5][1,3]thiazolo[3,2-*a*]benzimidazoles from 2-aryl-3-nitro-2*H*-chromenes and 1*H*-benzimidazole-2-thiol

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A number of 6-aryl-6*H*-chromeno[4′,3′:4,5][1,3]thiazolo[3,2-*a*]benzimidazole derivatives were synthesised by the reaction of 2-aryl-3-nitro-2*H*-chromenes with 1*H*-benzimidazole-2-thiol in the presence of $Cu(OAc)_2·H_2O$ in moderate yields *via* successive C–N and C–S bond formations. The structures of all the products were characterised thoroughly by NMR and HRMS spectroscopy together with X-ray crystallographic analysis.

Keywords: 3-nitro-chromene, Michael addition, $Cu(OAc)_2$, benzimidazole-2-thiol

Benzimidazole derivatives are an important class of molecules owing to their biological and pharmaceutical activities, such as antitumour,[1] antimicrobial,[2] antiasthma,[3] antiparasitic,[4] antitubercular[5] and antagonistic[6] activities.

Chromene derivatives have attracted wide interest due to their antifungal,[7] antioxidant[8] and anticancer[9] activities. Furthermore, chromene derivatives are also used as photochromic materials and as precursors of flavylium dyes.[10,11]

In continuation of our work on the synthesis of fused heterocyclic derivatives,[12–16] here we report the synthesis of 6-aryl-6*H*-chromeno[4′,3′:4,5][1,3]thiazolo[3,2-*a*]benzimidazole derivatives by the reaction of 2-aryl-3-nitro-2*H*-chromene with 1*H*-benzimidazole-2-thiol in the presence of $Cu(OAc)_2·H_2O$ *via* successive C–N and C–S bond formations (Scheme 1).

Results and discussion

The structures of all compounds **3a–i** were established by different spectroscopic techniques (NMR, IR and HRMS). The HRMS spectrum of **3e** gave the molecular ion peak at *m*/*z* 292.0965, which indicates the addition of one molecule of 1*H*-benzimidazole-2-thiol and elimination of –HNO and H_2O to provide **1**. The ^1H NMR spectrum of **3i** revealed four singlet signals at δ 3.87 ($–OCH_3$, 6H), 3.90 ($–OCH_3$, 3H), 6.18 (–CH) and 6.78 (ArH, 2H) ppm. The presence of signals at δ 7.19–8.14 ppm corresponded to the other eight aromatic protons.

The ^{13}C NMR spectrum of the product **3i** exhibited the presence of $–CH_3O$ carbon at δ 56.25 and 60.90 ppm. The signal at δ 78.17 ppm is assignable to the carbon of –CH. Furthermore, the structure of the products was confirmed by X-ray diffraction analysis of **3e** (Fig. 1).

A plausible reaction pathway for the formation of 6-aryl-6*H*-chromeno[4′,3′:4,5][1,3]thiazolo[3,2-*a*]benzimidazole **3** is illustrated in Scheme 2. First, the Michael addition of the benzimidazol-2-thiol **2** to 2-aryl-3-nitro-2*H*-chromene **1** obtained intermediate **A**; intermediate **B** was generated from the intermediate **A** through intramolecular cyclisation *via* C–S bond formation in the presence of $Cu(OAc)_2.H_2O$; and finally

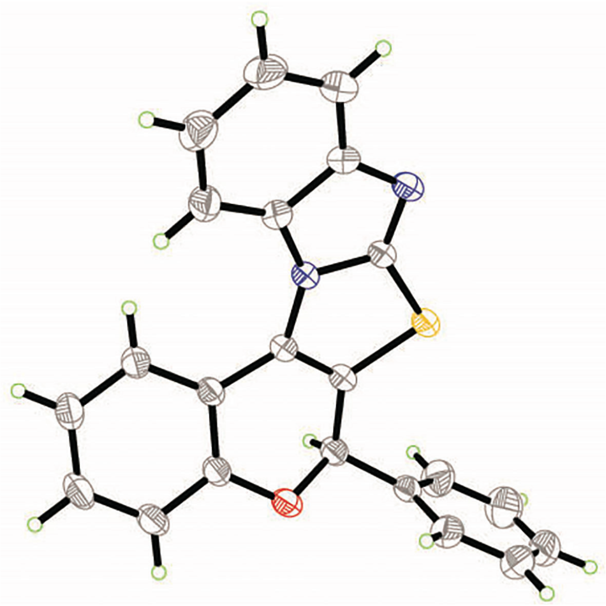
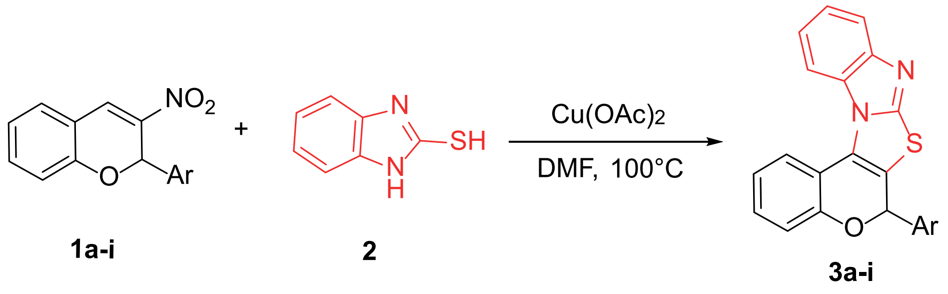


Fig. 1 ORTEP diagram of **3e** with 50% probability.



Ar: a, $4-FC_6H_4$; **b,** $4-ClC_6H_4$; **c,** $4-BrC_6H_4$; **d,** $4-CH_3C_6H_4$; **e,** $4-CH_3OC_6H_4$; **f,** $2,4-Cl_2C_6H_3$; **g,** C_6H_5; **h,** $4-COOCH_3C_6H_4$; **i,** $3,4,5-(CH_3O)_3C_6H_2$

Scheme 1 Synthesis of 6-aryl-6*H*-chromeno[4′,3′:4,5][1,3]thiazolo[3,2-*a*]benzimidazoles.

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Diastereoselective synthesis of spiro[pyrrolo[2,1-*b*][1,3] benzothiazole-3,5′-[1,3]thiazolo[3,2-b][1,2,4]triazol]-6′-ones *via* cycloaddition reaction of benzothiazolium salts

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The 1,3-dipolar cycloaddition reaction of (*Z*)-5-arylidene[1,3]thiazolo[3,2-*b*][1,2,4]triazol-6(5*H*)-one and azomethine ylide, which was generated *in situ* by the reaction of *N*-4-methoxyphenacylbenzothiazolium bromides and triethylamine, afforded novel 2-(aryl)-1-(4-methoxybenzoyl)-1,2-dihydrospiro[pyrrolo[2,1-*b*][1,3]benzothiazole-3,5′-[1,3]thiazolo[3,2-*b*][1,2,4]triazol]-6′-ones in moderate yields. The structures of all the products were characterised thoroughly by NMR, IR and HRMS spectroscopy together with X-ray crystallographic analysis.

Keywords: thiazolo[3,2-*b*][1,2,4]triazol, spirohetercycle, pyrrolo[2,1-*b*][1,3]benzothiazole 1,3-dipolar cycloaddition

Thiazolo[3,2-*b*][1,2,4]triazol derivatives are found in many synthetic derivatives due to their broad spectrum of biological activity, including antibacterial and antifungal activity,[1] antioxidant properties,[2] analgesic properties,[3] anti-inflammatory properties[4] and anticancer activity.[5]

The spiro ring system is a frequently encountered structural motif in many pharmacologically relevant alkaloids, as typified by corynoxeine and spirotryprostatins.[6] The synthesis of spiroheterocycle derivatives have attracted wide interest due to their wide biological applications as antimicrobial, antitumoural and antibiotic agents, and inhibitors of human NK-1 receptor.[7–10]

The 1,3-dipolar cycloaddition reactions of azomethine ylides — which are generated *in situ* by the reaction of *N*-phenacylbenzothiazolium bromides and triethylamine — with exocycle carbon–carbon double bonds can be used in the synthesis of complicated spiroheterocycle systems that cannot be obtained by other methods.[11–13]

In continuation of our work[14–18] on the study of cycloaddition reactions, here we report the synthesis of spiro thiazolo[3,2-*b*][1,2,4]triazole derivatives by the 1,3-dipolar cycloaddition reactions of azomethine ylide, which is generated *in situ* by the reaction of *N*-4-methoxyphenacylbenzothiazolium bromides and triethylamine, with (*Z*)-5-arylidene[1,3]thiazolo[3,2-*b*][1,2,4]triazol-6(5*H*)-ones (Scheme 1).

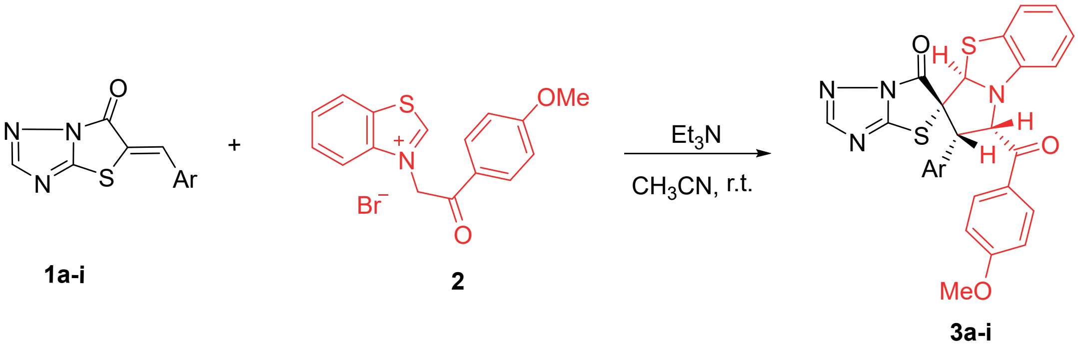
Results and discussion

The structures of all compounds **3** were established by different spectroscopic techniques (NMR, IR and HRMS). The HRMS spectrum of **3f** gave the molecular ion peak at *m*/*z* 559.0930. The IR spectrum of **3f** displayed $\nu_{C=O}$ at 1762.2 and 1676.5 cm^{-1}. The ^{1}H NMR spectrum of **3f** revealed four singlets at δ 2.40, 3.84, 6.40 and 8.11 ppm, which were assigned to –SCH$_3$, –OCH$_3$, H3a and H2′, respectively (the proton numbers are shown in Fig. 1), and two doublet signals at δ 4.42 (*J* = 7.5 Hz) and 5.99 (*J* = 7.5 Hz) ppm, which were assigned to H2 and H1. The presence of signals at δ 6.40–7.75 ppm corresponded to the aromatic protons. The ^{13}C NMR spectrum of the product **3f** exhibited the presence of –SCH$_3$ carbon at δ 15.06, –OCH$_3$ carbon at δ 55.54, C3a at δ 54.57, C2 at δ 77.93 and C1 at δ 78.51 ppm, The signal at δ 74.65 ppm represents the spiro carbon of C3. The two C=O signals at δ 164.94 and 193.87 ppm are assigned to the C6′ and benzoyl, respectively. These assignments were based on 2D NMR (COSY, HSQC, HMBC and NOESY). Some important HMBC correlations are shown in Fig. 1. Furthermore, the structure of the products was confirmed by X-ray diffraction analysis of **3f** (Fig. 2).

Four stereocentres were formed in the products. Spiroheterocycle products synthesised by the 1,3-dipolar cycloaddition of benzothiazolium bromides should have two possible diastereomer products.[11–13] However, our reaction showed diastereoselectivity, as only one product was detected and isolated.

Conclusion

We have developed a practical 1,3-dipolar cycloaddition reaction for the synthesis of (1*RS*,2*RS*,3*SR*,3a*SR*)-spiro[pyrrolo[2,1-*b*]



Ar: **a,** 4-ClC$_6$H$_4$; **b,** 2-ClC$_6$H$_4$; **c,** 4-FC$_6$H$_4$; **d,** 4-BrC$_6$H$_4$; **e,** C$_6$H$_5$;
f, 4-CH$_3$SC$_6$H$_4$; **g,** 2,4-Cl$_2$C$_6$H$_3$; **h,** 4-CH$_3$OC$_6$H$_4$; **i,** 4-CH$_3$C$_6$H$_4$

Scheme 1 Synthesis of spiro thiazolo[3,2-*b*][1,2,4]triazole derivatives.

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One-pot transformation of Me_3Si-/$Ph_2P(O)$-protected ethynes to unsymmetrical arylethynes

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Me_3Si-/$Ph_2P(O)$-protected ethynes were successfully transformed to unsymmetrical arylethynes *via* a one-pot $Ph_2P(O)$-deprotection/[Pd(dppf)Cl_2]-catalysed coupling and one-pot Me_3Si-deprotection/Sonogashira coupling under mild conditions and in high yield. Unsymmetrical phenylethynes, unsymmetrical extended phenylene ethynylenes and unsymmetrical anthrylethynes were successfully synthesised in good to excellent yields.

Keywords: one-pot, unsymmetrical ethynes, protecting group, deprotection, Sonogashira coupling

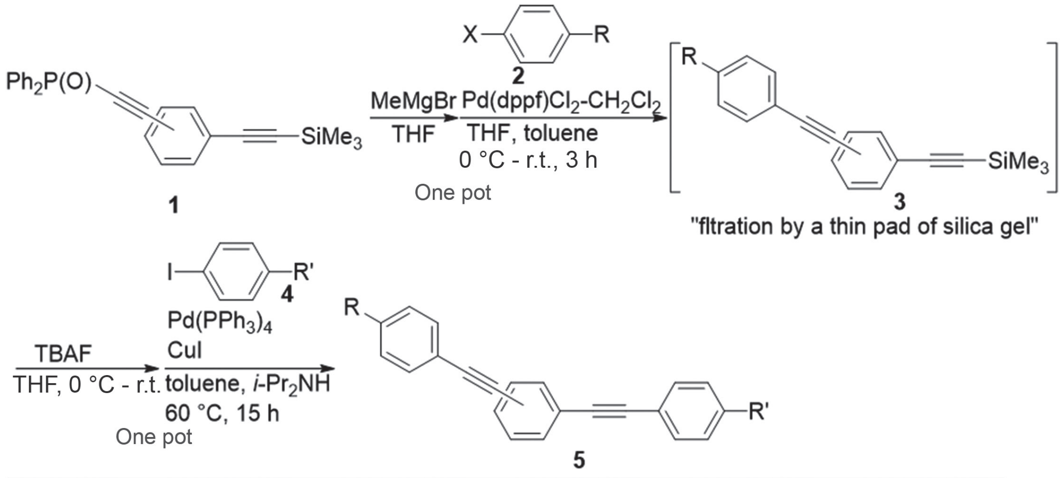
Highly π-conjugated unsymmetrical arylethynes, which have rigid structures and highly extended π-systems, are important organic materials used in organic field-effect transistors,[1] organic light-emitting diodes,[2–4] liquid crystals[5] and dye-sensitised solar cells[6,7]. The Sonogashira coupling is a powerful method for synthesising arylethynes from the corresponding aryl halide and terminal ethynes as starting materials. The traditional synthesis of unsymmetrical arylethynes often suffers from severe drawbacks, such as the difficult separation of the products that have similar R_f values to the starting materials and by-products as well as low overall yields and long synthetic steps.[8] Although trialkylsilyl groups such as trimethylsilyl (TMS) and *t*-butyldimethylsilyl (TBDMS) and the 2-hydroxy-2-propyl group are routinely used as protecting groups for terminal ethynes, the phosphoryl group ($Ph_2P(O)$) has been developed as a new protecting group.[9–13] The high polarity of the phosphoryl group enables the easy separation of the desired products from the less-polar hydrocarbon by-products.[10,12] Recently, a short one-pot synthesis of unsymmetrical arylethynes has been developed involving dephosphorylation followed by Sonogashira couplings. However, the isolation of products was tedious because of the similar R_f values of the products and by-products, and the yields of products required improvement.[10]

Therefore, a more efficient procedure leading to unsymmetrical arylethynes under mild reaction conditions, with easy purification and high yields was required. We now report our work on developing an efficient route to unsymmetrical arylethynes from Me_3Si-/$Ph_2P(O)$-protected arylethynes *via* a one-pot $Ph_2P(O)$-deprotection [Pd(dppf)Cl_2]-catalysed coupling followed by a one-pot Me_3Si-deprotection/Sonogashira coupling under mild conditions, with easy purification and in high yield.

Results and discussion

First, we tried a selective $Ph_2P(O)$-deprotection/[Pd(dppf)Cl_2]-catalysed coupling and Me_3Si-deprotection/Sonogashira coupling of the Me_3Si-/$Ph_2P(O)$-protected phenylethyne **1**. When **1** was treated successively with MeMgBr and then with the phenyl halide **2** and Pd catalyst, the corresponding Sonogashira coupling product **3** was obtained. The crude product **3** was subjected to a KOH-catalysed desilylation/[Pd, Cu]-catalysed Sonogashira coupling to afford product **5** as shown in Table 1. In the above procedure,

Table 1 Synthesis of unsymmetrical phenylethynes



Entry	**1** ($Ph_2(O)PC{\equiv}C$)	**2** (X; R)	**4** (R')	**5** ($RC_6H_4C{\equiv}C$; R')	yield (%)[a]
1	**1a** (*m*-$C{\equiv}CP(O)Ph_2$)	**2a** (Br; OMe)	**4a** (CN)	**5a** (*m*-$C{\equiv}CC_6H_4OMe$; CN)	86[b]
2	**1b** (*p*-$C{\equiv}CP(O)Ph_2$)	**2b** (I; ODMO)	**4b** (OMe)	**5b** (*p*-$C{\equiv}CC_6H_4ODMO$; OMe)	91
3	**1c** (*o*-$C{\equiv}CP(O)Ph_2$)	**2c** (I; H)	**4c** (H)	**5c** (*o*-$C{\equiv}CC_6H_5$; OMe)	87

ODMO: O-(3,7-dimethyloctyl)
dppf: 1,1'-bis(diphenylphosphino)ferrocene

[a]Isolated yields.
[b]The temperature of [Pd(dppf)Cl_2]-catalysed coupling was 0–80 (refers only to entry 1).

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A one-pot method for the synthesis of phenylalkynyl-substituted terminal alkynes by deprotection/stannylation followed by a Migita–Kosugi–Stille coupling

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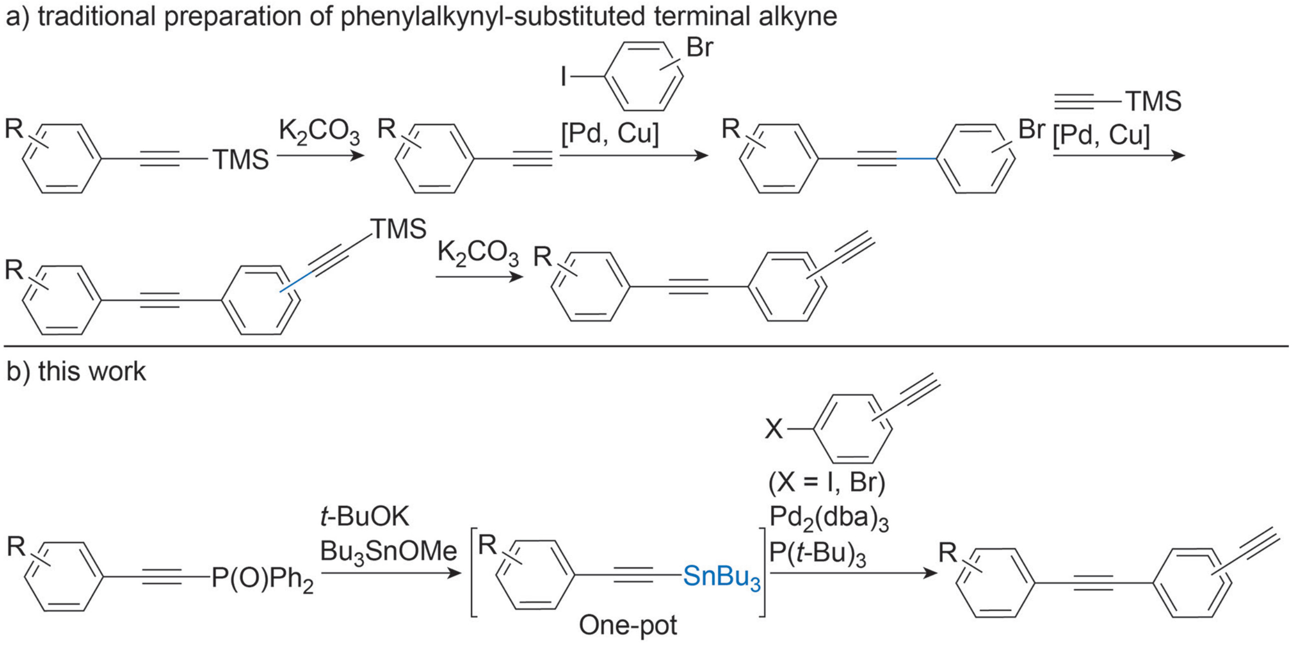
A practical one-pot approach for the synthesis of arylalkynyl-substituted terminal alkynes has been developed through a deprotection/stannylation of a phenylethynyl phosphine oxide followed by Migita–Kosugi–Stille coupling, avoiding the longer synthetic route involving repeated deprotection/Sonogashira coupling. Other features of this approach include mild reaction conditions, excellent yields, facile isolation of products and wide functional group tolerance.

Keywords: one-pot synthesis, alkynes, deprotection, Migita–Kosugi–Stille coupling, terminal alkynes

Alkynes are versatile building blocks for the synthesis of natural product analogues and hybrid structures.[1] For example, the hydrophobic, rigid and linear attributes of acetylenes produce derivatives with interesting physical properties and biological activity such as antibacterial,[2] antifungal,[3] pesticidal[4] and antitumour[5] activity. Aromatic acetylenes have structures with unique electronic properties due to their rigid skeleta and rich π electron density. The conjugated system of an aryl-ethynyl moiety produces important organic materials, such as organic field-effect transistors,[6] organic light-emitting diodes[7] and dye-sensitised solar cells.[8]

Phenylalkynyl-substituted terminal alkynes are important intermediates to prepare these conjugated aryl-ethynyl organic materials. The conventional synthesis of these phenylalkynyl-substituted terminal alkynes involves the Sonogashira coupling of aryl halides with alkynes protected with a trialkylsilyl group such as trimethylsilyl (TMS) and *t*-butyldimethylsilyl.[9] This traditional synthesis, though powerful, frequently suffers from some severe drawbacks, such as difficult isolation of the product with a similar R_f value to that of the starting material and by-products, low total yields and longer synthetic steps involving repeated deprotection/Sonogashira coupling (Scheme 1a).[10] Thus, the development of a practical procedure for the preparation of phenylalkynyl-substituted terminal alkynes with higher total yields, short synthetic steps and easy purification is required. Recently, we developed a new protecting group, $Ph_2P(O)$, which enabled the easy isolation of the Sonogashira coupling product because of its high polarity. We exemplified the usefulness of this protecting group in the synthesis of phenylalkynes.[11]

To overcome the drawbacks of the traditional synthesis of phenylalkynyl-substituted terminal alkynes, we have expanded the use of the $Ph_2P(O)$ protecting group to a one-pot synthesis of phenylalkynyl-substituted terminal alkynes through a deprotection/stannylation sequence followed by a Migita–Kosugi–Stille coupling (Scheme 1b).



Scheme 1 General methods for synthesis of phenylalkynyl-substituted terminal alkynes.

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Synthesis of octahydropyrano[2,3-*d*]pyrimidine derivatives *via* tetrahydropyrano[3,2-*e*][1,3]thiazolo[3,2-*a*]pyrimidine and 2,6-dichlorobenzonitrile oxide

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N^1-substituted octahydro-1*H*-pyrano[2,3-*d*]pyrimidines derivatives were prepared in moderate yield by the reaction of methyl [(4a*RS*,5*SR*,10a*RS*)-5-aryl-2-oxo-3,4,4*a*,10*a*-tetrahydro-2*H*,5*H*-pyrano[3,2-*e*][1,3]thiazolo[3,2-*a*]pyrimidin-8(9*H*)-ylidene]acetate and 2,6-dichorobenzonitrile oxide *via* a domino 1,3-dipolar cycloaddition/ring-opening/dethionation process. The structures of the products were characterised by spectroscopic and X-ray crystallographic analysis.

Keywords: pyrano[2,3-*d*]pyrimidine, pyrano[3,2-*e*][1,3]thiazolo[3,2-*a*]pyrimidine, cycloaddition, 2,6-dichorobenzonitrile oxide

Pyranopyrimidines and related fused-ring pyrimidinones have diverse and important bioactivities.[1] These compounds show antitumour and anti-allergic activities.[2] Some of them also show antifungal and herbicidal properties.[3] As a consequence, the synthesis of pyranopyrimidines and fused-ring pyrimidinones has been extensively researched in recent decades.[4,5]

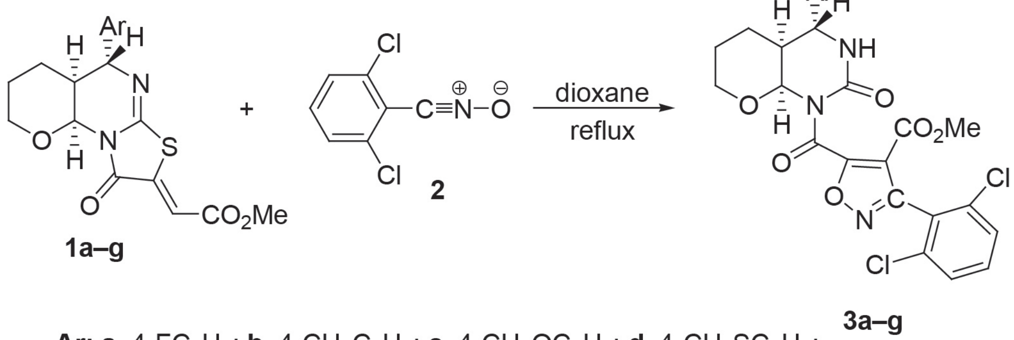
The isoxazole structure has been found in many natural products exhibiting a wide range of biological activities, including pharmacological and agrochemical applications, including anti-inflammatory, antibacterial, fungicidal and insecticidal activities.[6–8] In continuation of our work[9,10] on the synthesis of isoxazoline-containing heterocycles, we now report the synthesis of N^1-substituted pyrano[2,3-*d*] pyrimidines **3** by the reaction of methyl [(4a*RS*,5*SR*,10a*RS*)-5-aryl-2-oxo-3,4,4*a*,10*a*-tetrahydro-2*H*,5*H*-pyrano[3,2-*e*] [1,3]thiazolo[3,2-*a*]pyrimidin-8(9*H*)-ylidene] acetate **1** with 2,6-dichorobenzonitrile oxide **2**, as shown in Scheme **1**.

Results and discussion

The structures of compounds **3a–g** were established on the basis of ^{1}H NMR, ^{13}C NMR and mass spectral (MS) analysis. The mass spectrum of **3c** showed a molecular ion peak at *m/z* 560.0982 ([M+H]$^+$), which indicates **3c**. The ^{1}H NMR spectrum of **3c** revealed a doublet at δ (parts per million, ppm) 1.46 (*J* =13.5 Hz) and a multiplet in the range of δ 1.89–1.92 resulting from the methylene (Hb) of the pyran ring. The methylene (Hc) appeared as two multiplets in the range of δ 1.62–1.65 and 1.74–1.81, and the methylene (Ha) appeared as two multiplets in the range of δ 3.79–3.84 and 4.21–4.24. There was a multiplet in the range of δ 2.14–2.16 for proton Hd and a doublet at δ 5.73 (*J* =13.5 Hz) for proton He. The protons of the methoxy group (Hk) appeared as a singlet at δ 2.48, and another singlet appeared at δ 3.67 corresponding to the methoxycarbonyl protons (Hj). The benzylic proton (ArH) (Hg) appeared as a doublet at δ 4.87 (*J* = 11.0 Hz), there was a broad singlet at δ 5.32 for the NH proton of the pyrimidine ring, and several multiplets appeared in the range of δ 7.27–7.43 for the aromatic protons.

The ^{13}C NMR spectrum of the product **3c** shows the presence of three methylene carbons at δ 20.20 (Cb), 23.23 (Cc) and 68.46 (Ca), a methoxyl carbon (Ck) at δ 15.47, a O-CH_3 (Cj) at δ 52.17 and a benzylic carbon (Cg) at δ 53.22. The signals at δ 37.91 and 81.11 were assigned to the two carbons, Cd and Ce, respectively. The carbonyl carbons of the pyrimidine ring and the keto carbonyl group resonated at δ 159.27 (Cf) and 168.49 (Ch) ppm, respectively. Another signal at δ 160.20, corresponding to the carbomethoxy carbon (Ci) based on ^{1}H and ^{13}C heteronuclear multiple bond correlation (HMBC, Fig. 1). In addition, the structure of the product was confirmed by X-ray diffraction analysis of **3e** (Fig. 2).

Mechanistically, the 1,3-dipolar cycloaddition reaction of **1** and **2** results in the formation of intermediate **4**, which undergoes a subsequent ring-opening to form the corresponding intermediate **4′**(or **4″**). Finally, the S of **4′**(or **4″**) was substituted by O in the presence of nitrile oxide **2**,[11] which leads to the formation of the title product **3**, as shown in Scheme 2.



Ar: a, 4-FC_6H_4; **b**, 4-$CH_3C_6H_4$; **c**, 4-$CH_3OC_6H_4$; **d**, 4-$CH_3SC_6H_4$;
e, 4-ClC_6H_4; **f**, 3,4,5-$(OCH_3)_3C_6H_2$; **g**, 4-$CH_3O_2CC_6H_4$

Scheme 1 Synthesis of pyrano[2,3-*d*]pyrimidines derivatives.

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Synthesis of spiro[pyrrolo[2,1-*b*][1,3]benzothiazole-3,2′-[1,3]thiazolo[3,2-*a*] pyrimidine] *via* cycloaddition reactions

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The 1,3-dipolar cycloaddition reaction of ethyl-5-aryl-2-[(*Z*)-2-methoxy-2-oxoethylidene]-7-methyl-3-oxo-3,5-dihydro-2*H*-thiazolo[3,2-*a*] pyrimidine-6-carboxylates and azomethine ylide, which was generated *in situ* by the reaction of *N*-4-methoxyphenacylbenzothiazolium bromides and triethylamine, yielded novel 6′-ethyl-2-methyl-5′-aryl-1-(4-methoxybenzoyl)-7-methyl-3′-oxo-1,2-dihydro-5*H*-spiro[pyrrolo[2,1-*b*][1,3]benzothiazole-3,2′-[1,3]thiazolo[3,2-*a*]pyrimidine]-2,6′-dicarboxylates in moderate yields. The structures of all of the products were characterised by NMR, IR, HRMS spectrometry, together with X-ray crystallographic analysis.

Keywords: thiazolo[3,2-*a*]pyrimidine, spirohetercycle, pyrrolo[2,1-*b*][1,3]benzothiazole-1,3-dipolar cycloaddition

Spiroheterocycle derivatives are motifs in many pharmacologically important alkaloids, as typified by rhyncophylline, corynoxeine, mitraphylline, horsifiline and spirotryprostatins.[1] The derivatives of spiroheterocycles find very wide biological applications as antimicrobial, antitumour and antibiotic agents, as well as inhibitors of the human NK-1 receptor.[2–5]

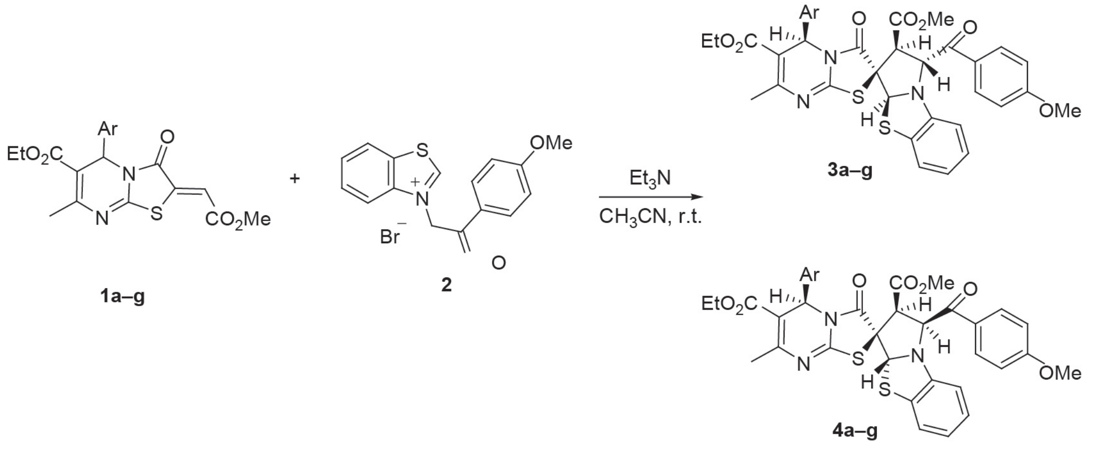
The 1,3-dipolar cycloaddition reaction of azomethine ylides, generated by a decarboxylative route from amino acids and isatin with exocyclic olefins, represents an efficient method for the construction of the spiroheterocycle structural unit.[6–7] The azomethine ylides generated by the reaction of *N*-phenacylbenzothiazolium bromides and triethylamine, which can be used in the synthesis of complex heterocycle systems, are less studied compared with azomethine ylides generated by a decarboxylative route.[8–10]

Thiazolo[3,2-*a*]pyrimidine derivatives are found in many synthetic derivatives due to their broad spectrum of biological activities, including as antagonists of 5HT2 serotonin receptors and dopamine D2 receptors,[11–12] antifungal[13] and anti-inflammatory properties[14] and CDC25 phosphatase inhibitor activity.[15]

In continuation of our work on the study of the cycloaddition reaction[16–19], we now report the synthesis of spiro[thiazolo[3,2-*a*] pyrimidine] derivatives by the 1,3-dipolar cycloaddition reactions of azomethine ylide generated *in situ* by the reaction of 3-(4-methoxyphenacyl)benzothiazolium bromides and triethylamine with ethyl-5-aryl-2-[(*Z*)-2-methoxy-2-oxoethylidene]-7-methyl-3-oxo-3,5-dihydro-2*H*-thiazolo[3,2-*a*] pyrimidine-6-carboxylates (Scheme 1).

Results and discussion

The structures of all compounds **3** and **4** were established by different spectroscopic techniques (NMR, IR) and HRMS. The high resolution mass spectrum of **3f** gave the molecular ion peak at *m/z* 716.1555. The IR spectrum of **3f** displayed $\nu_{C=O}$ at 1739.6, 1711.6, 1681.5 cm^{-1}. The ^{1}H NMR spectrum of **3f** revealed a triplet at δ 1.18 ppm (J = 7.0 Hz, $-CH_2\underline{CH_3}$), four singlets at 2.44, 2.51, 3.04 and 3.90, which were assigned to $-SCH_3$, 7-CH_3, $-CO_2CH_3$ and $-OCH_3$, respectively, a quadruplet at δ 4.08 ppm (J = 7.0 Hz, $-\underline{CH_2}CH_3$), two doublet signals at δ 4.47 (J = 8.5 Hz) and 5.38 (J = 8.5 Hz) assigned to H-2 and H-1, respectively, two singlets at δ 6.00 and 6.11 assigned to H-4 and H-5′, respectively. The presence of signals at δ 6.42–8.19 ppm corresponded to the aromatic protons. The ^{13}C NMR spectrum of the product **3f** exhibited the presence of $-SCH_3$ carbon at δ 15.32, $-OCH_3$ carbon at δ 55.60, 7′-CH_3 at 22.69, $-CH_2\underline{CH_3}$ at 14.07, $-\underline{CH_2}CH_3$ at 60.59, $-CO_2\underline{CH_3}$ at 52.64, C-5 at 55.13, C-4 at 80.92, C-1 at 65.31 and C-2 at 55.60. The signal at δ 69.64 represents the spiro carbon of C-3. The four C=O signals at δ 165.15, 167.68, 170.16, 195.49 are assigned to the carbons of $-CO_2Et$, $-CO_2Me$, C-3′ and benzoyl, respectively. These assignments were based on 2D NMR (COSY, HSQC, HMBC and NOESY), and some important 2D correlations are shown in



Ar: **a**, 4-$CH_3C_6H_4$; **b**, 4-ClC_6H_4; **c**, 2-ClC_6H_4; **d**, 4-FC_6H_4; **e**, 4-$CH_3OC_6H_4$; **f**, 4-$CH_3SC_6H_4$; **g**, 2,4-$Cl_2C_6H_3$

Scheme 1 Synthesis of spiro thiazolo[3,2-*a*]pyrimidine derivatives.

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RESEARCH PAPER

Spectrofluorometric determination of berberine using a novel Au nanocluster with large Stokes shift

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Abstract

Berberine hydrochloride (BHC), a natural isoquinoline alkaloid, is widely applied as a an agent in traditional Chinese medicine. Almost all the traditional methods for BHC detection require complicated preprocessing steps or expensive instruments. In this article, we report a simple, rapid, sensitive, and selective method for BHC detection using fluorescent gold nanoclusters (F-AuNCs) as the fluorescent probe with a large Stokes shift of 237 nm. The F-AuNCs prepared with citrate-stabilized stannous chloride and hydrogen tetrachloroaurate(III) as raw materials in an aqueous medium display strong and stable fluorescence at 566 nm. When F-AuNCs are mixed with BHC, the fluorescence of F-AuNCs is effectively quenched. Under optimized conditions, this method allows sensitive and selective measurements of BHC in a concentration ranging from 1.0×10^{-6} to 1.0×10^{-4} mol L^{-1} with a detection limit of 7.5×10^{-8} mol L^{-1}, which is relatively low among reported spectral methods. This method provides excellent selectivity for the detection of BHC against inorganic anions and natural amino acids. In addition, the BHC content in two different types of berberine tablets was successfully determined by this method and the results showed high accuracy.

Keywords Berberine hydrochloride · Gold nanoclusters · Fluorescent · Stokes shift

Introduction

Berberine hydrochloride (BHC) is an isoquinoline alkaloid isolated from *Rhizoma coptidis*, *Berberis aquifolium*, *Berberis vulgaris*, and other Chinese herbs [1]. Because of BHC's antibacterial, antilipid peroxidation, antiatherosclerotic, and neuroprotective properties as well as its property of relieving polycystic ovary syndrome [2–6], its quantification is crucial in the fields of clinic medical assay and optical probes [7–9]. Many analytical methods, including chromatography [10, 11], mass spectrometry [12], capillary electrophoresis [13], chemiluminescence [14], electrochemical analysis [15, 16], light scattering spectrometry [17, 18], colorimetric assay [19, 20] fluorescence spectra [21–23], and optical fiber sensing [24–26], for the quantification of BHC have been established. These methods have certain advantages, such as sensitivity and selectivity, but require expensive instruments or complicated procedures. On the basis of these methods, sensing methods using fluorescence, scattering, and the fluorescence spectrum have been rapidly developed in recent years [27–29], possessing simplicity in approach, shortened response time, and cost-effectiveness.

Recently, fluorescent probes using metal nanoclusters (NCs) with small particle size have drawn considerable research interest in the fields of analytical chemistry owing to their special characteristics, such as good biocompatibility, large surface area, low toxicity, and exceptional fluorescent properties [30–32]. By choosing different capping and stabilizing agents, researchers have developed various approaches to synthesize NCs and have applied them in chemosensing/biosensing [33]. However, the development of high-quality

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Aoli Wen, Xiaoxiao Peng, and Pingping Zhang contributed equally to this work.

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RESEARCH PAPER

Real-time monitoring of endogenous cysteine levels in living cells using a CD-based ratiometric fluorescent nanoprobe

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Abstract

A simple and readily available fluorescent probe is needed for the real-time monitoring of endogenous cysteine (Cys) levels in living cells, as such a probe could be used to study the role of Cys in related diseases. Herein, we report the first fluorescent probe based on carbon dots (CDs-FITA) for the selective and ratiometric imaging of endogenous Cys in live cells. In this ratiometric fluorescent probe, a fluorescein derivative (FITA) that recognizes Cys is covalently linked to the surfaces of carbon dots (CDs); employing CDs greatly improves the water solubility of the probe. Acrylate on FITA is selectively cleaved by Cys in aqueous solution under mild conditions, leading to a dramatic increase in the fluorescence from fluorescein. The probe therefore allows the highly selective ratiometric fluorescent detection of Cys even in the presence of various interferents. The as-prepared CDs-FITA showed excellent performance when applied to detect Cys in blood serum. In addition, due to its negligible cytotoxicity, the CDs-FITA can also be utilized for the real-time monitoring of endogenous cysteine (Cys) levels in living cells.

Keywords Carbon dots · Fluorescein · Ratiometric fluorescence · Cys · Living cell imaging

Introduction

Endogenous cysteine (Cys), a reactive sulfur species, plays a critical role in many biological processes [1, 2]. It is also thought to be a precursor in the production of the antioxidant glutathione and to be involved in detoxification and metabolism [3]. However, high levels of endogenous Cys in living systems are related to many diseases, including Parkinson's disease, liver damage, and Alzheimer's disease [4–8]. Hence, a simple and efficient method for detecting endogenous Cys in living systems could facilitate the early diagnosis and prevention of those diseases.

In recent years, fluorescence probes have become powerful tools for sensing and imaging living systems due to their simple operation and high sensitivity and selectivity and because they allow real-time in-situ imaging [9–25]. Indeed, numerous fluorescent sensors that are selective for Cys have been developed, mainly based on the Michael addition/cyclization reaction [26–36]. Despite these recent advances, most fluorescent Cys probes utilize small-molecule fluorophores and exhibit poor water solubility; they require a mixture of organic solvents and water [37–39]. While there are several probes that are water soluble and exhibit ratiometric fluorescence, they do

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Hong Wang and Peisheng Zhang contributed equally to this work.

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RESEARCH PAPER

A near-infrared fluorescent sensor with large Stokes shift for rapid and highly selective detection of thiophenols in water samples and living cells

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Abstract

The development of simple methods with high sensitivity and selectivity to differentiate toxic aromatic thiols (thiophenols) from aliphatic thiols (cysteine, homocysteine, and glutathione) and hydrogen sulfide (H_2S) is of great significance. Herein, we report on the fabrication of a novel near-infrared (NIR) fluorescent sensor for rapid and highly selective detection of thiophenols through the photoinduced electron transfer (PET) mechanism. In the presence of the thiophenols, an obvious enhancement of NIR fluorescence at 658 nm could be visualized with the aid of nucleophilic aromatic substitution (S_NAr) reaction. The sensor displays large Stokes shift (~ 227 nm), fast response time (< 30 s), high sensitivity (~ 8.3 nM), and good biocompatibility. Moreover, the as-prepared sensor possesses an excellent anti-interference feature even when other possible interferents exist (aliphatic thiols and H_2S) and has been successfully utilized for thiophenol detection in both water samples and living cells.

Keywords Thiophenols · NIR fluorescence · Live cell imaging

Introduction

The organic thiol species, including the aliphatic thiols and the thiophenols, play very important roles in biological systems and industrial processes [1]. Aliphatic thiols, such as glutathione (GSH), cysteine (Cys), and homocysteine (Hcy), are involved with various biological functions [2–4]. Despite of their widespread utility, aromatic thiols including thiophenols, being a serious toxic pollutants, show a median lethal dose (LC50) for fish in a low range from 0.01 to 0.4 mM [5, 6]. In addition, the experimental investigation has ascertained that superabundant intake of the thiophenols could result in a variety of disorders like central nervous system damage, muscle weakness, increased respiration, hind limb paralysis, and even death [7]. In view of their high toxicity, it is vital to explore novel strategies to effectively and accurately detect thiophenols and more importantly to differentiate the toxic thiophenols from aliphatic thiols of biological importance and hydrogen sulfide (H_2S) in both environmental and biological science.

Recently, a large amount of fluorescent sensors for thiols have been reported due to several excellent merits, such as high sensitivity, noninvasiveness, and real-time detection ability [8–26]. Despite of the extensive efforts, it remains a challenge to develop fluorescent sensors that can differentiate thiophenols from both the aliphatic thiols and the H_2S due to their similar physical and chemical properties. To solve the above problems, Wang et al. [27] for the first time reported a reaction-based fluorescent probe for detecting thiophenols among the thiols through the thiolysis of 2,4-dinitrobenzenesulfonamide based

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In-situ preparation of silver salts/collagen fiber hybrid composites and their photocatalytic and antibacterial activities

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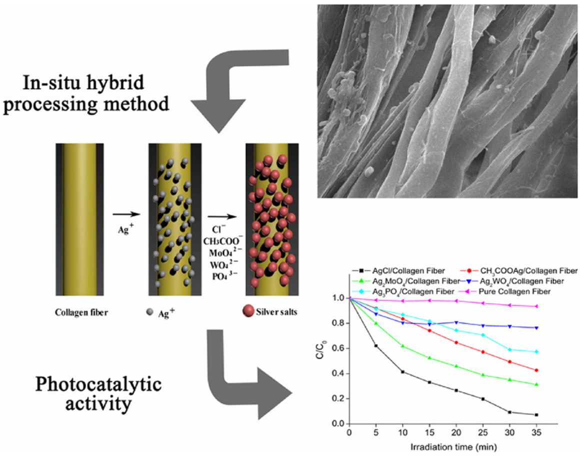
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Collagen fiber
Hybrid composites
Photocatalytic activity
Antibacterial activity

ABSTRACT

To promote the utilization of collagen fiber, silver salts/collagen fiber hybrid composites with photocatalytic and antibacterial activities were successfully prepared in this study via the in-situ organic-inorganic process. The surface morphology, chemical composition and structure were discussed. Scanning electron microscopy (SEM) observation showed that the silver salts/collagen fiber hybrid composites were successfully prepared with silver salt particles (300–500 nm) distributing evenly on the surface of collagen fiber. X-ray diffraction (XRD) patterns and Fourier transform infrared spectroscopy (FTIR) analysis provided strong evidence for the successful coating of silver salts on the surface of collagen fiber and the hybrid mechanism was subsequently discussed. The photocatalytic activity was evaluated by degrading methyl orange (MO) under ultraviolet (UV) light and visible light, respectively. The results indicated that AgCl/Collagen Fiber showed the most efficient photocatalytic activity under UV and visible light irradiation. Furthermore, the introduction of Ag^+ endowed the photocatalysts with antibacterial performance, which was investigated by measuring the width of the bacteriostatic belts. The results indicated the antibacterial activity of the composites, proving that the photocatalysts were durable and reusable.

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碳纳米管负载的Pd-Ag-Sn催化剂对甲酸的电氧化

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摘要：采用硼氢化钠还原的方法合成了碳纳米管负载的钯基纳米催化剂(Pd/CNT，Pd_7Ag_3/CNT，Pd_7Sn_2/CNT，$Pd_7Ag_1Sn_2$/CNT，$Pd_7Ag_2Sn_2$/CNT和$Pd_7Ag_3Sn_2$/CNT)。通过XRD，TEM和XPS对其进行了表征，结果表明，相比Pd/CNT和Pd-Ag(或Pd-Sn)催化剂的纳米颗粒，Pd-Ag-Sn催化剂展现出了更小的平均颗粒尺寸(2.3 nm)。此外，还通过循环伏安(CV)和计时电流法(CA)测试了这些催化剂对甲酸氧化的电活性，在酸碱介质中，Pd-Ag-Sn/CNT对甲酸氧化都表现出了更高的电流密度。其中，$Pd_7Ag_2Sn_2$/CNT催化剂在酸碱介质中的电流密度分别是108.8和211.3 $mA\cdot cm^{-2}$，相应的Pd质量电流密度高达1 364和2 640 $mA\cdot mg^{-1}$，远远高于商业Pd/C，表明Pd-Ag-Sn/CNT催化剂对甲酸氧化表现出了极好的电催化活性。

关键词：钯催化剂；甲酸氧化；燃料电池；电催化
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Carbon Nanotube-Supported Ternary Pd-Ag-Sn Catalysts for Formic Acid Electro-Oxidation

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Abstract: Carbon nanotube-supported Pd-based binary and ternary nanocatalysts (Pd/CNT, Pd_7Ag_3/CNT, Pd_7Sn_2/CNT, $Pd_7Ag_1Sn_2$/CNT, $Pd_7Ag_2Sn_2$/CNT and $Pd_7Ag_3Sn_2$/CNT) have been fabricated by the $NaBH_4$ reduction method. They have been characterized by using XRD, TEM and XPS techniques. The ternary Pd-Ag-Sn nanoparticles exhibit a smaller average particle size of *ca.* 2.3 nm compared to Pd/CNT and binary Pd-Ag (or Pd-Sn) nanoparticles. The electrocatalytic activity of these catalysts towards formic acid oxidation in both H_2SO_4 and NaOH solutions has been investigated using cyclic voltammetry (CV) and chronoamperometry (CA). In both acidic and alkaline media, the ternary Pd-Ag-Sn/CNT catalysts present higher anodic current density for formic acid oxidation than Pd/CNT and binary PdAg/CNT or PdSn/CNT catalysts. Among the prepared catalysts, the $Pd_7Ag_2Sn_2$/CNT catalyst displays the highest HCOOH oxidation current density of 108.8 $mA\cdot cm^{-2}$ in 0.5 $mol\cdot L^{-1}$ H_2SO_4 solution or 211.3 $mA\cdot cm^{-2}$ in 1 $mol\cdot L^{-1}$ NaOH solution, corresponding to the Pd mass current density of 1 364 or 2 640 $mA\cdot mg^{-1}$, respectively. These currents are extremely larger than those obtained from the commercial Pd/C. Results exhibit the excellent electrocatalytic activity of the ternary $Pd_7Ag_2Sn_2$/CNT catalyst towards formic acid oxidation.

Keywords: Pd catalyst; formic acid oxidation; fuel cell; electrocatalyst

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RESEARCH ARTICLE

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Determining the excited-state substituent constants of furyl and thienyl groups

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Abstract

Six series of styrene derivatives XCH═CHArY (total of 65) containing the styrene parent molecular skeleton were synthesized (here, Y is OMe, Me, H, F, Cl, CF_3, CN, and NO_2, and X is 2-furyl, 3-furyl, 2′-methyl-2-furyl, 2-thienyl, 3-thienyl, and 2′-methyl-2-theniyl). Their ultraviolet absorption spectra were measured in anhydrous ethanol, and their wavelength of absorption maximum λ_{max} was recorded. For the wavenumber ν_{max} (cm^{-1}, $\nu_{max} = 1/\lambda_{max}$) of the obtained λ_{max}, a quantitative correlation analysis was performed, and 6 excited-state substituent constants $\sigma^{ex}_{CC(p)}$ of groups X were obtained by means of curve-fitting method. Taking the ν_{max} values of total 90 compounds of styrene derivatives as a data set (including 25 compounds from reference and 65 compounds of this work), a quantitative correlation analysis was performed, and the reliability of the obtained $\sigma^{ex}_{CC(p)}$ was verified. In addition, 12 samples of disubstituted Schiff bases (XCH═NArY) involving the above groups X were synthesized, and their ν_{max} values were recorded. Using these 12 ν_{max} together with the 14 ν_{max} values of Schiff bases taken from reference (total of 26 compounds), it was further verified that the $\sigma^{ex}_{CC(p)}$ values are reliable by means of quantitative correlation method.

KEYWORDS

excited-state constant, furyl, styrene, thienyl, UV absorption spectrum

1 | INTRODUCTION

Substituted stilbenes XArCH═CHArY (XSBY), such as *p*/*m*-$XC_6H_4CH{=}CHC_6H_4Y$-*p*/*m* (X, Y = OMe, Me, H, F, Cl, CF_3, CN, and NO_2), are a typical conjugated organic compound with 2 aryl groups attached to a vinylidene.[1] It was widely used in medicines,[2–5] foods,[6] functional materials,[7,8] and other fields due to their specific structural features and characteristics. With the continuous discovery of various activities and the extension of application, stilbene compounds have attracted extensive attention. For example, diphenylethylene, dithienylethylene, and tetraphenylethylene show interesting optical properties.[9] Tetraphenylethylene has been extensively studied because of its tunable luminescent properties, and some of its derivatives show an interesting phenomenon of aggregation-induced emission,[10,11] that is, molecules, under photoexcitation, are not emissive in solution and are strongly luminescent in the solid state.[12,13] Moreover, regioselective functionalization of the thiophene rings in tetra(2-thienyl)ethylene can lead to the synthesis of a series of derivatives, which are suitable for investigating systematically their electronic, photophysical, and electrochemical properties.[9]

The ultraviolet (UV)-visible spectra of organic compounds are associated with transitions between electronic energy levels. Also, the energy of the wavelength of absorption maximum λ_{max} (nm) of a compound reflects

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RESEARCH ARTICLE

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Substituent effects on the UV absorption energy of 2,5-disubstituted pyrimidines

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Abstract

Pyrimidine-containing molecules have been extensively investigated in organic light emitting devices (OLEDs), solar cells, liquid crystals, and so on due to their perfect photoelectric properties. Ultraviolet (UV) absorption is one of the interesting photoelectric properties. Systematical study of the substituent effects on the UV absorption energy of pyrimidine derivatives will guide to design functional molecules with specific photoelectric properties. In this paper, thirty-seven 2-X-5-Y pyrimidines with various substituents (X/Y=NH_2, CH_3, OCH_3, NMe_2, CF_3, NO_2, Cl, Br, I) were synthesized, and their UV spectra were recorded in anhydrous ethanol. The maximum absorption wavelength λ_{max}(nm) were obtained and converted to wavenumber ν_{max}(cm^{-1}) ($\nu_{max} = 1/\lambda_{max}$) for quantitative structure-property relationship study. Hammett parameters (σ, σ_F, σ_R), electronegativity (χ), the excited-state substituent effect parameter (σ^{ex}_{CC}), and the heavy atom effect indicator (D) were employed as descriptors characterizing the molecular structure. By stepwise regression, a 5-descriptor linear regression model was built as $\nu_{max} = 35\,864.8122 + 6743.7901\sigma_R(X) + 8587.9937\sigma_R(Y) - 2042.7280\Delta\sigma^2 + 1106.0034D(X) + 1451.8873\chi(X)$ ($R = 0.9861$, S = 693.70, ARD = 1.49%, F = 218.68, $R_{cv} = 0.9775$, $S_{cv} = 881.25$, $ARD_{cv} = 1.82\%$, $n = 37$). The model is proved of good stability and predictive performance by leave-one-out cross validation. Compared with the benzylideneaniline derivatives with C═N bridge group, the substituent effects on the UV absorption energy of 2,5-disubstituted pyrimidines are quite different and much more complex.

KEYWORDS

2,5-disubstituted pyrimidine, quantitative structure-property relationship, substituent effect, UV absorption

1 | INTRODUCTION

Pyrimidine, a 6-membered aromatic heterocyclic compound with 2 nitrogen atoms, has some special properties such as high π-electron delocalization, high electron affinity, and so on.[1,2] Due to the strong aromaticity, presence of n-π electronic states, pyrimidine-containing molecules exhibit perfect photoelectric properties and have been extensively investigated in organic light emitting devices,[3–8] solar cells,[9,10] and liquid crystals.[11] 2,5-Disubstituted pyrimidines are the most interested model compounds. For example, Wong et al[4–6] synthesized a series of linear molecules with 2,5-pyrimidinylene unit and investigated their photophysical properties. Gompper[12] found that 2,5-diarylpyrimidines with donor-acceptor substituents have interesting nonlinear

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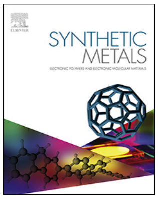

Small-molecule acceptors based on 4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophene units with near-infrared absorption for nonfullerene polymer solar cells

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ABSTRACT

Two small-molecule acceptors 1CIC and 2CIC based on 4*H*-cyclopenta[1,2-*b*:5,4-*b′*]dithiophene units and 1,1-dicyanomethylene-3-indanone were developed. Compared with 1CIC, 2CIC possesses red-shift absorption, higher HOMO and LUMO energy levels, and higher electron mobility. Nonfullerene polymer solar cells based on PTB7-Th:2CIC gave a power conversion efficiency (PCE) of 3.53%, with an open-circuit voltage (V_{oc}) of 0.75 V, a short-circuit current (J_{sc}) of 10.97 mA/cm^2. As contrast, PTB7-Th:1CIC cell gave a PCE of 0.26%. Our results indicated that the absorption spectra of small-molecule acceptors containing indaceno[1,2-*b*:5,6-*b′*]dithiophene (IDT) core can be efficiently extended to near-infrared region by replacing the aromatic benzene ring of with 2,2′-bithiophene.

1. Introduction

Polymer solar cells (PSCs) with bulk heterojunction (BHJ) architecture have attracted extensive attention due to their unique advantages such as low processing cost, flexibility, and light weight [1,2]. Generally speaking, PSCs employed conjugated polymers as electron donors, fullerenes or their derivatives, such as phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$), phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) and indene-C_{70} bisadduct ($IC_{70}BA$), as electron acceptors [2–5]. However, fullerene derivatives suffer from several drawbacks, like poor light absorption, limited tunability of chemical structures and energy levels, high-cost purification and morphology instability [6–9]. Therefore, non-fullerene electron acceptors, particularly small-molecule electron acceptors, have been developed rapidly in past few years [7–15]. Small-molecule acceptors with efficient absorption, tunable energy levels, good device stability, and easy synthesis and purification have become one of the hottest research topics in organic optoelectronic. Very recently, single PSCs based on small-molecule electron acceptors have successfully achieved power conversion efficiencies (PCEs) over 14%, and these have been considered as promising alternatives to fullerenes derivatives [16].

The optical and electronic properties of small-molecule acceptor materials with acceptor-donor-acceptor (A-D-A) structure can be easily tuned by varying the electron-donating cores or end-capping electron-withdrawing groups. Small-molecule acceptors based on indaceno[1,2-*b*:5,6-*b′*]dithiophene (IDT) [17], indacenodithieno[3,2-*b*]thiophene (IDTT) [7], indacenobis(dithieno[3,2-*b*:2′,3′-*d*]thiophene) (IBDT) [18], benzo[1,2-*b*:4,5-*b′*]di(cyclopenta[2,1-*b*:3,4-*b′*]dithiophene) [19], and other electron-rich units [20,21] have demonstrated excellent photovoltaic performance. 4*H*-Cyclopenta[1,2-*b*:5,4-*b′*]dithiophene (CPDT), where two thiophene units are rigidified by a covalent carbon, is an excellent unit for D-A copolymers or small molecules donor material in organic solar cells (OSCs) or dye-sensitized solar cells (DSSCs) [22–25]. Very recently, Chen et al. reported a new nonfullerene acceptor DF-PCIC with an unfused-ring core containing one 2,5-difluorobenzene and two CPDT moieties, which yielded a decent PCE of 10.14% [26]. In this work, two small-molecule electron acceptors 1CIC and 2CIC using CPDT as the core units and 1,1-dicyanomethylene-3-indanone (IC) as the ending group were synthesized (Fig. 1). In addition, 2CIC can be regarded as a derivative of IDIC by replacing benzene ring with 2,2′-bithiophene [17]. Compared with 1CIC, 2CIC with two CPDT units possesses broader absorption spectra even to near-infrared region with optical bandgap of 1.35 eV, which is much narrower than that of IDIC (1.62 eV) [17]. PSCs based on PTB7-Th:2CIC gave a PCE of 3.53%,

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A highly porous acylamide decorated MOF-505 analogue exhibiting high and selective CO_2 gas uptake capability†

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Porous metal–organic frameworks (MOFs) constructed from organic linkers and metal ions/clusters can provide special pore environments for selective CO_2 capture. In this work, we designed and synthesized a highly porous acylamide-functionalized MOF (HNUST-7) from a nanosized linear diisophthalate ligand with linking acylamide groups and Cu(II)-paddlewheel clusters. Structural analysis shows that HNUST-7 possesses a (4,4)-connected NbO-type 3D open framework incorporating two different types of metal–organic cages. After activation, HNUST-7 displays a high BET surface area of 2804 $m^2 g^{-1}$ and large CO_2 uptakes of 26.1 and 19.4 mmol g^{-1} under 30 bar at 273 and 298 K, respectively. In addition, with the optimized pores and functional sites (open copper sites and Lewis basic acylamide groups) integrated within the framework, HNUST-7 exhibits highly selective adsorption of CO_2 over CH_4 and N_2 under ambient conditions, which have been verified by both single compound gas sorption measurements and dynamic column breakthrough experiments.

1. Introduction

Metal–organic frameworks (MOFs, also known as porous coordination polymers, PCPs) have been rapidly emerging as a new class of crystalline hybrid porous materials with periodic network structures, which are readily assembled *via* metal coordination bonds from multidentate organic ligands acting as linkers and metal ions or metal clusters serving as connectors. Compared with conventional porous materials such as zeolites and activated carbons, MOFs possess large specific surface areas, and in particular, their overall structures (framework topology, pore size and geometry, and chemical functionalities) can be systematically tailored and/or finely tuned on the atomic level for targeted applications such as strategic gas storage/separation,[1] heterogeneous catalysis,[2] drug delivery,[3] luminescent sensing,[4] *etc.* Design and synthesis of porous MOFs with high performance has been attracting continuous and increasing attention over the past few decades, and the research in this area has become one of the most interesting fields in chemistry and materials science.[5]

Rational design/choice of organic linkers and inorganic moieties is crucial for the assembly of porous MOFs with desired structures and properties. We are especially interested in the design and construction of porous MOFs from nanosized multicarboxylate ligands linked by polar functional groups (*e.g.* acylamide, oxalamide, *etc.*) and dicopper(II) paddlewheel clusters, because such an approach may facilitate the generation of expanded and non-interpenetrated frameworks with high surface areas. In addition, both the pre-designed open copper(II) sites and polar acylamide functionalities within the frameworks can provide strong binding sites for target guest molecules associated with gas storage/separation, which has been unambiguously verified by both computational and experimental studies.[6,7] By working with the above consideration, we successfully synthesized several acylamide-functionalized MOFs and realized a balance between high gas binding affinity and large gas storage/separation capacity.[6] For example, by utilizing a nanosized rectangular acylamide-bridging tetra-carboxylate linker (bis(3,5-dicarboxyphenyl) terephthalamide = H_4BDPT), we recently reported an expanded NbO-type MOF (HNUST-1, HNUST denotes Hunan University of Science and Technology), which exhibits an exceptionally high CO_2 uptake capacity of 30.7

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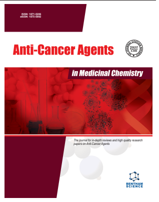
REVIEW ARTICLE



Indazole Derivatives: Promising Anti-tumor Agents

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Abstract: ***Background*:** Currently, cancer continues being a dramatically increasing and serious threat to public health. Although many anti-tumor agents have been developed in recent years, the survival rate of patients is not satisfactory. The poor prognosis of cancer patients is closely related to the occurrence of drug resistance. Therefore, it is urgent to develop new anti-tumor agents to make up for the deficiency. Indazoles is an important class of heterocyclic compounds possessing a variety of biological activities, such as anti-tumor, anti-bacterial, anti-inflammatory, anti-depressant and anti-hypertensive. This review focuses on the recent research advances of indazole derivatives in the aspect of anti-tumor.

***Methods*:** We have searched the recent literatures about indazole derivatives from the online resources and databases, such as pubmed, scifinder and google scholar.

***Results*:** In the recent years, many efforts have been taken to develop indazole derivatives as fibroblast growth factor receptor (FGFR) inhibitors, indoleamine-2,3-dioxygenase1 (IDO1) inhibitors, proviral integration site MuLV (Pim) kinase inhibitors, aurora kinases inhibitors, Bcr-Abl inhibitors, hypoxia inducible factor-1 (HIF-1) inhibitors and carbonic anhydrase (CA) inhibitors. Most compounds display good anti-tumor activities.

***Conclusion*:** Developing new anti-cancer agents with new scaffolds and high efficiency is a big challenge for researchers. Indazole derivatives are a class of important bioactive compounds. Making structural modifications on active indazole derivatives according to the corresponding structure-activity relationships is of benefit to obtain more potent anti-cancer leads or clinical drugs. This review will be useful for further development of new indazole-based derivatives as anti-cancer agents.

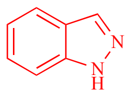
Keywords: Indazole derivatives, anti-tumor, biological activities, heterocyclic compounds, drug design, structure-activity relationship, inhibitors.

1. INTRODUCTION

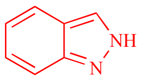
Cancer is a class of serious diseases to threaten our health severely, which displays the uncontrolled, rapid and pathological propagation for abnormal cells. In spite of the rapid development in diagnostic and therapeutic protocols, cancer is second only to cardiovascular disease as a cause of death in the world based on the World Health Organization [1]. In the USA, about 1,688,780 new cancer cases and 600,920 cancer deaths are reported in 2017 [2]. Besides surgery and radiation therapy, chemotherapy is a widely applied medical treatment for cancer, which has emerged as a new era of molecularly targeted therapeutics [3]. However, the survival rates of patients are still unsatisfactory mainly due to the arising of drug resistance, which remain unsatisfactory mainly because of drug resistance, which severely hinders the development of patient prognosis. And it is urgent to develop new agents to overcome the drawbacks of the current chemotherapy. Therefore, intense effort has been made to design and develop new anti-cancer agents with higher efficiency and less toxicity for scientists in the past few years [4].

Heterocyclic chemistry is a significant branch of organic chemistry. The compounds in the branch have drawn considerable attention not only because of their biological and industrial applicability but also due to the contribution to human society. These compounds could be obtained from laboratory or natural sources, which usually display some bioactivities. In addition, heterocyclic compounds are widely used in industry, which function as additives and modifiers, such as cosmetics, polymers and antioxidants [5]. Hence, effective synthesis of hetercycles has been a promising subject in the chemistry. Among these heterocyclic compounds, diverse indazole derivatives have aroused interest because of their wide variety of biological properties.

As the bioisostere of indole, indazole is a ten π electron aromatic heterocyclic system. It was firstly defined as a pyrazole ring condensed with the benzene ring by scientist Emil Fisher, also called as benzpyrazole compounds. The indazole ring has two annular tautomers owing to the position of NH hydrogen atom, named 1*H*-tautomer and 2*H*-tautomer. In general, the 1*H*-tautomer holds dominant position in the gas-phase, solution and solid state. Likewise, its derivatives are more stable than the corresponding 2*H*-forms in thermodynamics. Indazole ring has special structure (two nitrogen atoms, planarity of ring) that can afford many modified sites to provide an array of diverse derivatives with biological and therapeutic properties. In this review, we have focused on the recent development of indazole derivatives as anti-cancer agents in the past few years.



1*H*-tautomer



2*H*-tautomer

2. ANTI-CANCER ACITIVITIES

2.1. FGFR Inhibitors

The FGFR family is composed of four receptor tyrosine kinases (RTKs), that is FGFR1/2/3/4, which plays a prominent role in many biological events, such as embryogenesis, tissue homeostasis, tissue repair, wound healing and inflammation [6, 7]. In cancer cells, FGFR signaling could be activated by gene amplification, point mutations, or chromosomal translocations/rearrangements, which are associated with cell growth, angiogenesis, cell migration, invasion, and metastasis [8, 9]. Considerable evidences demonstrate that aberrant amplification of FGFR could be observed in multiple types

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Geometric deconstruction of core and electron activation of a π-system in a series of deformed porphyrins: mimics of heme†

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The predominant distortion of heme is responsible for its electronic activity, catalytic ability and spectral properties. In this work, altogether 12 new X-ray structures of saddled, waved and ruffled porphyrins are reported. Three types of deformed porphyrins as mimics of heme were evaluated and analyzed by geometric deconstruction, spectral comparison, and electrochemical tracking, which shows a unique relationship of deformation fashions and distortion degree to the geometry of the core and electron transfer ability of rings in these enzyme containing porphyrins. These mimics can adjust their core geometry for changing the structures of potential metals; while for rings themselves, they can also regulate the electron activity by switching the HOMO of the large π systems. These deformed porphyrins can be used as ideal mimics for heme. These findings help us to understand the principle and contribution of these deformations to electron transfer in catalytic oxidation and photoreactions. The nonplanar mimics have been synthesized through a modular synthetic approach under Adler–Longo or Lindsey condensation conditions.

Introduction

It is well known that the ligand geometry and chelating topology[1] in coordination compounds play an important role in regulating the properties of central metal species[2–4] such as valence[5,6] and magnetism.[7] For instance, the distortion of some planar tetrapyrrole macrocycles and the corresponding conformational change in several metalloenzymes significantly affects their key functions[8–12] that are closely related to the storage, transportation, and conversion of biologically important small molecules.[13–16] In particular, the highly flexible porphyrin planes in heme complexes are responsible for the stabilization of the low-valent Fe^{II} oxidation state[17] and the formation of the high-valent $Fe^{IV,V}$-oxo complexes,[18] which further drive the binding or conversion of NO[19] or O_2.[20] Therefore, in order to understand the mechanisms of the metal-mediated electron (or charge) transfer processes in naturally occurring tetrapyrroles, it is important to examine their geometry and geometric effects.[21,22]

Recently, we have demonstrated that the core contraction of porphyrins derived from ruffled and saddled deformations can not only induce a rotation of the *meso*-aryl group,[23] but also change the electronic structure of coordinated metal ions such as Fe^{III},[24,25] Co^{II},[26–28] Cu^{II},[29,30] and Zn^{II}.[31] Indeed, in catalysis related to naturally occurring tetrapyrroles, one can use a "domino effect" to describe the inter-relationship between ring distortion, the metal-center's property, the axially coordinated ligand, and the potential reactant where the ring distortion plays a decisive role (Fig. 1). In order to mimic the unique distortion in naturally occurring tetrapyrroles, three strategies have been developed to synthesize their artificial counterparts, namely, increasing peripheral crowdedness,[32] using size-mismatched metal cations, and adding straps.[3,33] The crowdedness strategy was initially utilized to prepare photoactive compounds[34] for photodynamic therapy[35,36] and photosynthetic antenna,[37] where the distortion was induced by the bulky substituents at *meso*- and *β*-positions of porphyrins.[38,39] Small (*e.g.* Li^{I} [40] and Ni^{II} [41]) or large (*e.g.* Pt^{II} [42] and Cd^{II} [43]) metal cations have also been extensively used to induce ring distortion.[44] Short straps can be incorporated running

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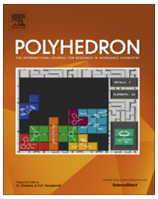

A 2D water-stable metal–organic framework for fluorescent detection of nitroaromatics

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ABSTRACT

By reacting $Zn(NO_3)_2{\cdot}6H_2O$ and H_2btca in the presence of iqo under hydrothermal conditions to give a 2D water-stable metal–organic framework (MOF), $\{[Zn(btca)(iqo)_2]\}_n$ (**1**) (H_2btca = benzotriazole-5-carboxylic acid, iqo = isoquinoline), which has been verified by combining X-ray single-crystal diffraction, thermogravimetric (TG) analysis, and infrared (IR) spectrum. Each five-coordinated Zn^{2+} in **1** exhibits a pentagonal bipyramid geometry defined by four N atoms from two btca^{2-} ligands and two iqo molecules, and one O atom from one carboxylate group of btca^{2-} ligand. Neighbouring Zn^{2+} are bridged by btca^{2-} ligands to form a 2D '**fes**'-type network, further generating a 3D supramolecular network through hydrogen bonds and $\pi \cdots \pi$ stacking interactions. Importantly, MOF **1** exhibits strong fluorescence in aqueous solution and can be used for detecting $Cr_2O_7^{2-}/CrO_4^{2-}$ and nitroaromatics compounds based on fluorescence quenching effects. Furthermore, experimental and theoretical calculations suggest that the fluorescence quenching effect could be mainly ascribed to the electron and energy transfer as well as electrostatic interactions between **1** and nitroaromatics analytes.

1. Introduction

Metal–organic frameworks (MOFs), as one of the most dramatic crystalline porous materials, have attracted predominant attentions owing to not only their abundant architectures, but also their wide applications in luminescent recognition, gas storage and separation, catalysis, and so on [1–5]. Among various applications, MOF-based sensors have been widely applied towards sensing of numerous analytes, which is mainly due to the following natural advantages compared with other luminescent sensors [5–11]. (i) The precise structures of MOFs are easily determined by X-ray single-crystal diffraction for their intrinsic crystallinity, which provide the possibility to investigate the recognition mechanisms at molecular level through structure–property correlations and host–guest interactions. (ii) The porous nature of MOFs can capture and preconcentrate the target analytes, enhancing the opportunity of host–guest interactions and increasing the sensitive detections. Moreover, functional groups and Lewis acidic or basic sites of organic ligands, as well as open metal sites, are liable to be employed into MOFs through pre-design of the structures or post-synthetic modifications, which further promote their detection selectivity. (iii) The rigid MOFs could effectively reduce the non-radiative relaxation and lead to the strong emissions in comparison with the free vibration and rotation of organic ligands. (iv) MOF-based sensors usually possess high thermal and chemical stabilities because of their relatively strong coordination interactions between metal centers and organic ligands, permitting them suitable even at elevated temperatures and broad range of pH values. Additionally, the permanent porosity allows them to recycle for many cycles without losing luminescence and crystallinity. As a result, an overwhelming number of MOF-based sensors for sensitive and selective detection of various analytes including ionic species, small organic molecules, gases, explosives, environmental toxins, biomolecules and many other have emerged in the past decade [5–11].

Nitroaromatics, as one type of important chemical materials, have been widely used in the explosives, pesticides, pharmaceuticals, leather and rubber. Meanwhile, nitroaromatics are also a class of compounds that greatly affect public safety, human health, and environment due to their explosibility and high toxicity [9–11]. With the rapid development of science and technology, various

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A theoretical investigation on Cu/Ag/Au bonding in $XH_2P\cdots MY$(X = H, CH_3, F, CN, NO_2; M = Cu, Ag, Au; Y = F, Cl, Br, I) complexes

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Intermolecular interaction of $XH_2P\cdots MY$ (X = H, CH_3, F, CN, NO_2; M = Cu, Ag, Au; Y = F, Cl, Br, I) complexes was investigated by means of an *ab initio* method. The molecular interaction energies are in the order Ag < Cu < Au and increased with the decrease of $R_{P\cdots M}$. Interaction energies are strengthened when electron-donating substituents X connected to XH_2P, while electron-withdrawing substituents produce the opposite effect. The strongest P···M bond was found in $CH_3H_2P\cdots AuF$ with −70.95 kcal/mol, while the weakest one was found in $NO_2H_2P\cdots AgI$ with −20.45 kcal/mol. The three-center/four-electron (3c/4e) resonance-type of P:-M-:Y hyperbond was recognized by the natural resonance theory and the natural bond orbital analysis. The competition of P:M–Y ↔ P–M:Y resonance structures mainly arises from hyperconjugation interactions; the bond order of $b_{P\text{–}M}$ and $b_{M\text{–}Y}$ is in line with the conservation of the idealized relationship $b_{P\text{–}M} + b_{M\text{–}Y} \approx 1$. In all MF-containing complexes, P–M:F resonance accounted for a larger proportion which leads to the covalent characters for partial ionicity of MF. The interaction energies of these Cu/Ag/Au complexes are basically above the characteristic values of the halogen-bond complexes and close to the observed strong hydrogen bonds in ionic hydrogen-bonded species. *Published by AIP Publishing.* https://doi.org/10.1063/1.5027605

I. INTRODUCTION

Noncovalent interactions have attracted widespread interest due to their indispensable role in supramolecular chemistry, molecular self-assembly, and materials science.[1–5] The hydrogen bonds are the most traditional research area for the noncovalent interactions, but recently, a new type of intermolecular interaction involving closed-shell molecules between a Lewis base B (where B is H_2O, H_2S, CO, N_2, PH_3, C_2H_2, C_2H_4, or C_3H_6) and a diatomic molecule M–X (where M is Cu, Ag, or Au and X is a halogen atom) has attracted a lot of attention both experimentally and theoretically.[6–13] Many studies have shown that the type of pairwise interaction B···M–X is isomorphic with its hydrogen-bonded (B···HX, where X is a halogen atom)[14–16] and halogen-bonded (B···XY, where XY is a dihalogen molecule)[17–20] interactions but is generally stronger. For instance, the gold bond was first proposed[21] by the theoretical study of strong bonded HF/$H_2O\cdots$AuOH; the significant charge transfer was from the lone pair HF/H_2O donors to AuOH during the complex formation, similar to that in the hydrogen bond. The Ag-bond in $H_2O/H_2S\cdots$AgCl investigated experimentally by Legon *et al.* is also analogous to the hydrogen bond.[22] These interactions have some similarities to the hydrogen bonding, but the details are not very clear and much effort has been put into revealing the nature of these interactions during the past decades.[23–25]

Computational studies showed that hyperconjugation interactions participated in noncovalent interactions.[26] Hydrogen-bond has been accurately decribed by resonance concept in terms of the three center/four-electron (3c/4e), and the resonance interactions are expressed as hyperbonds or ω bonds (the resonance hybrid of asymmetrically weighted neutral and proton-transferred resonance forms) to differentiate them from conventional 2c/2e bonding interactions.[27,28] The 3c/4e hyperbond goes beyond the typical Lewis structure[29] and can be described as resonance bonding, commonly originating in the very strong n → σ* donor–acceptor interaction. Cyclic 3c/4e hyperbonding resonance bonding patterns were also found in "phosphadioxirane" intermediates.[30] The 3c/4e hyperbond often exists in the transition metal coordination compound because the polar M–B bond is easily attacked from the back by a Lewis base. The hyperbonded triads generally have near-linear structures which can be compactly described as a resonance hybrid mixture of A:M–B ↔ A–M:B. Zhang *et al.*[31] studied the 3c/4e system in NgM–Y (Ng = He, Ne, Ar, Kr, Xe, Rn; M = Cu, Ag, Au; Y = F, Cl, Br, I) complexes: they introduced the resonance bonding model in H-bonding into

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Mini-review

Small-molecule Mcl-1 inhibitors: Emerging anti-tumor agents

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ABSTRACT

The anti-apoptotic members of B-cell lymphoma-2 (Bcl-2) proteins family, such as Bcl-2 and myeloid cell leukemia-1 (Mcl-1), are the key regulators of the intrinsic pathway of apoptosis and overexpressed in many tumor cells, which have been confirmed as potential drug targets for cancers. A number of Bcl-2 proteins inhibitors have been developed and conducted clinical trials, but no Mcl-1 inhibitors are presented in the clinics. In addition, Mcl-1 is an important reason for the resistance to radio- and chemotherapies, including inhibitors that target other Bcl-2 family members. For example, the recently launched Bcl-2-selective inhibitor ABT-199 displays highly potency in the treatment of chronic lymphocytic leukemia (CLL), but it cannot induce the apoptosis controlled by Mcl-1 in some tumor cell lines. Therefore, developing potent Mcl-1 inhibitors become urgently needed in clinical therapy. This review briefly introduces the structure of Mcl-1 protein, the role in cancers and focuses on the progress of small-molecule Mcl-1 inhibitors from 2012 to 2017.

1. Introduction

Tumor is a kind of serious and complexed diseases that cause abnormal cell proliferation. Evading apoptosis is an important hallmark of cancers, which is often a key factor for drug resistance in the chemotherapy [1]. There are two major pathways to induce apoptosis, named extrinsic pathway and intrinsic pathway. The extrinsic apoptosis pathway is triggered by extracellular ligands that bind cell surface receptors of the tumor necrosis factor receptors (TNFR) superfamily [2]. On the other hand, the intrinsic pathway conducts within the cell and mainly is regulated by Bcl-2 proteins family [3].

The Bcl-2 proteins family consists of anti-apoptotic proteins and pro-apoptotic proteins based on their functions. All of the members share at least one of four conserved Bcl-2 homology (BH) domains called BH1, BH2, BH3 and BH4. The anti-apoptotic proteins such as Bcl-2, Bcl-xL, Mcl-1, have three or four BH domains. The pro-apoptotic proteins are further grouped into multidomain proteins (e.g., Bax, Bak and Bok) and BH3-only proteins (e.g., Bad, Bim and Bik) [4]. The intrinsic pathway is regulated by the interaction between anti-apoptotic proteins and pro-apoptotic proteins. When cells are stimulated by apoptotic signals such as cell stress, DNA damage and ultraviolet irradiation, BH3-only proteins activate the apoptotic effectors Bax and Bak through two mechanisms. One is that they directly bind to Bax and Bak, while the other one is that they suppress anti-apoptotic proteins (such as Bcl-2, Bcl-xL, Mcl-1) to set free Bax and Bak. Subsequently, Bax and Bak form homo-oligomers to release cytochrome *c* into cytosol by mitochondrial outer membrane permeabilization (MOMP), which promotes the formation of apoptosome to drive the caspase cascade and result in apoptosis [5].

During the life of a cell, its fate is largely related to the relative ratio of anti-apoptotic and pro-apoptotic Bcl-2 proteins. When anti-apoptotic Bcl-2 proteins are expressed in large amount, they block cell death by binding to pro-apoptotic Bcl-2 proteins to sequester their pro-apoptotic effects. Since evading apoptosis is one characteristic of cancers, targeting anti-apoptotic Bcl-2 proteins to reinstate the apoptosis has been a promising strategy of anti-tumor research [6]. A number of small-molecule inhibitors targeting anti-apoptotic Bcl-2 proteins with different scaffolds have been reported in recent years. So far, there are three small molecule inhibitors, that is *R*-(−)-Gossypol (AT-101) [7], GX15-070 (Obatoclax) [8] and

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Research paper

Design, synthesis and biological evaluations of novel pyridone-thiazole hybrid molecules as antitumor agents

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ABSTRACT

A hybrid pharmacophore approach was adopted to design and synthesize new series of pyridone-thiazole hybrid compounds. The structures of the compounds were established by IR, ^1H NMR, ^{13}C NMR, and HRMS. All the newly prepared compounds (**3a-3m**) were *in vitro* evaluated for their anti-proliferative activity against three human cancer cell lines, namely Colon cancer (HCT-116), gastric carcinoma (MGC803) and hepatocellular cancer (Huh7). Bioassay results demonstrated that most of the tested compounds showed potent anti-tumor activities against various cancer cells *in vitro*, and some compounds exhibited stronger effects than positive control 5-Fluorouracil (5-FU). Compound **3b** showed the best anti-tumor activity with IC_{50} values of 8.17 μM and 3.15 μM against HCT116 and MGC803 cell lines, respectively, which was 1.4–8.1 times more potent than 5-Fluorouracil ($IC_{50} = 11.29$ μM and 25.54 μM against HCT116 and MGC803 respectively). These findings suggest that compound **3b** may have potential to be developed as a promising lead for the design of novel anticancer small-molecule drugs.

1. Introduction

Molecular hybridization is a valuable structural modification approach that comprises the incorporation of two or more pharmacophores into a single entity. In the last few years, hybrid drug design has emerged as a prime tool for the discovery of innovative anticancer therapies that can potentially overcome most of the pharmacokinetic drawbacks encountered when using conventional anticancer drugs.

The pyridin-2(*1H*)-one ring system present in various natural active substances [1,2]. The existence of a pyridin-2(*1H*)-one structural unit is a key to the pharmacological activities of many natural and synthetic drugs. A large number of compounds having pyridin-2(1*H*)-one ring system has been reported to possess different kind of biological activities like anti-tumor [3], cardiotonic [4], antituberculosis [5], antibacterial [6] and antihepatitis B virus [7]. Recently, pyridin-2(1*H*)-ones include 5-ethyl-1-phenyl-2-(1*H*)-pyridone [8], Camptothecin [9] and 3-(4,5,6,7-tetrahydro-3*H*-imidazo[4,5-*c*]pyridin-2-yl)-1*H*-quinolin-2-one [10] have been reported to show strong cytotoxicity against several human cancer cell lines.

Heterocycles containing the thiazole moiety are important targets in synthetic and medicinal chemistry because this fragment is a key moiety in a number of natural and synthetic biologically active agents [11,12]. In the last few decades, the clinical efficacy of tiazofurin and its analogs, and bleomycins (BLMs) has pointed out the importance of thiazole moiety for anticancer drug design. Bleomycins, glycopeptide antitumor antibiotics produced and isolated from *Streptomyces sp* have been clinically used to treat several types of cancers, like squamous cell carcinomas, malignant lymphomas and testicular cancers. In view of these reports and in continuation with the previous work, we therefore envisaged that integrating pyridin-2(1*H*)-one and thiazole moieties in one molecular platform could potentially produce novel compounds with significant synergistic antitumor properties (Fig. 1). These new pyridin-2(1*H*)-ones analogues bearing thiazole moiety (**3a-3m**) were prepared to verify their efficacy as potential anticancer agents.

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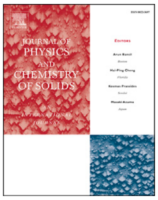

CeHIO$_6$·4H$_2$O: A novel, highly efficient catalyst for degrading organic dyes without light illumination at room temperature

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ABSTRACT

It is still desirable to obtain the catalysts to degrade organic dye pollutants at room temperature, which meets the current demands of pollutant-removing and energy-saving simultaneously. By a facile precipitation method, we prepared in this work a new, highly efficient CeHIO$_6$·4H$_2$O catalyst. By characterization, it was found that the CeHIO$_6$·4H$_2$O sample is in nature a yellow inorganic semiconductor with particle size of 0.2–10 μm, band gap of 2.75 eV, low surface area of 1.52 m^2 g^{-1} and amorphous structure. The CeHIO$_6$·4H$_2$O catalyst showed high activity in degradation of rhodamine B (RhB), methyl orange (MO) and methylene blue (MB) in the dark at room temperature. After being used for 3 cycles, it did not undergo significant loss of activity and kept its chemical composition unchanged in the degradation experiments. More importantly, its activity is remarkably higher than that of the previously reported Ce(IO$_3$)$_4$, CeGeO$_4$, ZrHIO$_6$·4H$_2$O and Ce-doped MoO$_3$ analogues. The major active species and the catalytic mechanism for the dye degradation were proposed.

1. Introduction

Organic dye pollutants have posed wide public concern with their severe harm to human health and ecosystems. In the recent decades, semiconductor photocatalysis technology has been extensively researched due to its application in degradation of organic dye pollutants with sustainable solar energy [1—13]. As solar radiation contains a small fraction of ultraviolet ray and abundant visible light, the core issue to utilize solar energy through photocatalysis is making full use of visible light from solar irradiation with visible-light-responsive photocatalysts [11,14]. However, it remains still a challenge to get visible-light-responsive photocatalysts with both high activity and high stability [11,14,15].

A solution to this energy-saving issue involved in photocatalysis technology is to decompose organic dye pollutants without light illumination through process of catalytic wet air oxidation (CWAO) [16—23]. Elaborate choice of catalyst is key to successful application of CWAO since a favourable catalyst is able to relief the severity of oxidation conditions like reaction temperature, reaction pressure, etc [16—23]. Up to now, several catalysts including Ce(IO$_3$)$_4$ [16], CeGeO$_4$ [17], ZrHIO$_6$·4H$_2$O [18], Fe$_2$O$_3$-CeO$_2$-TiO$_2$/γ-Al$_2$O$_3$ [19], Ce-doped MoO$_3$ [20,21], CuO-MoO$_3$-P$_2$O$_5$ [22], ZnO/MoO$_3$/SiO$_2$ [23] and Pt–HCa$_2$Nb$_3$O$_{10}$ [24] were employed in degrading organic dyes without light illumination at room temperature. Nevertheless, the CWAO degradation of organic dyes still has the problems of low efficiency or laborious synthesis of the catalysts. Continuing efforts to develop novel catalysts for the CWAO process under mild conditions is still desirable to provide more insights into the CWAO process and hence enhance the degradation efficiency.

In this work, we prepared a CeHIO$_6$·4H$_2$O compound by a simple precipitation method [25]. To the best of our knowledge, no research work has been conducted on its structure, physicochemical and functional properties including catalytic performance, etc. Interestingly, it was found applicable to degrade organic dyes even in the dark at room temperature. The CeHIO$_6$·4H$_2$O catalyst achieved higher catalytic performance than the previous Ce(IO$_3$)$_4$ [16], CeGeO$_4$ [17], ZrHIO$_6$·4H$_2$O [18] and Ce-doped MoO$_3$ [21] analogues. Also gratifyingly, it performed with high durability and high stability in the dye degradation experiments.

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Adsorption efficiency, thermodynamics, and kinetics of amino-functionalized mesoporous calcium silicate for the removal of heavy metal ions

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ABSTRACT

Amino-functionalized mesoporous calcium silicate (MCS-NH_2) was synthesized by past-grafting with calcium nitrate tetrahydrate and sodium metasilicate nonahydrate as raw materials, cetyl trimethyl ammonium bromide as the template, and 3-aminopropyltriethoxysilane as the modifying agent. The structure and composition of MCS-NH_2 were characterized, and the adsorption performance and thermodynamic and kinetic characteristics of MCS-NH_2 were investigated using Pb^{2+}, Cd^{2+}, Cr^{3+}, and Cu^{2+}. MCS-NH_2 maintained its mesoporous slit-pore structure with a specific surface area of 114.32 m^2/g, and pore size was mainly within 4.5–49 nm in the modification. The amount of $–NH_2$ grafted to MCS-NH_2 was 1.6106 mmol/g. The equilibrium data of Pb^{2+}, Cd^{2+}, Cr^{3+}, and Cu^{2+} adsorbed by MCS-NH_2 fitted the Langmuir and Redlich–Peterson models well but were more suitable for the latter. The maximum adsorption capacities deduced from the Langmuir model were 717.97, 631.43, 628.61, and 366.88 mg/g for Pb^{2+}, Cd^{2+}, Cu^{2+}, and Cr^{3+}, respectively. The adsorption processes were endothermic, entropy increasing, and spontaneous. The adsorption of Pb^{2+}, Cd^{2+}, Cr^{3+}, and Cu^{2+} by MCS-NH_2 was rapid and reached equilibrium within 60 min. The adsorption kinetics fitted the pseudo second-order model well, and the adsorption activation energy was 21.0187, 18.1051, 25.9062, and 16.8084 kJ/mol, respectively. The adsorption mechanisms included physical adsorption, chemical adsorption (especially surface complexing adsorption), and ion exchange, among which chemical adsorption was the dominant mechanism. The findings suggest that MCS-NH_2 can be used as an effective sorbent for removing Pb^{2+}, Cd^{2+}, Cr^{3+}, and Cu^{2+} and other related hazardous metal ions from wastewater.

Keywords: Amino-functionalized mesoporous calcium silicate; Heavy metal ion; Adsorption performance; Adsorption thermodynamics and kinetics; Adsorption mechanism

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The Polyurethane/5A Zeolite Hybrid Hydrogel with Thermal- and pH-Sensitivity for Removing Acid Fuchsin from Aqueous Solutions

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A series of polyurethane/5A zeolite hybrid hydrogels (5A hydrogels) were successfully prepared via wet phase inversion method for removal of acid fuchsin from aqueous solutions. The morphology, organic groups, phase transition temperature and crystallinity of the hydrogels were investigated by SEM, FTIR, DSC and XRD, respectively. The SEM observation didn't show that obvious coagulation in interior, until content of 5A zeolite exceeded 20%. The FTIR analysis revealed that the 5A hydrogels were synthesized successfully, and 5A zeolite had been filled in it. The DSC analysis and XRD analysis indicated that the regular arrangement of polyurethane network was destroyed by 5A zeolite particle. The adsorption experiments demonstrated that the adsorption capacity (q_e) of 5A hydrogels was still influenced by the external temperature after the introduction of 5A zeolite, which shown upward trend with content of 5A zeolite rose. In addition, the adsorption capacity (q_e) of 5A hydrogels increased under neutral pH conditions due to the introduction of 5A zeolite, differing with the polyurethane (PU) hydrogel. Hopefully, 5A hydrogels will be widely used in the water treatment, molecular imprint and separation etc.

Keywords: Polyurethane Hydrogel, Thermal- and pH-Sensitivity, 5A Zeolite, Acid Fuchsin.

1. INTRODUCTION

Dyes are widely used in many modern industries such as paint, plastic, leather and food industries etc.[1–3] Many dyes could be dissolved in water, which are toxic and even carcinogenic, thus damaging the human health and environment.[4,5] The treatment of dyes has aroused diffusely concern in recent years.[6,7] Several effective technologies have been applied to separate dyes from industrial wastewater, such as liquid–liquid extraction, separation and adsorption.[8,9] Among these methods, adsorption is the most economical and practical method owning to the advantages of cost, facility and operation.[10,11] Various adsorbents such as activated carbons,[12,13] chitosan,[14] agricultural peels[15] are used in separation of dyes from wastewater. In recent years, environmental-friendly polymer composites materials have caused extensive concern by researchers.[16–20] More and more research have provided opportunities for developing the treatment of wastewater by adsorption.[21,22] Smart hydrogels with excellent physics and chemistry property such as non-toxic, low cost and other characteristic, one of environmental-friendly polymer composites materials, have attracted much attention.[23,24]

Intelligent hydrogel is a kind of polymer with three-dimensional structure, which could reversibly adjust the internal structure responding to temperature, pH value,[25] magnetism[26] and metal ion.[27] The intelligent hydrogels have caused extensive concern due to their excellent performance in recent years.[28,29] In addition, intelligent hydrogels have been applied in field of drug delivery,[30,31] biochemical sensor[32] and separation.[22] It is well know that the temperature and pH value are the important factor of physiology. As the result, the thermal- and pH-sensitive hydrogels have researched and reported frequently.[33,34]

Nowadays, zeolite particles have various application such as gas separation,[35] oil purification,[36] separation,[37] because they have many advantages, such as adsorption, ion exchange, catalysis and heat resistance etc.[38] Because of the excellent properties of the zeolite, polymer/zeolite hybrid materials attract considerable attention gradually. Ryohei Shindo et al.[39] prepared polyimide/ZSM-5 zeolite

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Is there substituent cross-interaction effect in all the conjugated systems containing C═N polar bond? The substituent effects on the NMR chemical shifts of 2,5-disubstituted pyrimidines

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The cross-interaction effect ($\Delta\sigma^2$)
Quantitative structure-property relationship

A B S T R A C T

The substituent cross-interaction effect in the substituted benzylidene anilines (p-X–C_6H_4–CH═N–C_6H_4–Y-p) has been observed and widely investigated. In order to investigate whether the substituent cross-interaction effect exist in all the conjugated systems containing C═N polar bond, this paper employed 2-X-5-Y pyrimidines as the model compounds for study. The influences of substituents X and Y on the ^{1}H NMR and ^{13}C NMR chemical shifts of 2, 5-disubsitituted pyrimidines have been systematically investigated. Quantitative structure-chemical shifts relationship models have been built for $\delta(H_{4,6})$, $\delta(C_2)$, $\delta(C_{4,6})$ and $\delta(C_5)$ with four to six molecular descriptors. These models were confirmed of good stability and predictive performances by leave-one-out cross validation. This study indicates that the substituent effects of 2,5-disubstituted pyrimidines are much more complex than that of the substituted benzylidene anilines. More structural factors besides of Hammett parameter should be taken into consideration. Different from the substituted benzylidene anilines, the cross-interaction effect ($\Delta\sigma^2$) of substituents X and Y has little contribution to $\delta(H_{4,6})$, $\delta(C_2)$, $\delta(C_5)$ and $\delta(C_{4,6})$ of 2,5-disubstituted pyrimidines.

1. Introduction

Extensive investigations have been reported about the substituent effects on the electronic character of the C═N bridging group in Schiff bases due to the promising liquid-crystal and nonlinear optical properties of Schiff bases [1–3]. The substituted benzylidene anilines (p-X–C_6H_4–CH═N–C_6H_4–Y-p) are the most interested model compounds. Both Neuvonen [3,4] and Cao [5,6] have observed that the benzylidene substituent X and the aniline substituent Y exert different effects on δ_C(C═N) and δ_N(C═N): for substituent X, the electron-withdrawing substituent causes shielding and the electron-donating one results in deshielding; while for substituent Y, the electron-withdrawing substituent leads to deshielding and the electron-donating one behaves oppositely. In the early year, Kawasaki [7] and Akaba [8] qualitatively demonstrated that the substituent on the benzylidene ring can influence the sensitivity of the azomethine carbon to the aniline substituent. Neuvonen [3] also found that the neighboring aniline substituent Y can modify the sensitivity of the electronic character of C═N group to the benzylidene substituent X. The cross-interaction effect between substituents X and Y has been demonstrated and investigated systematically. Guo [9–12] developed the parameter σ_{XY} ($\sigma_{XY} = \sigma_X\sigma_Y$) to describe the cross-interaction effect of substituents X and Y in the investigation of the bond dissociation. Cao [5] proposed another parameter $\Delta\sigma^2 = (\sigma_X - \sigma_Y)^2$ to scale the substituent specific cross-interaction effect in the correlation of ^{13}C NMR chemical shifts of the C═N bridging group in the substituted benzylidene anilines. In the investigation of the substituent effects of X and Y on the δ_C of 4, 4′-disubstituted cinnamyl anilines (p-X–C_6H_4–CH═CH–CH═N–C_6H_4–Y-p), Chen [13] modified the substituent cross-interaction item ($\Delta\sigma^2$) by the bond number (m).

All the above studies focused on the substituent effects on the electronic character of the polar C═N bond in Schiff bases, which are very valuable for tailoring the specific properties of the mesogenic molecules or design of new materials for nonlinear optical purposes. The substituent cross-interaction effect has been observed in all the above investigations. However, the C═N groups in the above interested model compounds all situate in the open

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Solvent-free synthesis of novel spirocyclic oxindole derivatives *via* a Michael-aldol cascade by grinding

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A simple and novel synthesis of spirocyclic oxindole derivatives by the reaction of (*E*)-3-arylideneindole-2-ones and 1,4-dithiane-2,5-diol *via* a Michael-aldol cascade under solvent-free reaction conditions is reported. This method provides a new practical and facile approach to 4′-hydroxy-2′-aryl-4′,5′-dihydro-2′*H*-spiro[oxindole-3,3′-thiophen]-2-ones in moderate to good yields. The structures of all the products were characterised by NMR, infrared spectroscopy and HRMS.

Keywords: oxindole, spirocycle, Michael-aldol cascade, solvent free synthesis

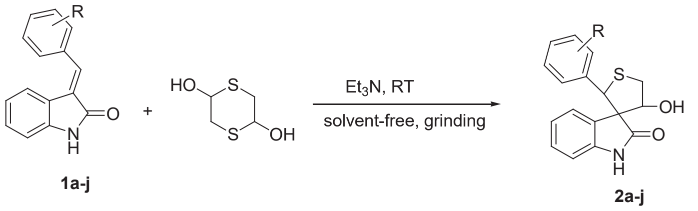
The oxindole moiety is an important structure responsible for the biological activity of alkaloids and pharmaceutically active compounds, such as pteropodine,[1] paraherquamide A,[2] tryprostatins B[3] and sunitinib.[4] Compounds with an oxindole unit have aroused great interest because of their broad spectrum of biological activities, such as antitumour,[5] anti-inflammatory, analgesic,[6] cyclooxygenase[7] and myosin inhibition[8] activity.

Spiroheterocycles are important structures found in many biologically active natural products[9] and their biological properties make them good targets for drug candidates and clinical pharmaceuticals.[10,11]

It is well known that there are pronounced advantages to solvent-free synthetic approaches, including easy work-up procedures, short reaction times and simple apparatus requirements, which has attracted considerable attention in recent years.[12–14] Here we report a facile synthesis of spirocyclic oxindole derivatives by the Michael-aldol cascade reaction of 1,4-dithiane-2,5-diol with (*E*)-3-arylideneindole-2-ones under solvent-free conditions (Scheme 1).

Results and discussion

The 4′-hydroxy-2′-aryl-4′,5′-dihydro-2′*H*-spiro[oxindole-3,3′-thio-phen]-2-ones **2** were synthesised in moderate to good yields by the Michael-aldol cascade reaction of (*E*)-3-arylideneindole-2-ones with 1,4-dithiane-2,5-diol in the presence of triethylamine under solvent-free conditions at room temperature. The reaction can be scaled up to 5 mmol with similar yields, for example, 5 mmol of **1a** gives 1.17 g of **2a** (79.0% yield) under the reaction conditions. The intermediate product (*E*)-3-arylideneindole-2-ones **1** were obtained by condensation of oxindole and various substituted benzaldehydes in the presence of triethylamine at room temperature.



2a: R = H, 2b: R = *o*-Cl, 2c: R = *m*-Cl, 2d: R = *p*-Cl, 2e: R = *p*-CH$_3$, 2f: R = *m*-CH$_3$, 2g: R = *p*-CH$_3$O, 2h: R = *o*-Br, 2i: R = *o*-F, 2j: R = *p*-F

Scheme 1 Synthesis of spiro oxindole-tetrahydrothiophenes.

The structures of all compounds **2a–j** were established by different spectroscopic techniques (NMR, IR) and HRMS. The high-resolution mass spectrum of **2d** gave the molecular ion peak at *m/z* 332.0515, which indicates the addition of one molecule of 1,4-dithiane-2,5-diol to **1d**. The IR spectrum of **2d** displayed $\nu_{C=O}$ at 1689.4 cm^{-1}. The ^{1}H NMR spectrum of **2d** revealed a doublet at δ 5.58 ppm (*J* = 6.0 Hz, OH), two singlets — a singlet at δ 10.40 ppm for –NH and another singlet at δ 4.94 resulting from –HCPh — a multiplet at δ 4.70–4.65 ppm for –CH–OH, a doublet of doublets at δ 3.32 ppm (J_1 = 10.0 Hz, *J2* = 6.0 Hz) and a triplet at δ 3.20 ppm (*J* = 10.0 Hz) resulting from H$_2$C5′, The presence of signals at δ 6.62–7.58 ppm corresponded to the aromatic protons.

The ^{13}C NMR spectrum of the product **2d** exhibited the presence of carbonyl carbons at δ 176.79 (C2). The signal at δ 79.45 represented the spiro carbon of C3. Furthermore, the structure of the product was confirmed by X-ray diffraction analysis of **2d** (Fig. 1).

There are three diastereoisomeric carbon atoms in the products **2a–j**; therefore, two diastereoisomers might exist in the obtained products. TLC and the ^{1}H NMR spectra of the reaction mixtures only showed one set of typical absorptions for the characteristic groups in the molecules, which indicated that the products **2a–j** existed as only one diastereoisomer with the structure being established *via* the single-crystal structure determination.

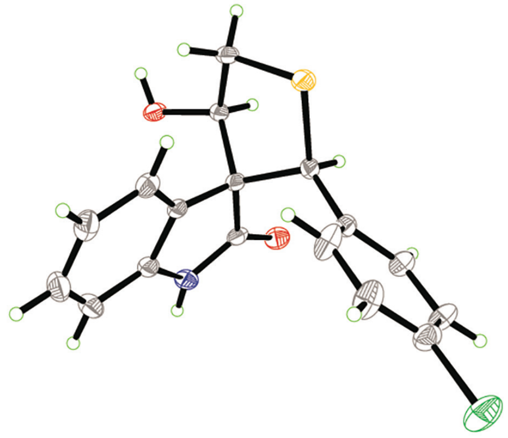


Fig. 1 ORTEP diagram of **2d** with 50% probability.

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Selectfluor-mediated benzo[*d*][1,2,3]triazole functionalisation of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene

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8-Aryl-1-(1*H*-benzo[*d*][1,2,3]triazole-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene and 8-aryl-3,5-di-(1*H*-benzo[*d*][1,2,3]triazole-yl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene derivatives were synthesised by the reaction of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene with benzo[*d*][1,2,3]triazole in the presence of Selectfluor in moderate to good yields. The reaction took placed regioselectively on the 3(5)-position carbon of 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, which was confirmed by X-ray analysis.

Keywords: 1*H*-benzo[*d*][1,2,3]triazole, 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene, Selectfluor.

4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) derivatives have attracted considerable attention in recent years due to their unique photophysical properties and high reactivities.[1] They have high molar absorption coefficients and fluorescence quantum yields as well as good stability, permeabilities and strong absorption/emission in the visible spectral range.[1] BODIPY derivatives have been widely applied as biomolecular probes,[2] in optoelectronics/photovoltaics[3] and as anion and cation sensors,[4] fluorescent switches[5,6] and photodynamic therapy (PDT) agents.[7]

The transition metal-catalysed amination of BODIPY halides with amines or nitrogen-containing heterocycles and the transition metal-promoted direct C–H amination of BODIPYs are efficient synthetic methods for the facile functionalisation of BODIPY, which can be used in biomolecular probes.[8,9] Both of these methods need the use of transition metals and bases, which make them uneconomic to prepare. As a result, the successful development of new synthetic methods for this class of structures would be of great interest.

Selectfluor, a commercially available reagent, has been widely used in organic synthesis, acting as a potential fluorinating reagent,[10,11] methylating agent[12] and strong oxidant.[13]

In continuation of our work on the synthesis of fluorophore derivatives, [14–21] we now report the synthesis of BHT-BODIPY derivatives by the reaction of BODIPY with benzo[*d*][1,2,3]triazole (BHT) in the presence of Selectfluor (Scheme 1).

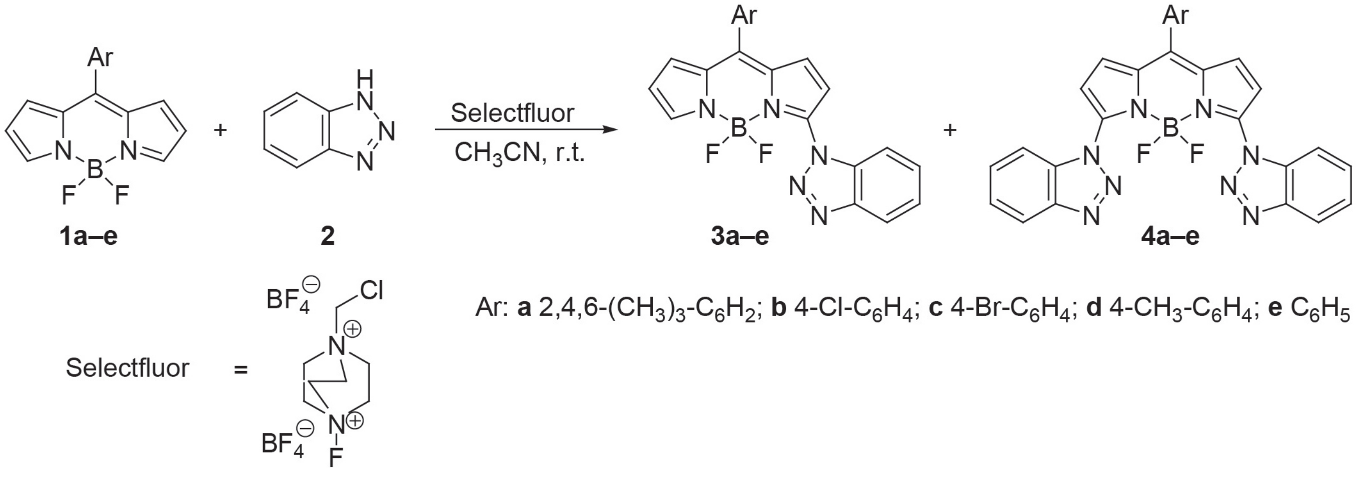
Results and discussion

The reaction of the BODIPY derivatives (**1a**–**e**) and BHT in the presence of Selectfluor in CH$_3$CN at room temperature for 3 h afforded novel BHT-BODIPY (**3a**–**e**) and di(BHT)-BODIPY derivatives (**4a**–**e**) in moderate to good yields with high regioselectivity. The structures of all of these compounds were established by various spectroscopic techniques (UV, NMR and HRMS).

The high-resolution mass spectrum (HRMS) of **3a** gave the molecular ion peak at *m/z* 428.1854, which indicates the addition of just one BHT to **1a,** while the corresponding spectrum of **4a** gave the molecular ion peak at *m/z* 545.2177, which indicates the addition of just two BHT moieties to **1a**.

The ^{1}H NMR spectrum of **3a** (298 K, CDCl$_3$) is characterised by four doublets at 6.56 (J = 4.0 Hz), 6.61 (J = 4.5 Hz), 6.80 (J = 4.0 Hz) and 6.84 (J = 4.5 Hz) ppm, which are assigned to the four protons of the pyrrole ring. Two singlets at 2.18 and 2.40 ppm are assigned to the three methyl groups. The signals at δ 7.01–8.19 ppm correspond to the aromatic protons and one proton of the pyrrole ring.

The ^{1}H NMR spectrum of **4a** (298 K, CDCl$_3$) is characterised by two doublets at 6.67 (J = 4.5 Hz) and 6.96 (J = 4.5 Hz) ppm, which are assigned to the four protons of the pyrrole ring. Two singlets, at 2.27 and 2.42 ppm, are assigned to the three methyl groups. The signals at δ 7.06–8.08 ppm correspond to the aromatic protons.



Scheme 1 Synthesis of BHT-BODIPY derivatives.

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ARTICLE

Substituent Effects on ^{13}C NMR and ^{1}H NMR Chemical Shifts of CH=N in Multi-substituted Benzylideneanilines

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Fifty-three samples of multi-substituted benzylideneanilines XArCH=NArYs (abbreviated XBAYs) were synthesized and their NMR spectra were determined. An extensional study of substituent effects on the ^{1}H NMR chemical shifts ($\delta_{\rm H}$(CH=N)) and ^{13}C NMR chemical shifts ($\delta_{\rm C}$(CH=N)) of the CH=N bridging group from di-substituted to multi-substituted XBAYs was made based on a total of 182 samples of XBAYs, together with the NMR data of other 129 samples of di-substituted XBAYs quoted from literatures. The results show that the substituent specific cross-interaction effect parameter $\left(\Delta\left(\sum\sigma\right)^2\right)$ plays an important role in quantifying the $\delta_{\rm C}$(CH=N) values of XBAYs, but it is negligible for quantifying the $\delta_{\rm H}$(CH=N) values; the other substituent parameters also present different influences on the $\delta_{\rm C}$(CH=N) and $\delta_{\rm H}$(CH=N). On the whole, the contributions of X and Y to the $\delta_{\rm C}$(CH=N) of XBAYs are balanced, but the $\delta_{\rm H}$(CH=N) values of XBAYs mainly rely on the contributions of X.

Key words: Multi-substituted benzylideneanilines, Substituent effects, ^{1}H NMR chemical shifts, ^{13}C NMR chemical shifts, Substituent specific cross-interaction effect

I. INTRODUCTION

In the molecules of benzylideneanilines XArCH=NArYs (abbreviated XBAYs), CH=N is a bridge linking two aromatic rings, of which one ring carries substituent X, and another ring carries substituent Y. The changes of X and Y can affect the molecular overall electron distribution and the properties of optoelectronic materials containing the molecule of XBAY. Therefore, the effects of substituents X and Y on the performance of the CH=N bridging group play an important role. On the other hand, NMR shielding is affected by the electron density, and the field of resonance increases with the increasing electron density of the protons and carbon nucleus in molecules [1, 2]. So the NMR chemical shifts of CH=N ($\delta_{\rm H}$(CH=N) and $\delta_{\rm C}$(CH=N)) were always applied to investigate the substituent effects in past years [3–11].

Neuvonen *et al.* [12, 13] analyzed the substituent effects on the $\delta_{\rm C}$(CH=N) of 4,4′-substituted XBAYs by employing several different single and dual substituent parameter approaches, and the relatively best model equation (shown as Eq.(1)) has been obtained. In their research, they pointed out that the substituent specific cross-interaction between X and Y existed, but they didn't quantify it. Nonetheless, their work strongly promoted the research of the substituent effects on the $\delta_{\rm C}$(CH=N) of substituted XBAYs. In Eq.(1), $\sigma_{\rm F}$ is the inductive effect parameter, $\sigma_{\rm R}$ is the conjugative effect parameter, ρ are the coefficients of corresponding parameter.

$$\delta_{\rm C}({\rm CH{=}N}) = {\rm constant} + \rho_{\rm F}({\rm X})\sigma_{\rm F}({\rm X}) + \rho_{\rm F}({\rm Y})\sigma_{\rm F}({\rm Y}) + \rho_{\rm R}({\rm X})\sigma_{\rm R}({\rm X}) + \rho_{\rm R}({\rm Y})\sigma_{\rm R}({\rm Y}) \qquad (1)$$

Afterwards, Cao *et al.* [14] studied the substituent effects on the $\delta_{\rm C}$(CH=N) of 4,4′-substituted XBAYs further. The substituent specific cross-interaction effect was quantified with the item $\Delta\sigma^2$ and a more effective five parameter equation (Eq.(2)) was proposed to quantify the $\delta_{\rm C}$(CH=N) of XBAYs by adding $\Delta\sigma^2$ to Eq.(1). In Eq.(2), $\Delta\sigma^2 = (\sigma({\rm X}) - \sigma({\rm Y}))^2$.

$$\delta_{\rm C}({\rm CH{=}N}) = {\rm constant} + \rho_{\rm F}({\rm X})\sigma_{\rm F}({\rm X}) + \rho_{\rm F}({\rm Y})\sigma_{\rm F}({\rm Y}) + \rho_{\rm R}({\rm X})\sigma_{\rm R}({\rm X}) + \rho_{\rm R}({\rm Y})\sigma_{\rm R}({\rm Y}) + \rho_{(\Delta\sigma^2)}\Delta\sigma^2 \qquad (2)$$

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REGULAR ARTICLE

Computational study of mbandakamine A: a dimeric naphthylisoquinoline alkaloid with antimalarial activity

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Abstract

Mbandakamine A is one of the naphthylisoquinoline alkaloids isolated from the leaves of Congolese *Ancistrocladus* species and shows good antimalarial activity. It is also one of the first discovered dimeric naphthylisoquinolines with an unsymmetrically coupled central biaryl axis. The molecule consists of two units, with each unit containing one naphthalene moiety and one isoquinoline moiety. The substituents on the rings comprise four OH groups and four OCH_3 groups. Each OH group can be H-bond donor, either to the methoxy group in the same moiety or to another OH from another moiety; they can also be H-bond acceptors to another OH. Conformers can have up to three O–H···O intramolecular hydrogen bonds (IHBs) simultaneously, O–H···N or N–H···O and also other H-bond-type interactions (O–H···π, C–H···O and C–H···N). A detailed conformational study was performed *in vacuo* and in three solvents with different polarities and different H-bonding abilities (chloroform, acetonitrile and water), using two levels of theory, HF/6-31G(d,p) and DFT/B3LYP/6-31+G(d,p). Because IHBs have a relevant role in determining conformational preferences, all combinations of IHBs and IHB-type interactions were considered, for a total of 107 conformers. The results highlight the stabilizing effect of the various types of IHBs and also of the mutual orientation of the four aromatic moieties and of the presence of stacking interactions.

Keywords Alkaloids · Antimalarials · Intramolecular hydrogen bonding · Mbandakamine A · Naphthylisoquinoline alkaloids · Mutual orientation of aromatic moieties · Solute–solvent interactions

1 Introduction

Malaria is a transmittable disease caused by plasmodia. It remains a serious world health problem, with almost 200 million cases and 600,000 deaths per year in tropical and sub-tropical regions [1]. Ninety per cent of the deaths occurs in Africa, most of which concerning children under 5 years of age. The fast development of resistance to new drugs few years after they get into clinical use complicates the possibility of treating malaria by requiring the introduction of newer drugs with different modes of actions every few years. Natural products represent a potentially vast source of novel compounds, with diverse molecular structures and pharmacophores and, therefore, diverse mechanisms of action. The very rich biodiversity of Africa offers a high number of natural compounds with antimalarial activity.

Mbandakamine A (Fig. 1, denoted by the acronym MBK in the rest of the text) is one of the naphthylisoquinoline alkaloids isolated from the leaves of Congolese *Ancistrocladus* species and showing good antimalarial activity ($IC_{50} = 0.148$ μM, where IC_{50} indicates the amount of a particular drug that is needed to inhibit 50% of a given biological process or component of a process, such as an enzyme, cell, cell receptor or microorganism). It was also one of the first dimeric naphthylisoquinoline alkaloids with an unsymmetrically coupled central biaryl axis to be discovered [2]. It has a peri–peri coupling (Fig. 2a), which makes the molecule to have stacking interactions (Fig. 2b).

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00214-018-2323-z) contains supplementary material, which is available to authorized users.

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Full Paper

Metal–Organic Frameworks

Highly Selective Carbon Dioxide Capture and Cooperative Catalysis of a Water-Stable Acylamide-Functionalized Metal–Organic Framework

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Abstract: Incorporation of specific functionalities within the framework offers a significant opportunity to produce high-performance gas storage/separation and catalysis MOF materials. In this work, multifunctionalities, including hydrophobic methoxy groups, polar acylamide functionalities, and open copper(II) sites, have been successfully integrated into a twofold interpenetrated microporous MOF (HNUST-6, HNUST represents Hunan University of Science and Technology). HNUST-6 possesses permanent porosity, with a moderate BET surface area of 1093 $m^2\ g^{-1}$ and high CO_2 adsorption capacity (111 $cm^3\ g^{-1}$ at 1 bar), with good selectivity for CO_2 over CH_4 (6.6) and N_2 (30.3) at 273 K. Remarkably, this MOF material exhibits excellent water stability and its framework structure is retained after being immersed in boiling water. In addition, HNUST-6 demonstrates efficient catalytic activity as a cooperative catalyst in a tandem one-pot deacetalization Knoevenagel condensation reaction.

Introduction

Metal–organic frameworks (MOFs) are highly porous and crystalline multifunctional materials that are composed of multidentate organic linkers coordinated to metal ions or metal-containing clusters. Due to the hybrid inorganic–organic compositions and inherent modular nature, the pore size and geometry, framework topology, and chemical functionality of MOFs can be finely tuned for targeted applications, such as strategic gas storage[1] and separation,[2] heterogeneous catalysis,[3] and chemical sensing.[4] To develop high-performance porous MOFs for such applications, how to simultaneously address materials with high porosity, excellent hydrostability, and enhanced supramolecular host–guest interactions, is one of the key challenges we now face in MOF chemistry. Remarkable breakthroughs in the construction of MOFs with ultrahigh porosity (experimental BET surface area exceeds 5000 $m^2\ g^{-1}$) can be achieved currently under the concept of reticular chemistry,[5] but most of such MOFs are not hydrostable enough, which greatly hinders their practical applications. To improve the water stability of MOF materials, several strategies have been extensively explored and shown to be effective: (i) strengthening the metal–ligand coordination bonds by judicious choice of metal ions/clusters and organic ligands;[6] (ii) interpenetration or catenation;[7] (iii) introduction of hydrophobic groups (e.g., methyl, ethyl ester, etc.);[8] and so on. In addition, in pursuit of new high-performance MOF materials for high-energy gas (hydrogen, methane) storage and carbon dioxide separation, it has been well documented that functionalization of MOF materials is a primarily important and effective method to enhance the interaction/affinity between the guest and the MOF framework.[9] There are principally three strategies to generate functional MOF materials: (i) insertion or attachment of various functional groups (–CONH–, –NH–, $–NH_2$, –F, –Cl, –Br, $–NO_2$, $–SO_3H$, etc.) into the framework backbones;[10] (ii) incorporation of open metal sites (OMSs);[11] and (iii) encapsulation of new ionic components into MOF channels, pores, and/or cages through ion exchange.[12]

We are interested in the design and construction of porous MOFs from large multidentate carboxylate ligands with linking acylamide groups (–CONH–) and dicopper(II) paddlewheels,[13] because such an approach may facilitate the generation of expanded MOFs with high surface areas. Furthermore, both the predesigned OMSs and polar acylamide functionalities within the framework can provide strong binding sites for target guest molecules associated with gas storage/separation and catalysis, which has been unambiguously verified by both computational and experimental studies.[14] In this contribution, we present a new 2-interpenetrated microporous acylamide-functionalized MOF decorated by methoxy groups, HNUST-6 (HNUST denotes Hunan University of Science and Technology), designed from a nanosized flexible tetracarboxylate linker 5,5′[(5methoxy-iso-

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RESEARCH ARTICLE

Cooperative effects between F . . . Ag bonded and X . . . Br (Cl) halogen-bonded interaction in BrF(ClF) . . . AgX . . . BrF(ClF) (X = F, Cl, Br) complexes: a theoretical study

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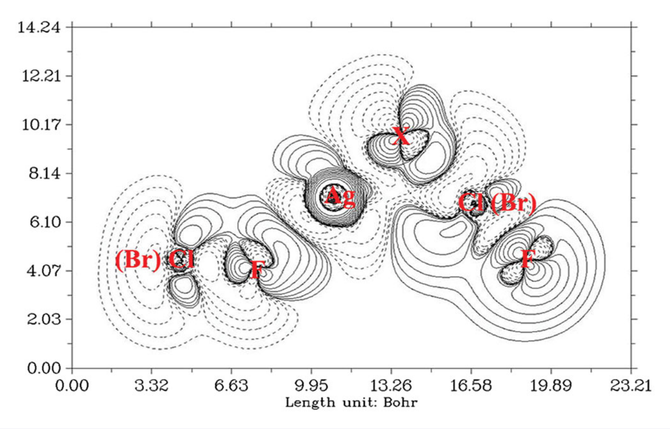
ABSTRACT
The equilibrium structures, interaction energies and binding properties of ternary BrF(ClF) . . . AgX . . . BrF(ClF)(*X* = F, Cl, Br) complexes and the corresponding binary systems have been studied by DFT method at the X3LYP/aug-cc-pVQZ level. Cooperative effects are probed by analysing charge transfer, electronic properties and orbital interactions when F . . . Ag bond and X . . . Br (Cl) halogen bond coexist in the same complex. The results indicate that the X . . . Br (Cl) halogen bond has a greater enhancing effect than the F . . . Ag bond does, resulting in a shorter binding distances, larger interaction energies and greater electron densities for the ternary complexes than for the corresponding binary ones. In addition, the origins of both the F . . . Ag bond and X . . . Br (Cl) halogen bond have been deduced via energy decomposition.



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KEYWORDS
Cooperative effects; electron density; halogen bonds; molecular electrostatic potential; orbital interaction; energy decomposition

1. Introduction

Non-covalent interactions have attracted widespread interest due to their indispensable role in supramolecular chemistry, molecular self-assembly and materials science [1–3]. The hydrogen bonds are the most traditional research for the non-covalent interactions, but recently a new type of intermolecular interaction involving closed-shell molecules between a Lewis base B and a diatomic molecule M–X (where M is Cu, Ag or Au, and X is a halogen atom) have attracted a lot of attention both experimentally and theoretically [5]. The experimental approach is to generate B . . . MX by laser ablation of a metal M in the presence of a gas pulse composed of small amounts of B and a molecular source of halogen atoms X undergoing supersonic expansion, then interrogated by microwave spectroscopy [5]. Legon *et al.* have conducted extensive and systematic study of complexes formed by metal halides and simple Lewis bases such as N_2, H_2, CO, NH_3, H_2O, H_2S, C_2H_4 and C_2H_2. Such complexes have been synthesised in the gas phase and char-

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An Improved Quantitative Structure Property Relationship Model for Predicting Thermal Conductivity of Liquid Aliphatic Alcohols

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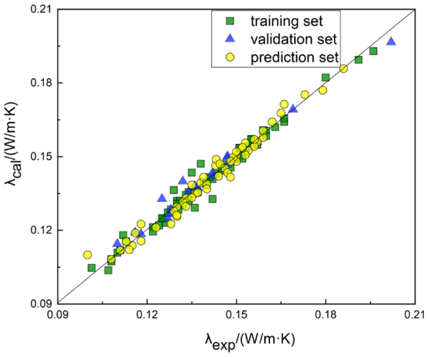
Supporting Information

ABSTRACT: The quantitative structure property relationship (QSPR) for thermal conductivity of liquid aliphatic alcohols was developed on the basis of 139 thermal conductivity data points of liquid aliphatic alcohols, which were divided into a 65-member training set, a 20-member validation set, and a 54-member prediction set. Four parameters (temperature-*T*, the intrinsic state pseudoconnectivity index-type 1s-*Psi_i_1s*, the sixth eigenvalue from augmented edge adjacency matrix weighed by edge degree-*Eig06_AEA(ed)*, and the global topological charge index-*JGT*) were screened to develop the model by using the stepwise regression and the best subset regression method. For the training set, validation set and prediction set, the square correlation coefficient (R^2) is 0.9769, 0.9726, and 0.9738, respectively. The mean relative deviation values of training set, validation set, and prediction set were 1.4%, 1.6%, and 1.6%. The QSPR model can provide not only basic data for the engineering application but also theoretical guidance for designing and seeking specific thermal conductivity materials.



1. INTRODUCTION

Thermal conductivity is the essential physical property of chemicals and a fundamental property for the chemical industry, technological design, and energy engineering, and closely related to its composition, structure, density, pressure, and temperature.[1,2]

In the production process, people have developed many measuring methods in order to obtain thermal conductivity data. However, each measurement method has its limitation of applications. There are two reasons for this. One is that thermal convection and diffusion within fluids and the heat loss in experiments (especially at high temperatures) have not been solved, which make the measurement errors of liquid thermal conductivity very big. The other reason is that some compounds are easily decomposed and volatile, which makes thermal conductivity inaccessible in experiments. Therefore, the thermal conductivity data of many compounds is lacking.[3,4]

Under this circumstance, some calculation methods are deduced to predict thermal conductivity. The results of these methods for calculating thermal conductivity of alcohols are listed in Table 1. However, these methods are empirical, and they need experimental data to support. First and foremost, each formula's error in calculation is also relatively big, generally between 3 and 10%.

Table 1. Results of Some Empirical Methods for Calculating Thermal Conductivity of Alcohols

author	Rodenbush	Nagvekar	Baroncini et al.
no. of data point	267	634	592
MRD (%)	2.7	6.3	7.7
ref	5	6	7

Considering the limitation of empirical methods, some researchers have attempted to predict thermal conductivity of compounds based on QSPR models. They estimated the physical properties of compounds with molecular descriptors.[8−10] The possibility of estimation can be substantial and the accuracy in calculation can be increased.[11] The research on QSPR models for predicting thermal conductivity is listed in Table 2. It can be seen that using QSPR to predict the properties of organic compounds is simple and efficient.

At present, diverse linear and nonlinear methods are used to develop QSPR models.[16−20] Linear QSPR model can be used to reveal the parameters affecting the properties of compounds, and predict the properties of compounds simply and conveniently.

Aliphatic alcohol is an important category of organic compounds and an important raw material in daily life and chemical production, and thermal conductivity is an important data in the industrial production and utilization of such compounds.

The present work intends to (1) collect thermal conductivity data of liquid aliphatic alcohol from literatures and experiments; (2) extract and find out molecule characteristic

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Phase transformation synthesis of TiO_2/CdS heterojunction film with high visible-light photoelectrochemical activity

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Abstract

CdS/TiO_2 heterojunction film used as a photoanode has attracted much attention in the past few years due to its good visible light photocatalytic activity. However, CdS/TiO_2 films prepared by conventional methods (successive ionic layer adsorption and reaction, chemical bath deposition and electrodeposition) show numerous grain boundaries in the CdS layer and an imperfect contact at the heterojunction interface. In this study, we designed a phase transformation method to fabricate CdS/TiO_2 nanorod heterojunction films. The characterization results showed that the CdS layer with fewer grain boundaries was conformally coated on the TiO_2 nanorod surface and the formation mechanism has been explained in this manuscript. Moreover, the prepared CdS/TiO_2 films show a high photocatalytic activity and the photocurrent density is as high as 9.65 mA cm^{-2} at 0.80 V versus RHE. It may be attributed to fewer grain boundaries and a compact heterojunction contact, which can effectively improve charge separation and transportation.

Supplementary material for this article is available online

Keywords: nanowire, titanium dioxide, cadmium sulfide, heterojunction, photoanode

(Some figures may appear in colour only in the online journal)

1. Introduction

Photoelectrochemical (PEC) hydrogen generation is considered as a low-cost and eco-friendly approach to obtaining hydrogen fuel [1–4]. Since Fujishima and Honda reported the discovery of PEC water splitting to generate hydrogen on a TiO_2 photoelectrode in 1972 [5], TiO_2 has been intensively studied as a photoanode material because of its nontoxicity, low cost, high charge mobility and excellent photostability [6–9]. In particular, TiO_2 film with a nano-array structure, such as nanowires [10–12], nanotubes [13–15] and nanorod arrays [16–18], has generated extensive interest recently as a photoelectrode due to its unique advantages of a large surface area and oriented charge transport pathway [19–21]. Moreover, compared to films with

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NOTE

环苯基六炔烃的制备: 脱 $Ph_2P(O)$/分子内 Eglington 偶联环化反应

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摘要　脱二苯膦酰($Ph_2P(O)$)保护基/分子间炔烃偶联环化反应可一锅进行, 高效形成环苯基六炔烃. 与 Haley 等的脱硅基/Eglington 偶联分步反应的制备方法相比, 极性 $Ph_2P(O)$保护基使产物与少量剩余原料具有不同极性而易分离, 且本反应与产物 R_f 值相近的分子间偶联副产物量较少, 使得产物易分离. 且一锅反应可避免脱 $Ph_2P(O)$的后处理, 减少化合物损失, 有效提高了环苯基六炔烃的产率. 此外, 本方法还具有中间体易制备、反应条件温和等优点.

关键词　一锅反应; 二苯基膦酰基保护基; 环苯基多炔烃

Synthesis of Cyclic Phenyl Polyynes: $Ph_2P(O)$-Deprotection/Intramolecular Eglington Coupling Cyclization

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Abstract　$Ph_2P(O)$-deprotection/intramolecular Eglington coupling cyclization, proceeding in one-pot manner, can be applied to synthesize cyclic phenyl polyynes. Compared to Micheal M. Haley's stepwise desilylation/Eglington coupling reaction, the polar $Ph_2P(O)$ protecting group enabled facile seperation of product from remaining starting compound for their different polarity, and it also led to easy separation of target compound because the amont of by-products which showed similar R_f to target compound decreased. Furthermore, our one-pot reaction, avoiding the workup after $Ph_2P(O)$-deprotection and reducing losses of materials, increased the yield of cyclic aromatic polyynes. This method showed some other outstanding features including easy synthesis of intermediates and mild reaction conditions.

Keywords　one-pot reaction; diphenylphosphoryl protecting group; cyclic phenyl polyyne

环苯基多炔烃具有 π 共轭体系、刚性平面结构和丰富的碳原子, 是多碳功能分子和聚合物分子的合成前体[1], 在液晶材料[2]、有机光电材料[3]及高分子材料[4]等领域有广泛应用. 苯基环炔烃最初通过 α,ω-双炔烃的二聚/环化齐聚反应制备, 由于反应物与产物极性相近, 产品分离纯化较为困难[5]. Haley 等[6]通过反复 Sonogashira 偶联/脱硅基保护基分步反应、碘化及脱硅基/Eglington 偶联分步反应合成了环苯基六炔烃(Scheme 1). 但在上述反应中需使用活泼试剂三甲基硅基丁二炔($Me_3SiC\equiv CC\equiv CH$, 需要在 −30 ℃以下储存); 碘化反应中需使

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有机化学 DOI: 10.6023/cjoc201805009 研究论文
Chinese Journal of Organic Chemistry ARTICLE

膦酰保护基促进选择性 Hay 偶联制备非对称 1,3-二炔

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摘要　报道了芳香末端炔烃与单膦酰基–保护二炔的选择性 Hay 偶联反应. $Ph_2P(O)$的极性使得产物非对称 1,3-二炔易与副产物分离. 单膦酰基–保护二炔的低反应活性减少了自身氧化偶联, 从而提高了目标产物的产率. 很多芳香末端炔烃与单膦酰基–保护二炔都能应用于本 Hay 偶联反应, 且相应非对称 1,3-二炔产物的产率为中等到好. 产物非对称 1,3-二炔能用于合成非对称炔–二炔烃及环多炔烃.

关键词　Hay 偶联; 非对称 1,3-二炔; 末端炔烃; 膦酰保护基

Phosphoryl Protecting Group Enabled Facile Synthesis of Unsymmetrical 1,3-Diynes by Selective Hay Coupling

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Abstract　A selective Hay coupling reaction of aromatic terminal acetylenes and monophosphoryl-protected diynes was developed. The polarity of $Ph_2P(O)$ realized facile isolation of the desired unsymmetrical 1,3-diynes from by-products. The low reactivity of monophosphoryl-protected diynes reduced the oxidative homocoupling of itself and enhanced the yields of desired products. A number of aromatic terminal acetylenes and monophosphoryl-protected diynes were tolerated in this reaction, and all the corresponding unsymmetrical 1,3-diynes could be obtained in moderate to good yields. The unsymmetrical 1,3-diynes could be applied to synthesize unsymmetrical yne-diynes and cyclic polyynes.

Keywords　Hay coupling; unsymmetrical 1,3-diyne; terminal acetylene; phosphoryl protecting group

1　Introduction

Unsymmetrical 1,3-diynes are important compounds in organic chemistry, and important intermediates in organic synthesis.[1,2] The structural motif of 1,3-diyne, which is a constituent part of natural products,[3] such as panaxydol,[4] panaxytriol,[5] oploxyne,[6] petrosiol[7] and so on, has been recognized as an ubiquitous functionality in organic materials, such as dye for dye sensitized solar cell,[8] fluorophores,[9] liquid crystal[10] and so on.

A number of transition-metal catalyzed oxidative homocoupling reactions of terminal acetylenes, such as Glaser,[11] Eglinton,[12] Hay,[13] Cadiot coupling[14] and their alternative approaches are effective to produce 1,3-diyne structural motif. Although these kind of oxidative homocoupling reactions of an acetylene gave symmetrical 1,3-diynes in good yields, it is difficult to afford unsym-

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Prompting peroxidase-like activity of gold nanorod composites by localized surface plasmon resonance for fast colorimetric detection of prostate specific antigen†

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The interaction between incident light and surface electrons in conductive nanoparticles produces localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, and dielectric environment. Hybrid heterostructure materials combining two or more materials in one structure represent a powerful way to achieve unique properties and multifunctionality compared to those of the individual nanoparticle components. Hybrid gold nanorods and gold nanoclusters (GNR/AuNCs) heterostructures prepared by intimate integration of GNRs with AuNCs exhibit both localized surface plasmon resonance (LSPR) property and peroxidase-like activity. It is found that the catalytic activity of the AuNC/GNR heterostructure could be remarkably enhanced by LSPR induced by photon–plasmon coupling in the visible to near-infrared (NIR) region. Meanwhile, the catalytic activity of enzyme-like AuNC/GNRs may be regulated by immunoreactions to realize specific recognition of a target analyte. Accordingly, a fast colorimetric assay within 5 min for the detection of prostate specific antigen (PSA) was developed based on a AuNC/GNRs heterostructure mask regulated by the target molecule under photon-plasmon coupling. The color intensity is inversely proportional to the PSA concentration, and quantitative analysis may be achieved in a range of 10 and 200 pg mL^{-1}. This sensor was practically applied to detect PSA levels in prostate cancer serum samples and the determined values agreed well with those measured by the hospital using standard methods. This indicates that the AuNC/GNRs heterostructure-based assay has high accuracy for the analysis of practical samples. Moreover, the new method has the advantages of very fast determination and low sample volume requirements.

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Introduction

Localized surface plasmon resonance (LSPR) is an optical phenomenon generated by the interaction of incident light with surface electrons in conductive nanoparticles,[1–3] which produces coherent localized plasmon oscillations with a resonant frequency that strongly depends on the composition, size, geometry, and dielectric environment.[4–7] The versatility of the LSPR effect is an advantage and can be exploited by simply manipulating the nanoparticle size and shape, opening new possibilities for visible and near-infrared (NIR) light utilization.[8–11] One of the most commonly studied metals for the LSPR effect is Au, including monometallic nanoparticles,[12–14] bimetallic nanoparticles,[15–17] and metal oxide-supported metal nanoparticles.[18–20] Gold nanorods (GNPs) possess two plasmonic absorption bands capable of absorbing and scattering light at very specific regions of the visible and NIR range.[21,22] The tailorable LSPR properties and biocompatibility enable GNRs to have attracted considerable attention for use in biosensors,[23,24] bioimaging,[25,26] photothermal therapeutics,[27,28] and drug delivery.[29,30] Meanwhile, GNRs have recently proven to be promising in harvesting photon energy for chemical reactions.[31–33] As another Au nanoscale material, gold nanoclusters (AuNCs) consist of tens to hundreds of metal atoms showing distinguished optical and electric properties due to their transition states from continuous to discrete energy levels, which have been reported to have versatile roles in catalysis,[34,35] environmental monitor-

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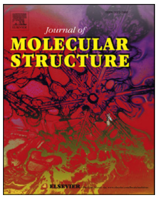

A new 2-D layer-like organic-inorganic hybrid tungstobismuthate constructed from $[Bi_2W_{20}O_{70}]^{14-}$ units and dimeric $[Cu_2(dien)_2]_2^{4+}$ complex cations

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ABSTRACT

The reaction of the lacunary polyoxotungstate $[B\text{-}\alpha\text{-}BiW_9O_{33}]^{9-}$ with $Cu(Ac)_2 \cdot H_2O$ in the presence of diethylenetriamine under hydrothermal conditions generating a new 2-D layer-like organic-inorganic hybrid tungstobismuthate $[Cu(dien)(H_2O)]_2[Cu_2(dien)_2]_2H_2[Bi_2W_{20}O_{70}] \cdot 15H_2O$ (**1**) (dien = diethylenetriamine). **1** has been carefully characterized by IR spectroscopy, elemental analysis, thermogravimetric analysis (TGA), X-ray single-crystal diffraction. **1** crystallizes in the orthorhombic *Pbca* space group with $a = 21.077(2)$ Å, $b = 21.788(2)$ Å, $c = 22.821(2)$ Å, $V = 10480.1(17)$ Å^3, $Z = 4$, $GOOF = 1.043$, $R_1 = 0.0454$, $wR_2 = 0.0710$. Structural analyses show that **1** exhibits an organic-inorganic hybrid 2-D layer-like architecture constructed by $[Bi_2W_{20}O_{70}]^{14-}$ polyanions by means of the $[Cu_2(dien)_2]^{4+}$ bridges. Notably, the dien ligand presents two kinds of coordination modes in **1**, which has been rarely observed in previously reported polyoxometalates. The magnetic study of **1** demonstrates the existence of ferromagnetic coupling interactions between Cu^{2+} ions in dimeric $[Cu_2(dien)_2]^{4+}$ groups.

1. Introduction

Polyoxometalates (POMs), as a series of early-transition-metal oxide clusters, have owned more and more interest due to their structural versatility and abroad applications such as catalysis, optical materials, medicine, magnetism, *etc.* [1–3]. In particular, lacunary POMs, as classical inorganic ligands, gained extra attentions due to their thermally and oxidatively robust, which are able to incorporate various types of oxophilic heterometal centers, resulting in an abundant and various structural topology [4–7]. The lacunary polyoxotungstates, consisting of the subvalent main group atoms As^{III}, Sb^{III} and Bi^{III} as heteroatoms, display meaningful structures and properties because of the stereochemical effect of the lone pair orbital electrons located on top of the trigonal pyramid, which can coordinate with transition metal and/or rare earth ions to generate a large number of POM-based complexes that show abundant properties [8].

Compared with the As^{III} and Sb^{III} contained POMs which have been intensively studied [9–12], only a little work has been documented about POM analogues based on Bi^{III} heteroatoms. In the large family of POMs, the polyanions $[\{(M(H_2O)_3)_2(M'(H_2O)_2)_2\}(B\text{-}\beta\text{-}XW_9O_{33})_2]^{n-}$ ($M = Mn^{2+}$ or Co^{2+}; $M' = W^{VI}$) with B-β-type lacunary tungsten-oxygen architectures can be well known as Krebs-type POMs. As we known, it is inevitably that the isomerization from α to β and partial decomposition of the lacunary POM precursor in solution, even if the reaction environment is mild. The structural isomerization of the trivicant precursor $[B\text{-}\alpha\text{-}XW_9O_{33}]^{9-}$ can be achieved by the introduction of 2–4 additional $\{WO_6\}$ octahedra into the transition metal belt [8,13]. In 1997, Krebs and co-workers successfully obtained a series of polyoxotungstates $[X_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$ ($X = Sb^{III}$, Bi^{III}; $M^{n+} = Fe^{3+}$, Co^{2+}, Zn^{2+}) comprising two trilvacant $[\beta\text{-}BiW_9O_{33}]^{9-}$ units bridged through two $\{WO_2\}$ groups [14]. However, according to the documents, only few tungstobismuthate containing $\{B\text{-}\beta\text{-}BiW_{10}O_{35}\}$ or $\{B\text{-}\beta\text{-}BiW_9O_{33}\}$ building blocks have been reported up to now [15–17].

In recently, we focus on the assembly chemistry of Bi^{III}-based POMs units and transition metal ions. Herein we present a new 2-D layer-like organic-inorganic hybrid tungstobismuthate $[Cu(dien)(H_2O)]_2[Cu_2(dien)_2]_2H_2[Bi_2W_{20}O_{70}] \cdot 15H_2O$ (**1**)

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Discovery and development of substituted tyrosine derivatives as Bcl-2/Mcl-1 inhibitors

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ABSTRACT

Anti-apoptotic Bcl-2 family proteins are vital for cancer cells to escape apoptosis, which make them attractive targets for cancer therapy. Recently, a lead compound **1** was found to modestly inhibit the binding of BH3 peptide to Bcl-2 protein with a K_i value of 5.2 μM. Based on this, a series of substituted tyrosine derivatives were developed and tested for their binding affinities to Bcl-2 protein. Results indicated that these compounds exhibited potent binding affinities to Bcl-2 and Mcl-1 protein but not to Bcl-X_L protein. Promisingly, compound **6i** inhibited the binding of BH3 peptide to Bcl-2 and Mcl-1 protein with a K_i value of 450 and 190 nM respectively, and showed obvious anti-proliferative activities against tested cancer cells.

1. Introduction

Apoptosis is vital for normal tissue homeostasis by removal of damaged or unwanted cells. It is generally considered that evasion of apoptosis is a critical attribute of cancer cells. Among all kinds of proteins involved in apoptosis, the B-cell lymphoma 2 (Bcl-2) family proteins are one of the most well-characterized ones. These proteins are pivotal regulators of the intrinsic apoptosis pathway by the way of governing mitochondrial outer membrane (MOM) integrity. There are three groups of structurally related Bcl-2 family proteins: the multi-domain anti-apoptotic proteins (Bcl-2, Bcl-X_L, Mcl-1, Bcl-W, A1/BFL-1), the pro-apoptotic BH3-only proteins (BIM, BID, PUMA, NOXA, BAD, BMF, BIK, HRK), and the multi-domain pro-apoptotic proteins (Bak and Bax). In response to apoptotic stimuli (*e.g.*, DNA damage and growth factor withdrawal), the BH3-only proteins are upregulated by transcriptional and/or posttranscriptional pathways. This will unbalance anti- and pro-apoptotic Bcl-2 family proteins, and then lead to activation of BAK and BAX. Activated BAX/BAK oligomerize and permeabilize the mitochondrial outer membrane. Subsequently, mitochondrial proteins (*e.g.*, cytochrome *c*) are released to cytosol, which triggers caspase cascades leading to cell death.[1–4]

However, cancer cells can upregulate anti-apoptotic Bcl-2 proteins in various different ways to escape apoptosis.[5] In this case, small molecule inhibitors targeting these anti-apoptotic proteins have been developed to restore apoptosis. Molecules which mimic the BH3 domain of the BH3-only proteins to bind anti-apoptotic Bcl-2 proteins are called 'BH3 mimetics'. It is well known that developing small molecules capable of effectively interfering the protein–protein interactions between pro- and anti-apoptotic Bcl-2 proteins is challenging. However, progress has been so far made.[6,7] For example, **Venetoclax/ABT-199** (Fig. 1) has been approved to treat patients with 17p deletion chronic lymphocytic leukemia (CLL) on April 11, 2016.[8] This shows great promise to develop novel small molecule Bcl-2 inhibitors to cancer treatment.

In our previous work, thiazolidinones, thiadiazoles and pyrrolidines have been developed as Bcl-2 inhibitors.[9–15] Interestingly, an intermediate (**1**, Fig. 1) to synthesize these compounds was found to modestly inhibit the binding of BH3 peptide to Bcl-2 protein with a K_i value of 5.2 μM. In our on-going studies, we developed a series of substituted tyrosine derivatives based on this compound. This paper shows the synthesis and biological evaluation of these tyrosine derivatives.

2. Chemistry

Tyrosine derivatives were synthesized as outlined in Scheme 1.[13,16] As starting material, L-tyrosine **2** was protected by Cu^{2+}, reacted with benzyl bromides, and then protected by Boc group to yield key intermediates **3a–3e**. Then intermediates **3a–3e** were treated with different benzenesulfonamides to give target compounds **4a–4m**. The Boc groups of **4a–4m** were removed to generate target compounds **5a–5f**. Compounds **5a–5f** did coupling reactions with carboxylic acids to obtain

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Molecular iodine-mediated synthesis of thiocarbamates from thiols, isocyanides and water under metal-free conditions†

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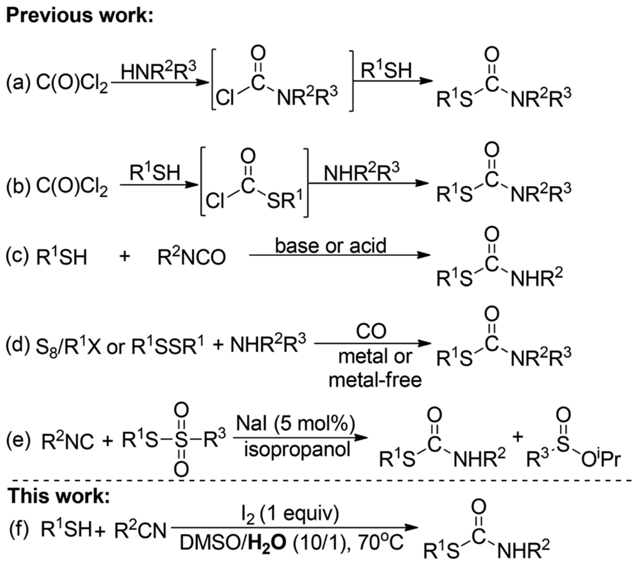
A simple and practical molecular iodine-mediated method for the efficient construction of thiocarbamates from isocyanides, thiols and water under metal-free and mild conditions has been developed. A variety of thiocarbamates were easily synthesized through this methodology, which has the advantages of simple operation, eco-friendly conditions, good functional group tolerance, and readily accessible raw materials.

Introduction

Thiocarbamates are extremely valuable compounds in organic synthesis and pharmaceutical chemistry, and have increasingly attracted the synthetic pursuit of chemists due to their wide spectrum of biological activities including bactericidal,[1] anesthetic,[2] antiviral,[3] pesticidal,[4] and fungicidal[5] properties. Conventionally, thiocarbamates were prepared by two-step reactions of phosgene with an amine and thiol (Scheme 1a)[6] or the reverse (Scheme 1b),[7] the addition reaction of a thiol with isocyanate (Scheme 1c),[8] and the carbonylation of an amine with carbon monoxide (CO) and disulfide or elemental sulfur (Scheme 1d).[9] However, most of these reactions require the employment of toxic oxalyl chloride, phosgene, CO or isocyanates as the raw materials. In recent years, some alternative protocols have been developed to avoid these hazardous reagents.[10–14] In this context, Lee and co-workers reported the synthesis of thiocarbamates from CBZ(Boc)-protected amines and thiophenols in a one-pot procedure.[12] Mandal *et al.* developed the Boc-Oxyma mediated reaction of hydroxamic acid with thiophenol leading to thiocarbamates through Lossen rearrangement.[13] In 2016, Maes and co-workers presented a NaI-catalyzed method for the construction of secondary thiocarbamates from isocyanides and thiosulfonates by using isopropanol as a solvent (Scheme 1e), which led to the inevitable formation of equal amounts of alkyl sulfinate side-products.[14] However, these well-developed reactions still encountered certain drawbacks including the need for extra steps to prepare the complex starting materials, narrow substrate scope, harsh reaction conditions, and toxic wastes. Thus, the development of a facile and efficient protocol for the synthesis of thiocarbamates from simple and readily available starting materials in pharmaceutical and synthetic chemistry still remains challenging.

Recently, molecular iodine as an alternative and promising metal-free reagent, has drawn much attention owing to its



Scheme 1 Synthesis of thiocarbamates.

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Metal-free difunctionalization of alkynes leading to alkenyl dithiocyanates and alkenyl diselenocyanates at room temperature†

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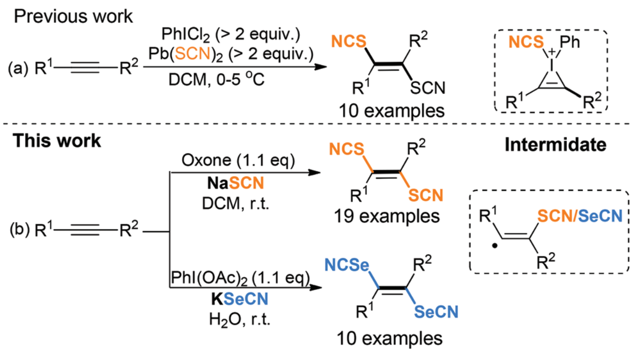
A simple and practical method for the synthesis of alkenyl dithiocyanates and alkenyl diselenocyanates has been developed *via* stereoselective difunctionalization of alkynes with NaSCN or KSeCN at room temperature. Through this methodology, a series of alkenyl dithiocyanates and alkenyl diselenocyanates could be efficiently and conveniently obtained in moderate to good yields under mild and metal-free conditions by the simple use of oxone and $PhI(OAc)_2$ as the oxidants.

Introduction

As a key structural motif, the thiocyanato group is widely present in a variety of natural products, biologically active compounds and synthetic intermediates.[1] Thus, the introduction of the thiocyanato group into organic molecules has drawn much attention from chemists in terms of their important biological properties[2] and widespread synthetic applications for the construction of diverse valuable sulfur-containing compounds such as disulfides,[3] thioethers,[4] thiocarbamates[5] and sulfonylcyanides.[6] Although many methods have been established to synthesize alkyl[7] and aryl thiocyanates,[8] the construction of alkenyl thiocyanates has not been fully developed, in spite of their versatile transformation abilities in organic synthesis. Generally, alkenyl thiocyanates are prepared through the nucleophilic substitution of vinyl halides with thiocyanate salts.[9] Other elegant methods for the synthesis of alkenyl thiocyanates have also been developed.[10] Among them, the functionalization of alkynes with [SCN] reagents represents one of the most powerful and straightforward methods for the construction of alkenyl thiocyanates due to their high atom economy and reaction efficiency. For example, Jiang and coworkers presented silver catalyzed hydrothiocyanation of haloalkynes with KSCN in AcOH at 100 °C leading to *Z*-alkenyl thiocyanates.[10c] In the same year, Yan and coworkers developed a facile and mild protocol to obtain allyl isothiocyanates through iodothiocyanation of allenes with KSCN and molecular iodine.[10d] In 2017, Sridhar Reddy *et al.* described the addition reaction of electron-deficient alkynes with KSCN in acetic acid for the synthesis of alkenyl thiocyanates.[10e] Very recently, our group also reported ultrasound-promoted Brønsted acid ionic liquid catalyzed hydrothiocyanation of activated alkynes with KSCN to access *Z*-alkenyl thiocyanates.[10f] However, all of these methods are limited to the hydrothiocyanation of alkynes leading to mono-alkenyl thiocyanates. To the best of our knowledge, only one example has been reported on the construction of alkenyl dithiocyanates from alkynes, (dichloroiodo)benzene and lead(II) thiocyanate through an iodirenium ion intermediate[11] (Scheme 1a). Obviously, the utilization of stoichiometric amounts of lead(II) reagent would increase the risk for traces of toxic metals in the products and limit their wide applications in the field of synthetic and pharmaceutical chemistry. Therefore, the development of a facile, efficient,



Scheme 1 Methods for the synthesis of alkenyl dithiocyanates and alkenyl diselenocyanates.

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Metal-free deoxygenative sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process†

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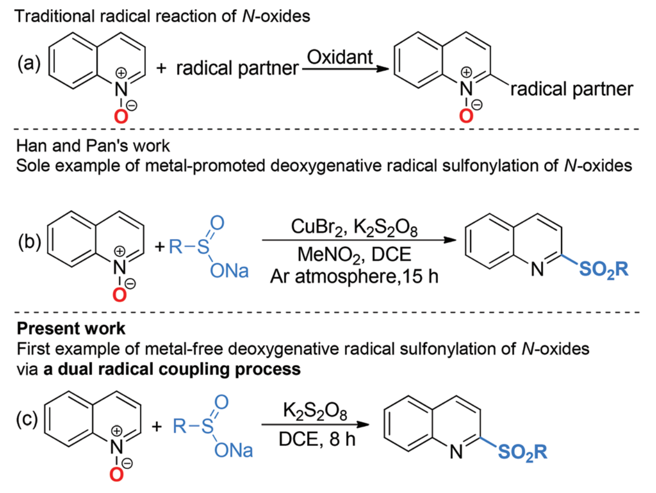
The first example of a metal- and reductant-free deoxygenative sulfonylation of quinoline *N*-oxides with sodium sulfinates *via* a dual radical coupling process is reported. In this reaction, sodium sulfinates play dual roles of a sulfonylation reagent and activating agent. This procedure is expected to complement the current methods for the radical reaction of quinoline *N*-oxides.

Introduction

Radical chemistry has played an increasingly important role in modern synthesis. The utilization of a controlled radical reaction to synthesize structurally diverse organic molecules has been of increasing interest in both academia and industry.[1] In recent decades, a large number of radical reactions have been catalyzed by various transition metal complexes, which result in inevitable metal residuals in the terminal products and disposal of these metal salts often causes environmental pollution.[2] Therefore, the development of metal-free radical reactions is of great importance and has been extensively studied over the past years.

The C–H bond functionalization of quinoline *N*-oxides has received extensive attention in organic synthesis, as it has been demonstrated to be a powerful and versatile tool for direct incorporation of new functionalities at the C-2[3] and C-8 positions[4] of quinoline skeletons with excellent atom economy. However, although the nucleophilic addition to quinoline *N*-oxides generating 2-substituted quinolines has been well established, direct construction of such motifs[5] *via* radical pathways remains a long-standing challenge. In fact, most radical reactions of quinoline *N*-oxides through C–H bond activation result in substituted quinoline *N*-oxides (Scheme 1a).[6] These protocols require additional deoxygenative functionalization with superstoichiometric amounts of harmful reagents as reductants for obtainment of the expected 2-substituted quinolines. The one-pot synthesis of 2-sulfonylquinolines from quinoline *N*-oxides through C–H bond activation[7] has attracted considerable attention due to their potential biological activities and valuable synthetic utilities as well as the availability of readily accessible quinoline *N*-oxides.[8] However, to the best of our knowledge, the only example of direct synthesis of 2-sulfonylquinolines *via* deoxygenative radical sulfonylation[9] of quinoline *N*-oxides in the presence of copper salts as the catalyst under an argon atmosphere was reported by Pan and Han (Scheme 1b).[10] Considering the inconveniences and manufacturing costs in eliminating the trace metal contami-



Scheme 1 Radical coupling reactions of *N*-oxides.

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Waste-Minimized Protocol for the Synthesis of Sulfonylated *N*-Heteroaromatics in Water

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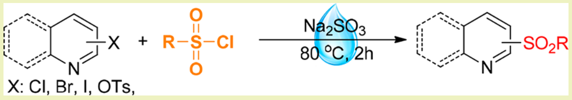
Supporting Information

ABSTRACT: An ecofriendly and practical method for the efficient synthesis of various sulfonylated *N*-heteroaromatics in water under metal-free, organic-solvent-free, neutral, and mild reaction conditions was developed. The employment of readily available reagents, wide substrate scope, high chemoselectivity, and regioselectivity make this protocol very practical. Importantly, the pure products can be easily obtained via filtration and washing by alcohol without extraction and recrystallization.



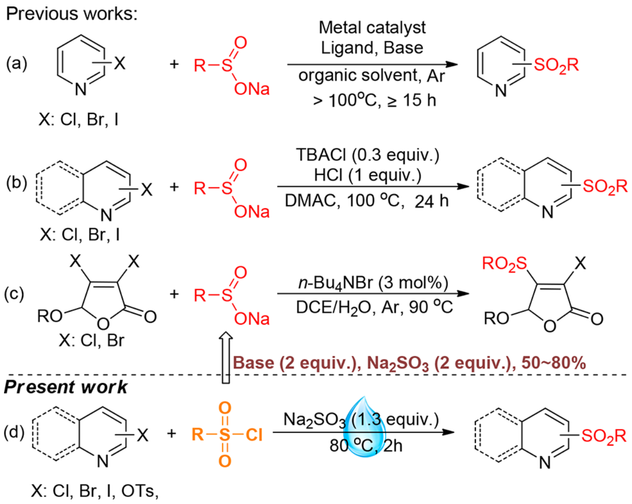
KEYWORDS: *In water, Sulfonyl chlorides, Sulfonylation, Sulfonylated N-heteroaromatics, Metal-free*

INTRODUCTION

The development of step- and atom-economical aqueous organic reactions[1−24] that can be conducted under neutral, metal-free, and mild reaction conditions in which the desired products can be obtained after the reaction through simple filtration without organic solvent extraction and recrystallization is one of the important targets in green chemistry. Over the past decades, the achievement of general and efficient protocols for the synthesis of sulfonylated *N*-heteroaromatics has attracted extensive attention of organic chemists because they have a wide range of applications in organic synthesis, pharmaceuticals, and functionalized material science.[25−27] Thus, tremendous efforts have been dedicated to construct such motifs.

Generally, the methodologies for the synthesis of sulfonylated *N*-heteroaromatics can be divided into two categories according to the reaction substrates: those that utilize heteroaromatic *N*-oxide substrates[28−38] and those that functionalize the halogenated or sulfonate *N*-heteroaromatics.[39−44] Both protocols continue to find widespread use, but they also have inevitable limitations. The limitation of sulfonylation[45−58] of *N*-heteroaromatic *N*-oxides is that the functionalization occurs at the 2-position, but a competing reaction at the other position is often observed, especially in the case of isoquinolines[33−36] and six-membered heteroaromatic *N*-oxides. The major advantage of the functionalization of halogenated or sulfonate *N*-heteroaromatics is the specific completely controllable regioselectivity. Since the first examples of $Pd_2(dba)_3$-catalyzed coupling of 2-bromopyridine with sodium *p*-toluenesulfinate in the presence of Cs_2CO_3 in toluene reported by Cacchi in 2004,[39] considerable progress has been achieved over the past years.[40−43] However, all of these protocols have the need for environmentally unfriendly transition metal catalysts and (super)stoichiometric amount of bases to facilitate this transformation (Scheme 1a). In 2011, Maloney and Kuethe developed a metal-free nucleophilic S_NAr reaction for the synthesis of sulfonylated *N*-heteroaromatics from halogenated *N*-heteroaromatics and sodium sulfinate salts (Scheme 1b).[44] All of the methods mentioned above can regioselectively construct the desired sulfonylated *N*-heteroaromatics, but these reactions are conducted in harmful

Scheme 1. Synthesis of Sulfonylated *N*-Heteroaromatics



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Metal-free Deoxygenative 2-Amidation of Quinoline *N*-oxides with Nitriles via a Radical Activation Pathway

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Abstract: A metal-, base- and reductant-free approach for the efficient synthesis of various *N*-acylated 2-aminoquinolines was reported. In this work, readily available nitriles are used as the amide source, and methyl carbazate as both the radical activating reagent and oxygen source. This is the first report on the ester-radical-activated highly regioselective addition of nitriles to quinolone *N*-oxides. This procedure is expected to complement the current methods for functionalization of *N*-oxides via an electrophilic activation mechanism.

Keywords: quinoline *N*-oxide; 2-amidation; radical activator; *N*-acylated 2-aminoquinoline; nitrile

Introduction

Quinolines are extremely important because of their abundance in various biologically active natural products and synthetic pharmaceuticals.[1] Consequently, the construction of valuable quinoline derivatives from readily available precursors under transition-metal-free conditions is a prominent research objective, especially in the pharmaceutical industry.[2] The regioisomers of quinoline molecules usually have contrasting indications or even opposing pharmacological activities. Therefore, the construction of various substituted quinolines from readily accessible quinoline *N*-oxides[3] via nucleophilic (Scheme 1a) and Minisci-type radical addition[4] (Scheme 1b) pathway under metal-free conditions represents a highly attractive approach because of excellent regioselectivity and high efficiency. However, compared with the well-established functionalization of quinoline *N*-oxides activated by various electrophiles (sulfonyl chlorides,[5] acyl chlorides,[6] anhydrides,[7] PyBroP,[8] *H*-phosphonate,[9] iodine reagents,[10] boron reagents,[11] etc.[12]), the regioselective nucleophilic substitution of *N*-oxides activated by a free radical activator have not been reported.

N-acylated 2-aminoquinolines are found in many natural products, biologically active compounds and pharmaceuticals.[13] The construction of *N*-acylated 2-aminoquinolines through nucleophilic substitution of electrophilic O-activation of *N*-oxides with various amide source[14] has been successfully developed. To the best of our knowledge, there is no example of direct synthesis of *N*-acylated 2-aminoquinolines from quinoline *N*-oxides via a radical activation pathway. As part of our ongoing interest in the green chemistry,[15] we have reported the synthesis of 2-substituted quinoline from quinoline *N*-oxides through electrophilic activation pathway.[16] In this paper, we report for the first time a metal-, base- and reductant-free deoxygenative 2-amidation of quinoline *N*-oxides with nitriles via a radical activation pathway (Scheme 1c). Our present strategy not only provides a novel, mild and efficient protocol for the synthesis of structurally important *N*-acylated 2-aminoquinolines, but also complements existing electrophilic activation mechanism for functionalization of *N*-oxides.

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Research Article

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Brønsted Acidic Ionic Liquid-Promoted Amidation of Quinoline *N*-Oxides with Nitriles

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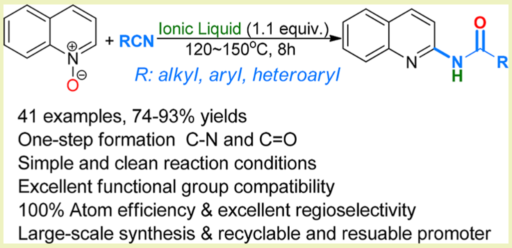
Supporting Information

ABSTRACT: An economic and eco-friendly straightforward synthesis of highly diversified *N*-acylated 2-aminoquinolines is successfully achieved via Brønsted acidic ionic liquid-promoted amidation of quinoline *N*-oxides with nitriles. The advantage of this present process is highlighted by its easily accessible starting materials, excellent functional group tolerance, 100% atom economy, operational simplicity, and clean reaction profile.



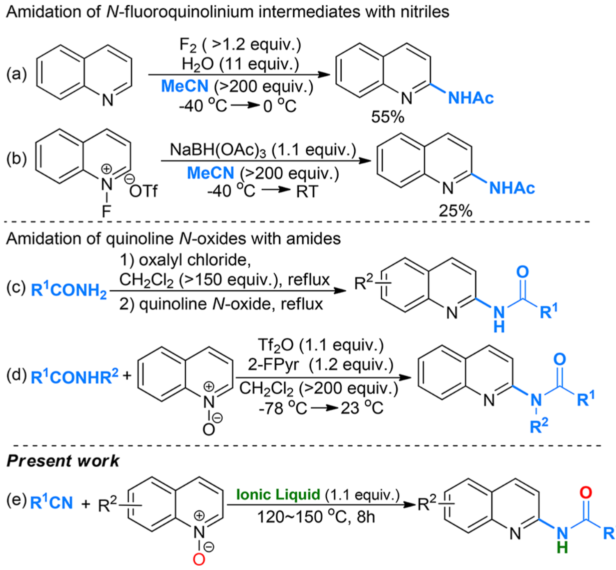
41 examples, 74-93% yields
One-step formation C-N and C=O
Simple and clean reaction conditions
Excellent functional group compatibility
100% Atom efficiency & excellent regioselectivity
Large-scale synthesis & recyclable and resuable promoter

KEYWORDS: *Ionic liquid, Quinoline N-oxide, Nitrile, Amidation reaction, Atom economy*

INTRODUCTION

Organic compounds containing *N*-acylamide(s) are versatile components of pharmaceuticals, agrochemicals, and organic functional materials.[1,2] Among the aromatic compounds with amide linkages, *N*-acylated 2-aminoquinolines are very common structural motifs and are found in a number of biologically active molecules.[3−7] Therefore, considerable efforts have been devoted in recent years to their preparation. The traditional synthetic strategies for *N*-acylated 2-aminoquinolines are based on acylation of 2-aminoquinolines[8] or coupling of amides with 2-haloquinolines.[9] However, the limited scope of 2-amino-/haloquinolines, low atom economy, and harsh reaction conditions often suppress the application of these methods. In contrast, the direct preparation of *N*-acylated 2-aminoquinolines from *N*-activated quinolines via C−H bond activation represents an attractive alternative. In 1994, Kiselyov and Strekowski reported one example of sequential *N*-fluorination and amidation of quinoline[10,11] through *N*-fluoroquinolinium intermediate in acetonitrile at ultralow temperature by using fluorine gas (F_2) as a fluorinating reagent (Scheme 1a).[12] However, the high toxicity, corrosivity, and explosivity of F_2 severely restrict its application. In 2005, Kiselyov employed the *N*-fluoroquinolinium as reaction substrate to construct 2-amidoquinoline, but only one example (*N*-(quinolin-2-yl)acetamide) was presented in low yield (Scheme 1b).[13] To overcome the above-mentioned disadvantages, *N*-fluoroquinolinium salts have been replaced with abundant and easily accessible quinoline *N*-oxides.[14−26] In 2006, Couturier's group first reported the amidation of quinoline *N*-oxides with carbonyl isocyanate (Scheme 1c), which was conducted by using stoichiometric amounts of harmful oxalyl chloride in harsh reaction conditions.[27] A trifluoroacetic anhydride (Tf_2O)-promoted amidation of quinoline *N*-oxides with secondary amides in the presence of superstoichiometric amounts of 2-fluoropyridine as the base

Scheme 1. Synthesis of *N*-Acylated 2-Aminoquinolines



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Palladium-catalyzed selective synthesis of 3,4-dihydroquinazolines from electron-rich arylamines, electron-poor arylamines and glyoxalates†

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A simple palladium-catalyzed selective synthesis of structurally diverse 3,4-dihydroquinazolines from electron-rich arylamines, electron-poor arylamines and glyoxalates has been developed under mild conditions. This reaction is carried out in a tandem manner constituted by the condensation of arylamines and glyoxalates, the selective Diels–Alder cycloaddition and oxidation processes, in which 4-nitrothiophenol was used as the key ligand.

Introduction

3,4-Dihydroquinazolines are significant scaffolds in biological and medicinal chemistry due to their multiple pharmacological activities,[1] such as anti-inflammatory,[2] antiviral,[3] antimicrobial,[4] anti-tremor,[5] and hypotensive properties.[6] In particular, some 3,4-dihydroquinazoline derivatives are employed as promising cancer treatment agents[7] and antiepileptic drugs.[8,9] For example, as shown in Fig. 1, compounds **I** and **II** are used as T-type Ca^+ channel blockers to suppress the growth of human cancer cells;[7a,b] compound **III** was found to be an effective trypanothione reductase (TryR) inhibitor,[8] and compound **IV** exhibits potent anti-cancer activities against human lung cancer A549 cells.[9]

Consequently, various synthetic methods have been established for the construction of 3,4-dihydroquinazoline skeletons.[10–19] Generally, 3,4-dihydroquinazolines are prepared by the reactions of 2-aminobenzylamines or anthranilamides with ketones,[11] aldehydes,[12] acyl chlorides,[13] or anhydrides.[14] Alternative strategies, including aza-Wittig/carbodiimide-mediated cyclizations,[15] intramolecular Michael addition of amidines,[16] intramolecular cycloadditions between ketenimines and imines,[17] as well as the Staudinger/aza-Wittig reactions have also been developed.[18] However, most of these methods suffer from limitations such as tedious procedures, low atom economy, or require relatively complex precursors. Recently, $CuBr_2$ [19] or I_2-catalyzed[20] cascade imino Diels–Alder and oxidation processes of arylamines and ethyl glyoxalates have been reported for the synthesis of 3,4-dihydroquinazolines. Nevertheless, both elegant methods are still restricted to the Diels–Alder cycloaddition of the two same imines. To date, it is still a challenge to deliver diversely substituted 3,4-dihydroquinazolines *via* the cross Diels–Alder process of imines with different electronic properties.

In light of the unique pharmacological activities of 3,4-dihydroquinazolines, and also with our continuing interest in heterocyclic chemistry,[21] herein, we wish to report a convenient palladium-catalyzed selective construction of structu-

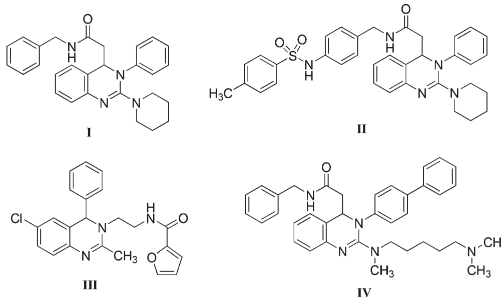

Fig. 1 Structures of biologically active 3,4-dihydroquinazolines.

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Palladium-Catalyzed Reductive Coupling of Nitroarenes with Phenols leading to *N*-Cyclohexylanilines

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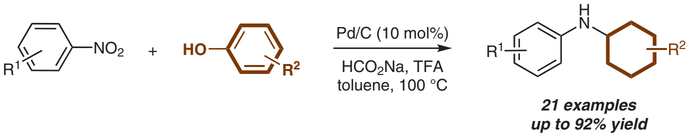

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Abstract A direct and efficient palladium-catalyzed reductive coupling reaction of nitroarenes with phenols has been developed. A series of *N*-cyclohexylaniline derivatives was easily and efficiently obtained in moderate to good yields via C–N bond formation by the simple use of safe and inexpensive sodium formate as the hydrogen donor.

Key words green chemistry, palladium catalysis, reductive coupling, nitroarene, phenol, cyclohexylamine

Nitroarenes are a stable, cheap, and readily available starting material in synthetic chemistry and the reduction of nitro compounds is an important step in the preparation of biologically active compounds and fine chemicals.[1] Although numerous procedures have been established for the reduction of nitro compounds,[2] the selective reduction and further transformation of nitroarenes under mild reaction conditions is still a challenging problem.[3]

On the other hand, as an important class of compounds, arylamines exhibit a wide range of applications in pharmaceuticals, agrochemicals, dyes, and functional materials.[2b,4] In recent years, transition-metal-catalyzed or metal-free methods for the synthesis of *N*-substituted arylamines via C–N bond formation from nitroarenes have attracted great attention of chemists.[5–8] For examples, in 2009, Li and co-workers reported the peroxide-mediated direct amination of simple cycloalkanes with nitroarenes leading to secondary arylamines [Scheme 1 (a)].[5] Tokunaga and co-workers utilized Au/Fe_2O_3[6a] and Sreedhar and co-workers[6b] utilized gum acacia stabilized palladium (GA-Pd) nanoparticles catalyzed hydrogenation/reductive amination to form aniline derivatives from nitroarenes and aldehydes under a H_2 atmosphere [Scheme 1 (b)]. The methods for the one-pot synthesis of arylamines from nitroarenes and alcohols catalyzed by ruthenium, rhodium, or gold complex have also been developed [Scheme 1 (c)].[7] The Deng and Lemaire groups independently described efficient palladium-catalyzed diarylamine formation from nitroarenes and cyclohexanone derivatives using borrowed hydrogen strategy [Scheme 1 (d)].[8] Although these methods are undoubtedly useful, there is still a great demand for the development of new, efficient, and practical methods to access arylamines from simple and easily accessible coupling partners.

Phenols are important structural units of renewable biomass, which can be readily obtained from naturally abundant lignins.[9] The direct use of non-preactivated phenols as aromatic coupling partners and cyclic C_6 feedstocks has attracted increasingly synthetic pursuit of chemists in terms of their easy available and renewable features.[10] Recently, palladium-catalyzed reductive coupling of phenols with amines to afford cyclohexylamines[10g] and cross-coupling of phenols with amines to access aromatic amines[10h] have been successfully established by Li and co-workers. Palladium-catalyzed reduction of nitroarenes to anilines with formic acid has been also developed by Johnstone and

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Chinese Journal of Organic Chemistry ARTICLE

无溶剂下胺、炔、炔反应选择性构筑季碳炔丙基胺

王 峥[a] 杨 柳[a] 刘慧兰[a] 谭英芝[a] 包文虎[a]
汪 明[b] 唐子龙[b] 何卫民*,[a]
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摘要 在无溶剂下以胺、炔、炔为原料通过“一锅法”串联的反应方便、高效地合成了季碳炔丙基胺. 脂肪炔和芳香炔都可以适用于该反应体系. 在脂肪炔反应体系中, AgOTf 催化促进胺–炔–炔“马氏”反应进程; 当芳香炔作为反应底物时, $CuBr_2/Zn(OTf)_2$ 用于共催化剂. 该串联反应展示出优异的原子利用效率, 为季碳炔丙基胺的制备提供了一种极具有吸引力的绿色合成方法.

关键词 炔丙基胺; 季碳; 炔; 无溶剂; 绿色有机合成

Selective Synthesis of Quaternary Carbon Propargylamines from Amines, Alkynes, and Alkynes under Neat Condition

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Abstract An efficient and facile method has been developed for the synthesis of quaternary carbon propargylamines via a one-pot tandem reaction of amines, alkynes, and alkynes under neat condition. Both aliphatic and aromatic terminal alkynes are well compatible with the established reaction, with respect to aliphatic alkynes, AgOTf was used as catalyst for the Markovnikov amine-alkyne-alkyne coupling process. When aromatic alkynes were used as substrates, the reaction was promoted by $CuBr_2/Zn(OTf)_2$ co-catalytic system. This tandem reaction exhibits excellent atom efficiency and provides an attractive approach to a diverse range of quaternary carbon propargylamines.

Keywords propargylamines; quaternary carbon; alkynes; neat condition; green organic synthesis

1 Introduction

The development of atom-economical tandem reactions is one of the primary challenges for synthetic chemists in contemporary organic synthesis and has attracted great interest.[1] Accordingly, the hydroamination reactions are among the most atom economic processes, in which all of the reactant atoms are incorporated into the desired products without formation of any side products and therefore proceed theoretically with 100% atom efficiency. Especially, hydroamination of alkynes represents the most valuable transformations for the preparation of enamines and imines, which are important synthetic intermediates or building blocks for the synthesis of various highly substituted nitrogen-containing molecules and carbonyl compounds.[2] Recently, tandem reactions involving hydroamination of alkynes as a key step have attracted extensive attention.[3] For example, Che and co-workers[4] reported a gold(I) catalyzed tandem synthesis of pyrrolo[1,2-α]quinolines via the intramolecular hydroamination of alkyne and subsequent cyclization process. Li and co-workers[5] reported the synthesis of 1,2-dihydroquinoline derivatives

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Biomolecular Chemistry

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Direct synthesis of alkenyl iodides *via* indium-catalyzed iodoalkylation of alkynes with alcohols and aqueous HI†

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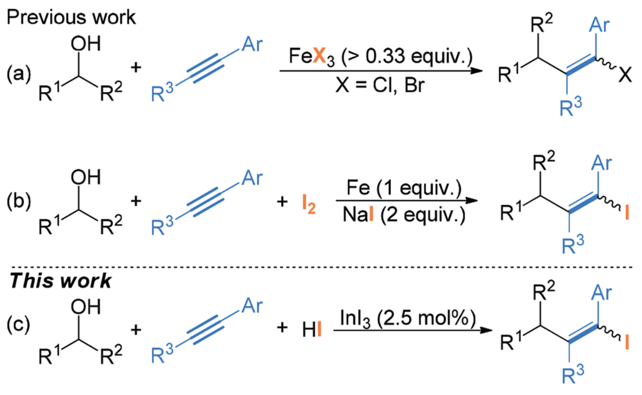
A convenient and efficient indium-catalyzed approach to synthesize alkenyl iodides has been developed through direct iodoalkylation of alkynes with alcohols and aqueous HI under mild conditions. This catalytic protocol offers an attractive approach for the synthesis of a diverse range of alkenyl iodides in good to excellent yields.

Introduction

Alkenyl iodides are very important compounds in organic synthesis,[1] and they have increasingly attracted the attention of synthetic chemists due to their wide applications as building blocks in transition-metal-catalyzed cross-coupling reactions such as Heck, Suzuki, Stille, Sonogashira and Negishi reactions.[2] In general, the classical preparation of alkenyl iodides relies heavily on the hydroiodination of alkynes with iodinating reagents such as PI_3, HI or AcI.[3,4] For the synthesis of versatile functionalized alkenyl iodides, various synthetic methods on iodoalkylation of alkynes have been developed over the past decades such as Ti, Zr, or Ni salt-mediated coupling of organometallic reagents or unsaturated compounds with alkynes followed by iodination of the resulting alkenyl organometallics,[5–10] the intramolecular reaction of complex alkynes such as substituted propargylic aryl ethers or 1,5-enynes,[11] radical addition of perfluoroalkyl iodides to alkynes induced by radical initiators,[12] and the use of activated alkynes such as ethyl propiolate or α,β-acetylenic ketones to react with iodide salts and ketones or aldehydes to obtain alkenyl iodides.[13] Nevertheless, most of these methods are accompanied by limitations such as the need for stoichiometric organometallic reagents, extra steps to prepare the starting materials, multistep reactions, poor substrate scope, and harsh reaction conditions. Therefore, the development of a simple, mild, convenient, and efficient method to obtain alkenyl iodides from simple and readily available starting materials is still highly desirable.

Recently, some elegant methods have been developed for the synthesis of alkenyl halides through the direct coupling reaction of benzyl alcohols and alkynes using FeX_3 (>33.3 equiv., X = Cl or Br) as promoters and halide sources (Scheme 1a).[14] However, the synthesis of alkenyl iodides could not be achieved by this procedure due to the unavailability of FeI_3.[15] In 2012, Ji group disclosed an iron-mediated method for the synthesis of alkenyl iodides *via* a coupling reaction of alcohols and alkynes in the presence of I_2 (1 equiv.) and NaI (2 equiv.) (Scheme 1b).[16] Nevertheless, the use of a stoichiometric amount of iron powder may limit the wide applications



Scheme 1 Synthesis of alkenyl halides.

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Amplified Split Aptamer Sensor Delivered Using Block Copolymer Nanoparticles for Small Molecule Imaging in Living Cells

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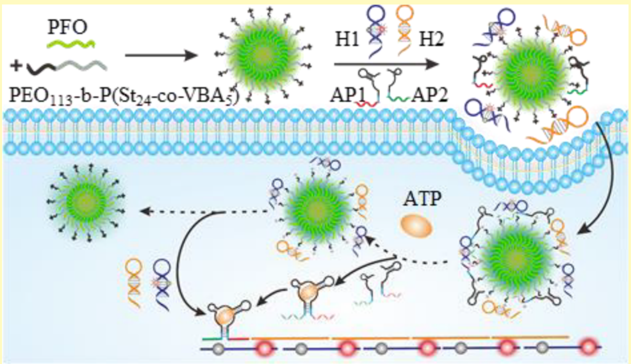
Supporting Information



ABSTRACT: We develop a novel amplified split aptamer sensor for highly sensitive detection and imaging of small molecules in living cells by using cationic block copolymer nanoparticles (BCNs) with entrapped fluorescent conjugated polymer as a delivery agent. The design of a split aptamer as the initiator of hybridization chain reaction (HCR) affords the possibility of enhancing the signal-to-background ratio and thus allows high-contrast imaging for small molecules with relatively weak interactions with their aptamers. The novel design of using fluorescent cationic BCNs as the nanocarrier enables efficient and self-tracking transfection of DNA probes. Results reveal that BCNs exhibit high fluorescence brightness allowing direct tracking of the delivery location. The developed amplified split aptamer sensor is shown to have high sensitivity and selectivity for in vitro quantitative detection of adenosine triphosphate (ATP) with a detection limit of 30 nM. Live cell studies show that the sensor provides a "signal on" approach for specific, high-contrast imaging of ATP. The DNA sensor based HCR system may provide a new generally applicable platform for detection and imaging of low-abundance biomarkers.

KEYWORDS: *split aptamer, enzyme-free amplification, block copolymer nanoparticles, small molecule imaging, sensor*

Monitoring and visualization of bioactive species in living cells is essential for understanding their physiological functions and pathological effects.[1] Development of sensors with selective, sensitive, and quantitative signals for live cell studies are in high demand.[2] Nucleic acids have proved to be a useful tool for biological analysis in living systems.[3] However, their detection sensitivity is one of the major challenges in intracellular applications, especially for those biomolecules which are in very low abundance. Therefore, signal amplification based protocols are drawing increasing attention.[4,5] Enzyme-free amplification assay is an emerging technology for ultrasensitive intracellular detection, avoiding cell damage caused by delivering exogenous enzymes or proteins while allowing monitoring targets in low abundance with high signal gain. Among them, hybridization chain reaction (HCR)[6] and catalytic hairpin assembly (CHA)[7] based amplification methods have been demonstrated for visualization of RNA,[8,9] enzyme activity,[10] and metal ions[11] inside living cells. However, detection of small molecules based on enzyme-free amplification assays in living cells has not been reported.

Efficient methods for delivering nucleic acids are another vital factor for live cell analysis. Nanocarriers offer a useful platform for delivery of nucleic acid probes. Recently, others and our group have explored some delivery systems for constructing intracellular enzyme-free amplification sensors. Although the use of commercially available liposomes has shown some success,[8] the delivery efficiency of this method cannot reach a satisfying level for a lot of cell types. We developed gold nanoparticle peptide based core−shell nanoparticles for electrostatically assembled DNA probes to realize sensitive mRNA detection in living cells.[9] Despite the high cellular delivery efficiency, the nanocomplex suffers from complex preparation processes. Other groups developed a GO-based delivery system for HCR and CHA probes. However, these methods may involve nonspecific dissociation of the probes and produce false positive signal.[10,12] Therefore, to

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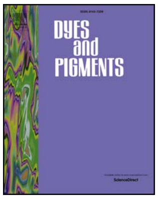

A 3D supramolecular network as highly selective and sensitive luminescent sensor for PO_4^{3-} and Cu^{2+} ions in aqueous media

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ARTICLE INFO

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Luminescent
Hydrothermal method
Benzotriazole-5-carboxylic acid

ABSTRACT

A 2D coordination polymer, $\{[Zn(btca)(py)_2]\}_n$ (**1**), (H_2btca = benzotriazole-5-carboxylic acid, py = pyridine), has been prepared with high yield by the hydrothermal reaction of H_2btca and $Zn(NO_3)_2{\cdot}6H_2O$ in the presence of py, which has been further characterized by kinds of methods combining elemental analysis, thermogravimetric (TG) analysis, infrared (IR) spectrum, powder X-ray diffraction (PXRD), and X-ray single-crystal diffraction. In **1**, each Zn^{2+} adopts a five-coordinated pentagonal bipyramid geometry with one O atom from one carboxylate group of $btca^{2-}$ ligand and four N atoms from two $btca^{2-}$ ligands and two py molecules. Adjacent Zn^{2+} are connected by $btca^{2-}$ ligands to generate a 2D layer with the '**fes**'-type topology, which could further form a 3D supramolecular network through hydrogen bonds interactions. Furthermore, the luminescent results reveal that the detection limit of **1** as a luminescent sensor to probe Cu^{2+} and PO_4^{3-} could reach 3 and 45 ppm, respectively, suggesting that **1** can sensitively and selectively detect Cu^{2+} and PO_4^{3-} in aqueous solution.

1. Introduction

The detection and sensing of ions in aqueous solution is of significant importance for environmental science, disease diagnosis and biological process monitoring [1–4]. Compared with various of detection techniques for ions such as electrochemical sensing, inductively coupled plasma atomic emission spectrometry, inductively coupled plasma atomic spectrometry and so on, the luminescent-based sensors have drawn increasing attention because of their simplicity, cost-effectiveness, high sensitivity and fast response [1–4]. Among anions and cations, Cu^{2+} is one of the most essential ions in biological systems, particularly in the brain, the appropriate concentration of Cu^{2+} plays an important role in the enzyme activity since the redox-active nature. But, if the concentration is excess in the body, it would bring about gastrointestinal disturbance and even damage to the liver and kidneys such as copper metabolism disordered Wilson's disease [3]. While PO_4^{3-} as an integral part of nucleotides, plays a key role in energy storage and signal transmission in biological systems, as well as environmental systems [4]. Numerous of luminescent-based sensors for sensing ions have been designed and prepared in the past decade [1–4], only a few sensors can simultaneously detect two different ions [5], however, to our best knowledge, one sensor simultaneously target Cu^{2+} and PO_4^{3-} has not been reported. Moreover, quite a number of sensors are not suitable for detecting Cu^{2+} or PO_4^{3-} in a quantitative fashion in aqueous systems, which may be mainly attributed to the poor water stability and selectivity of the sensors. Therefore, it is necessary to exploit highly selective and sensitive luminescent sensors for the straightforward and efficient detection of Cu^{2+} and PO_4^{3-} in aqueous systems.

Coordination polymers (CPs), as one type of important function materials, which are usually constructed by metal ions/clusters and organic ligands through coordination interactions, have been drawing fascinated interest because of their interesting architectures and potential applications in chemical recognition, magnetism, catalysis, gas storage and separation [6–9]. Metal ions with closed d-shells like d^{10} (such as Zn^{2+} and Cd^{2+}) usually produce broad emissions as well as large stokes shifts. On the other hand, the organic ligands with π-acceptor including aromatic rings are suitable for developing luminescent

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Polyoxometalate-Based Metal−Organic Frameworks as Visible-Light-Induced Photocatalysts

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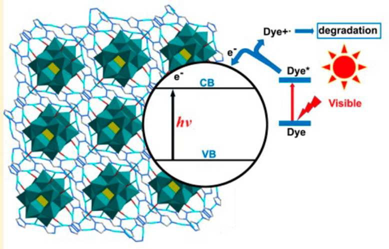
Supporting Information



ABSTRACT: Two stable 3D polyoxometalate-based metal−organic frameworks (PMOFs), $[Cu^{I}_{12}(trz)_8(H_2O)_2][\alpha\text{-}SiW_{12}O_{40}]\cdot 2H_2O$ (**1**) and $[Cu^{I}_{12}(trz)_8Cl][\alpha\text{-}PW_{12}O_{40}]$ (**2**) (Htrz = 1-*H*-1,2,4-triazole) based on Keggin-type POMs were successfully obtained and fully characterized. The basic building units of the two PMOFs are $[Cu^{I}_{12}(trz)_8]$, but polyoxoanion (POA) template effect leads to different structures and properties: **1** represents an interesting example that $[\alpha\text{-}SiW_{12}O_{40}]^{4-}$ locate in the nine-membered Cu-trz rings through Cu···O weak interactions to form a 3D framework, whereas **2** shows a 3D structure constructed from 2D bilayer cationic network $[Cu^{I}_{12}(trz)_8Cl]^{3+}$ and $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ lying in the adjacent layers via Cu···O weak interactions. PMOF **1** as unusual visible-light photocatalyst exhibit significantly enhanced photocatalytic activity under visible-light and excellent stability during the photocatalysis process for recovering and recycling, as well as photocatalytic hydrogen evolution activity.

INTRODUCTION

Because of a global energy shortage and environmental pollution, solar energy has been proposed as the most promising alternative energy source with abundant and environmentally friendly properties. Great efforts have been devoted for the usage of solar energy via various approaches such as photoelectrochemical cells and photovoltaics in the past two decades.[1] Photocatalysis is also an effective approach to remedying environment and converting solar energy. Especially, photocatalytic water splitting for hydrogen production has attracted tremendous attention because it is not only a green route to convert solar energy into renewable hydrogen energy but also a promising technology to reduce fossil fuels consumption.[2] As photocatalysts, polyoxometalates (POMs) acting as inorganic metal-oxide clusters have prominent photocatalytic activity under visible-light because they share very similar light absorption and electrochemical band-edge positions with TiO_2.[3] However, high solubility in solution makes them very difficult in recovering and recycling, which is highly critical to meet the industrial requirements. Furthermore, POMs as inorganic crystalline materials have their own shortages in compatibility and processability, hindering the further engineering of POMs into multifunctional materials. Therefore, the design and assembly of novel POM-based organic−inorganic hybrids with charming structures and optimizing properties has been an attractive and challenging topic.[4]

Metal−organic frameworks (MOFs), as one of the most attractive porous organic−inorganic hybrid materials, have attracted great interest because of their versatile structures and potential applications.[5] Especially, MOFs have widely served as porous supports for the heterogeneous catalysts.[6] As a consequence, one promising approach to solve the disadvantages of significant solubility and poor recyclability is to incorporate homogeneous POMs with porous MOFs with the following advantages:[7] (i) POM-based MOFs (PMOFs) usually possess high thermal stability and can be easily recycled as heterogeneous catalysts; (ii) the crystalline PMOFs with definite structures and chemical components are conducive for the study of catalytic mechanism; (iii) the porous MOFs with advantages including large surface area, high metal content, and flexibility in the design of the active sites in the framework facilitate the diffusion of substrates and products through the channels and make them as ideal platform to hierarchically organize light-harvesting antennae and catalytic centers to achieve solar energy conversion. Nevertheless, these two moieties (POMs and MOFs) have distinct solubility in either hydrophilic or hydrophobic solvents, which lead the preparation of PMOFs extremely difficult. Hydrothermal method has been proven to be an effective method in synthesis of organic−inorganic hybrid POMs,[8] because the increased solubilities of materials and the reduced viscosity of water under

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Two luminescent lanthanide(III) metal–organic frameworks as chemosensors for high-efficiency recognition of Cr(VI) anions in aqueous solution†

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Two new lanthanide(III) metal–organic frameworks (MOFs) $\{[(CH_3)_2NH_2]_2[Ln_4(FDA)_7(DMF)_2]\cdot 0.5DMF\}_n$ [Ln = Eu (**1**), and Tb (**2**)] based on furan-2,5-dicarboxylic acid (H_2FDA) have been successfully assembled and well characterized in detail. These MOFs are isostructural and demonstrate 12-connected ***sqc15*** topologies, which are rarely observed in MOF chemistry, especially in lanthanide(III) MOFs. Moreover, these two MOFs could show a tolerance towards moisture and organic solvents and satisfactory chemical stabilities. More importantly, they exhibit sensitive and selective luminescence quenching response towards $Cr_2O_7^{2-}$ and CrO_4^{2-} anions in aqueous solution with the average quenching K_{sv} values of 1.25×10^4 L mol^{-1} ($Cr_2O_7^{2-}$) and 3.56×10^3 L mol^{-1} (CrO_4^{2-}) for **1** and 1.46×10^4 L mol^{-1} ($Cr_2O_7^{2-}$) and 4.35×10^3 L mol^{-1} (CrO_4^{2-}) for **2** and the detection limits of 1.14×10^{-4} mol L^{-1} ($Cr_2O_7^{2-}$) and 1.12×10^{-4} mol L^{-1} (CrO_4^{2-}) for **1** and 7.42×10^{-5} mol L^{-1} ($Cr_2O_7^{2-}$) and 1.27×10^{-4} mol L^{-1} (CrO_4^{2-}) for **2**. The high quenching K_{sv} values and low detection limits make them more feasible in sensing Cr(VI) anions in aqueous solution. The possible detection mechanism has been discussed in detail.

Introduction

Hexavalent chromium ions, especially $Cr_2O_7^{2-}$ and CrO_4^{2-} anions, have been widely employed in diverse industrial productions, such as pigment printing, leather tanning, electroplating and other relevant fields.[1] Conversely, they have also been confirmed to be two of the most severe environmental nonbiodegradable pollutants and can accumulate in living organisms, severely causing several adverse human health problems such as cancer, deformity and gene mutation.[2] In particular, excessive $Cr_2O_7^{2-}$ and CrO_4^{2-} anions have lethal effects on organisms and the maximum contamination standard of hexavalent chromium ions in drinking water has been defined by the United States Environmental Protection Agency (EPA).[3] Therefore, it is highly necessary to explore an effective method for detecting these hexavalent chromium ions sensitively and rapidly in aqueous solution, which is strikingly significant for environmental protection and human health. Indeed, many sophisticated analytical techniques such as atomic absorption spectroscopy, chromatography, inductively coupled plasma mass spectrometry and electrochemical analysis have been available to detect them efficiently.[4] However, the drawbacks of these methods such as being time consuming, high cost, complicated pretreatment and the need for trained personnel are conspicuous as well. Therefore, seeking a new convenient, practically feasible, inexpensive and quantitative method for hexavalent chromium ion detection is imperative.

Recently, luminescent chemosensors have proven to be promising and compelling alternatives for detection because of their advantages in providing the opportunity of online monitoring with instantaneous and quantitative detection while the samples do not need redundant pretreatment.[5] As a new class of chemosensors, luminescent metal–organic frameworks (MOFs) have recently attracted intensive interest because of their luminescence and accessible porosity, endowing them with the capability of luminescence changes *via* the host–guest interactions, and providing an opportunity of their superior performance in chemical sensing applications.[6] For example, in 2017, our group reported two zinc(II)-lanthanide(III) MOFs to detect aniline and the corresponding detection limit could reach 7.5 μmol L^{-1} and 5.2 μmol L^{-1}, respectively.[7] Subsequently, we synthesized a zinc(II) MOF to be used as a

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Sensitive luminescent probes of aniline, benzaldehyde and Cr(VI) based on a zinc(II) metal-organic framework and its lanthanide(III) post-functionalizations

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Zinc(II) metal-organic framework
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Turn-off luminescent sensors
Aniline and benzaldehyde
Cr(VI) ions

ABSTRACT

A novel zinc(II) metal-organic framework (MOF) $\{[(CH_3)_2NH_2]_2\ [Zn_5\ (TDA)_4\ (TZ)_4]\cdot 4DMF\}_n$ (**1**) (H_2TDA = thiophene-2,5-dicarboxylic acid and HTZ = 1*H*-1,2,4-Triazole) based on $Zn_5(COO)_2\ (TZ)_4$ pentametallic clusters and thiophene-2,5-dicarboxylic acid was synthesized and structurally characterized via the mixed-ligand strategy. This MOF exhibits a uninodal 6-connected anionic framework with **pcu** topology and shows solvent stability. Post-functionalization via cation exchange of **1** with Eu^{3+} and Tb^{3+} afforded two lanthanide (III) functionalized MOFs: **Eu^{3+}@1** and **Tb^{3+}@1**. **1** as well as **Eu^{3+}@1** and **Tb^{3+}@1** were utilized as a highly selective and sensitive turn-off luminescent sensors for detecting aniline, benzaldehyde in DMF and $Cr_2O_7^{2-}$, CrO_4^{2-} in water with low detection limits. More importantly, it is rather rare in MOF-based luminescent probes that **1** and its lanthanide (III) post-functionalized materials (**Eu^{3+}@1** and **Tb^{3+}@1**) can detect aniline, benzaldehyde, $Cr_2O_7^{2-}$ and CrO_4^{2-}. Furthermore, the sensitivity of **1** as luminescent probes for detecting aniline and benzaldehyde could be improved via post-functionalization with Eu^{3+} ions.

1. Introduction

Aniline and benzaldehyde have been widely employed in fine chemicals because of their important industrial applications in intermediate for manufacturing dyes and medicines, precursor ligands for organic synthesis, analytical reagents and other significant raw materials [1]. However, they are also known as toxic chemicals. The excessive exposure of them in air beyond the normal range can cause health problems by irritating eyes, the respiratory system and skin, leading to cancer and deformity [2]. Additionally, similar toxicity can be observed in chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) anions due to their facile accumulation in organisms, thus resulting in human lesion such as cancer and deformity [3]. Consequently, they seriously harm human health and severely contaminate natural environment. Therefore, it is extremely urgent to explore an effective access for simultaneous response and selective detection of aniline, benzaldehyde, $Cr_2O_7^{2-}$ and CrO_4^{2-} anions to avoid the threat to human health and environment. Indeed, several analytical methods have been available for the determination of these substances, such as gas chromatography-mass spectrometry, raman spectroscopy and ion mobility spectrometry [4]. Nevertheless, the defects of low sensitivity and poor selectivity for these methods still remain. Especially, the simultaneously selective detection of them is not practically feasible, which is still a challenge.

Actually, metal-organic frameworks (MOFs) as luminescence sensors are promisingly optimal candidates with high sensitivity and excellent selectivity for sensing small organic molecules [5], such as explosives, aniline and cations [6], including Ca^{2+}, Hg^{2+} and Cr^{3+}, anions [7], such as $Cr_2O_7^{2-}$, CrO_4^{2-} and F^-, pH values [8] and temperature [9]. As a result, many efforts have been made on preparing such luminescence MOF-based probes via multifarious synthetic methods. One such attractive synthetic method for preparing luminescence MOF-based probes is the post-functionalization via ion exchange strategy, which provides an opportunity of the alternative charged guest motifs such as cations, anions, organic dyes or small coordinative molecules into MOFs, endowing MOFs with promising fuctionazation [10].

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Redox-responsive Pickering emulsion derived from the fabricated sheddable polymeric micelles

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HIGHLIGHTS

- Novel method for graft copolymers with cleavable side chains was demonstrated.
- Sheddable micelles exhibiting switchable emulsifying performances were prepared.
- A novel Pickering emulsion with redox-triggered demulsification was fabricated.

ARTICLE INFO

Keywords:
Polyurethane
Reversible addition–fragmentation chain transfer
Reversible covalent bond
Pickering emulsion
Redox-responsiveness

ABSTRACT

Amphiphilic graft copolymers with cleavable side chains exhibit many superiorities in some fields, such as the encapsulation, drug delivery and release, etc. In this study, we demonstrated a redox-responsive Pickering emulsion that was stabilized by sheddable polymeric micelles with many reversible S-S linkages at core-shell interfaces. The sheddable polymeric micelles were achieved by the self-assembly of amphiphilic polyurethane-*g*-poly (N,N-dimethyl acrylamide) (PU-*g*-PDMA) copolymers whose PDMA side chains were tethered on PU backbones by means of the reversible S-S linkages. Such PU-*g*-PDMA copolymers were synthesized via the combination of the polyaddition reaction with the reversible addition–fragmentation chain transfer (RAFT) polymerization reaction. The structure, molecular weight and molecular weight distribution of the polymers were characterized by ^{1}H NMR and GPC analysis. Emulsifying experiments indicated sheddable polymeric micelles possessed perfect emulsifying performances, and highly stable oil-in-water Pickering emulsion could be formed at a low content of emulsifiers. At the same time, the S-S reversible linkages retained at core-shell interfaces of polymeric micelles allowed hydrophilic PDMA shells to be detached through the thiol–disulfide exchange reaction under a reductive environment, which also allowed the resultant Pickering emulsions with redox-responsive demulsification.

1. Introduction

Graft copolymer refers to a kind of polymer that side chains are regularly or densely tethered on a linear backbone. The physical properties of graft copolymers, especially for those with a high graft density, are different distinctly from those of normal linear polymers, endowing graft copolymers with many applications in diverse fields, such as coating and encapsulation, biomedicine and nanoscience etc [1,2]. During the past years, considerable efforts have been devoted to the synthesis of well-defined graft copolymers with desired chemical compositions and adjustable grafting densities. The developed strategies for the synthesis of graft copolymers included “graft through”, “graft from” and “graft onto” [2–12]. Commonly, side chains of the graft copolymers are tethered on the backbones by means of C–C covalent linkages. The C-C covalent linkage endows the graft copolymers with the high stabilities, whose side chains can not be easily cleaved from the backbones. However, graft polymers with cleavable side chains are preferable in some fields, such as the drug delivery and

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Platinum-based metallomesogens bearing a Pt(4,6-dfppy)(acac) skeleton: synthesis, photophysical properties and polarised phosphorescence application†

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Duncan W. Bruce *[d] and Yafei Wang *[a,b]

Polarised phosphorescence has a bright future in backlighting for conventional liquid crystal displays due to its theoretical 100% internal quantum efficiency and low cost. However, there are scarce reports on polarised phosphorescence from metallomesogens. In this contribution, a platinum-based metallomesogen containing a mesogenic biphenyl (**Pt1**) was prepared and characterised. To further explore the effect of the substituent on mesophase and emission properties, a related complex **Pt2** containing a tetraphenylethene (TPE) moiety was also synthesised. Both complexes melt at elevated temperatures but thereafter do not appear to crystallise on cooling. Complex **Pt1** shows an enantiotropic nematic phase from which a broad emission can be seen when spread as a film; in solution, an intense, sky-blue emission is observed. For **Pt2**, which shows a monotropic SmA phase, the emission in the condensed phase is suppressed and there is only weak emission in solution. Polarisation-dependent photoluminescence with a polarised ratio of 5.4 was obtained for the aligned film of a **Pt1**:polyimide mixture. Using **Pt1** as an emissive layer, non-doped, polarised organic light-emitting diodes presented a broad emission spectrum in the range of 450–900 nm with a polarised ratio of 1.33 and the highest external quantum efficiency of 1.1%. This research has an important significance for achieving broad-based polarised phosphorescence from platinum complex-based metallomesogens.

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Introduction

Linearly polarised electroluminescent (EL) light is potentially useful as a backlight in traditional liquid crystal displays (LCDs) due to its low cost and reduced power consumption.[1–3] Over the past two decades, considerable work on polarised EL emission based on fluorescent liquid crystal materials (including polymers, oligomers and small molecules) has been reported.[4–8] Although relatively high dichroic ratios were realised for these fluorescence-based EL devices, the performance was limited by the intrinsic 25% internal quantum efficiency.

Phosphorescent metallomesogens, that is the metal-containing liquid crystals, are of interest to both chemists and physicists because of their unique mesomorphic properties based on the inclusion of the metal atom and the theoretical 100% internal quantum efficiency.[9–12] To date, a considerable number of phosphorescent metallomesogens have been designed and prepared[13–17] and the most effective strategy for the design of such materials has been the modification of known chromophores in such a way as to introduce the anisotropy necessary for liquid crystal phase formation. For example, phosphorescent metallomesogens based on lanthanides,[18–21] platinum,[22–34] iridium,[35–39] and palladium[40] have been reported. Among these, platinum-based metallomesogens were developed rapidly owing to their efficient emission and diverse emission states and the fact that the planar geometry of platinum(II) is well suited to the formation of

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Preparation of an environmentally friendly antifouling degradable polyurethane coating material based on medium-length fluorinated diols

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ABSTRACT

A novel medium-length fluorinated diols and poly(L-lactide) (PLLA) were synthesized via Michael addition reaction and ring-opening polymerization, respectively. Subsequently, Synthetic medium-length fluorinated diols and PLLA were combined to prepare new polyurethane composites with degradability and low surface energy. The compositional analysis and structural characterization of synthetic materials were characterized by using fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance spectra (^{1}HNMR). Thermogravimetric analysis(TGA) indicated that the introduction of medium-length fluorinated diols improved the thermal stability of the polyurethane. The biodegradation and low surface energy of the polyurethane were investigated by static hydrolysis experiment and water contact angle test. It was found that the degradation rate of the polyurethane increased as measurement time went on when the PLLA content was under 40%, and the water contact angle increased from 71.12° to 108.24° with the increase of fluorine content, which indicated that the degradable and low surface energy polyurethane has a potential as a coating material for a marine antifouling coating application.

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KEYWORDS
Low surface energy; degradation; polyurethane; environmentally friendly; fluorinated diols

1. Introduction

Polyurethanes (PUs) have attracted a significance scientific attention in recent years and have been widely used for various applications, such as drug delivery systems,[1] marine antifouling coating and metal coatings, [2–4] emissive materials[5–6] biomedical engineering scaffolds,[7–8] and implantable bioelectronics,[9] due to its unique properties including good biocompatibility and mechanical properties.[10] Polylactic acid (PLA), which is an environmentally friendly and renewable material derived from starch, has attracted a lot of attention. Owing to its desirable mechanical property,[11] thermoplastic processibility,[12] biocompatibility and biodegradability,[13–14] it has received extensive investigation in polymer material application and should be including: tissue engineering,[15] package material,[16] thermoplastic plastics and films as well as fiber,[17–19] and etc. A kind of renewable, degradable and environmentally friendly polylactides composite material can be formed by means of block, blending and co-polymerization. Marc A. and co-workers[20] fabricated PLA-PM-PLA triblock copolymer materials via atom transfer radical polymerization (ATRP), they found this kind of polymer possessed a low transmission temperature and an increased degradation rate. Yihui Xu[21] reported that MWNT-PBA were blended with PLLA and they found that the volume electrical resistance of PLLA/ MWNT-PBA nanocomposites decreased by 10 orders and the temperature of cold crystallization increased when the content of MWNT-PBA increased.

Due to high thermal stability,[22] good chemical resistance,[23] low water absorptivity and attractive surface properties[24–25] of fluorinated polymers, fluorinated polymers have been widely used in numerous practical applications including: aerospace engineering,[26] surface coatings for textile[27] and leather,[28] To extend its application, combination of degradable Polyurethane and low surface energy Polyurethane is expected to be effective to increase the performances of the resulting materials, such as high thermal stability, good chemical resistance, low water absorptivity, good biocompatibility and degradable property.

Herein, we reported the novel degradable and low surface energy polyurethane based on poly (L-lactide) and medium-length fluorinated diols to broaden the applications of this compound materials. We performed a detailed characterizations of structure of novel degradable and low surface energy polyurethane. Thermal stability of the degradable and low surface energy polyurethane was investigated by the thermogravimetry. Static hydrolysis experiment was used to test its degradation property and contact angles were measured by the kruss drop shape analysis system.

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NMR study on the coordination of diperoxovanadium(V) complexes with 2-hydroxymethyl pyridine derivatives

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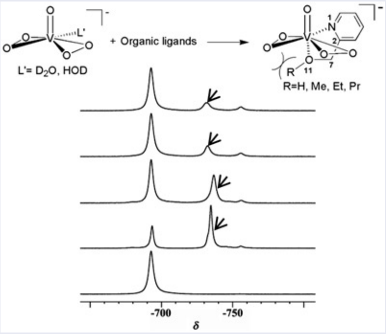
ABSTRACT

To understand the substitution effects of 2-hydroxymethyl pyridine on the reaction equilibrium, the interactions between a series of 2-hydroxymethyl pyridine derivatives and diperoxovanadium(V) complex $[OV(O_2)_2(D_2O)]^-$/$[OV(O_2)_2(HOD)]^-$ in solution were explored by the combined use of multinuclear (^{1}H, ^{13}C, and ^{51}V) magnetic resonance together with HSQC in 0.15 mol L^{-1} NaCl ionic medium for mimicking the physiological conditions. Some direct NMR data are given for the first time. The relative reactivity among the 2-hydroxymethyl pyridine ligands is 2-hydroxymethyl pyridine (**1**) > 2-methoxymethyl pyridine (**2**) > 2-ethoxymethyl pyridine (**3**) > 2-propoxymethyl pyridine (**4**). The competitive coordination results in the formation of a series of new seven-coordinate diperoxovanadium species $[OV(O_2)_2L]^-$ (L = **1**, **2**, **3**, and **4**). The results of density functional calculations indicated that steric effects play an important role in these reactions, providing a reasonable explanation on the relative reactivity of the 2-hydroxymethyl pyridine derivative.



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Diperoxovanadium; 2-hydroxymethyl pyridine derivatives; steric effect; NMR; DFT-calculation

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Chemistry of Heterocyclic Compounds **2018**, *54*(12), 1117–1120

1,3-Dipolar cycloaddition of diphenylnitrilimine and 5-arylmethylidene-1-phenyl-1,5,6,7-tetrahydro-4*H*-indazol-4-ones to afford novel spiro[indazole-5,3'-pyrazole] derivatives

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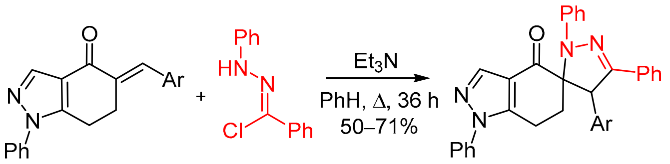


Ar = Ph, 4-ClC$_6$H$_4$, 2-ClC$_6$H$_4$, 4-FC$_6$H$_4$, 4-MeOC$_6$H$_4$,
4-MeSC$_6$H$_4$, 4-MeC$_6$H$_4$, 3,4,5-(MeO)$_3$C$_6$H$_2$

Novel 4'-aryl-1,2',5'-triphenyl-2',4',6,7-tetrahydrospiro[indazole-5,3'-pyrazol]-4(1*H*)-ones have been synthesized in moderate yields by 1,3-dipolar cycloaddition of 5-arylmethylidene-1-phenyl-1,5,6,7-tetrahydro-4*H*-indazol-4-ones and diphenylnitrilimine, generated *in situ* from *N*-phenylbenzohydrazonoyl chloride and triethylamine. According to structural analyses by NMR spectroscopy and single crystal X-ray diffraction method, the reaction proceeds regioselectively affording products with C(5)–C(3') connectivity at the spiro center.

Keywords: indazole, nitrilimine, pyrazole, spiro heterocycle, 1,3-dipolar cycloaddition.

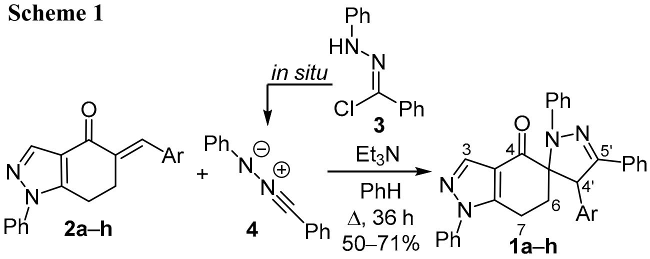
Indazole is an important structural motif in a number of biologically active natural compounds, such as nigellidine and its derivatives,[1] nigellicine,[2] and nigeglanine.[3] Indazole unit is also incorporated in many synthetic compounds that possess antitumor,[4] antiarrhythmic, and analgesic[5] activity and act as NO synthase[6] and HIV protease inhibitors[7] and selective ligands for estrogen receptor beta.[8]

As other important structural fragments, spiro heterocycles are included in different natural products.[9] Frequently, the presence of a spiro carbon enhances antimicrobial, antitumor, and antibacterial activity and inhibitory properties.[10] 1,3-Dipolar cycloaddition is a conventional method for the synthesis of spiro heterocycles.[11] For example, nitrilimines have been used as 1,3-dipoles in reaction with 4-arylmethylidene-1-phenylpyrazolin-5-ones to afford the respective spiropyrazoles.[12]

In continuation of our previous studies regarding 1,3-dipolar cycloaddition reactions,[13] we report herein the synthesis of spiro[indazole-5,3'-pyrazole] derivatives **1a**–**h** from 5-arylmethylidene-1-phenyl-1,5,6,7-tetrahydro-4*H*-indazol-4-ones **2a**–**h** and *N*-phenylbenzohydrazonoyl chloride (**3**) (Scheme 1). The 1,3-dipolar cycloaddition of nitrilimine **4**, generated *in situ* from hydrazonoyl chloride **3** and Et$_3$N, and compounds **2a**–**h** provided the respective 4'-aryl-1,2',5'-triphenyl-2',4',6,7-tetrahydrospiro[indazole-5,3'-pyrazol]-4(1*H*)-ones **1a**–**h** in moderate yields.

The structures of products **1a**–**h** were established by IR and ^{1}H, ^{13}C NMR spectroscopy and HRMS. The high-resolution mass spectrum of spiro[indazole-5,3'-pyrazole] **1h** contained a signal of molecular ion with *m*/*z* 585.2496 and thereby confirmed the addition of one equivalent of diphenylnitrilimine (**4**) to 5-arylmethylidene compound **2h**. The IR spectrum of product **1h** displayed a characteristic absorption of carbonyl group at 1685 cm^{-1}. Furthermore,

Scheme 1



a Ar = Ph, **b** Ar = 4-ClC$_6$H$_4$, **c** Ar = 2-ClC$_6$H$_4$, **d** Ar = 4-FC$_6$H$_4$
e Ar = 4-MeOC$_6$H$_4$, **f** Ar = 4-MeSC$_6$H$_4$, **g** Ar = 4-MeC$_6$H$_4$,
h Ar = 3,4,5-(MeO)$_3$C$_6$H$_2$

Synthesis of 2*H*-chromene-4-carbonitriles *via* trimethylsilyl cyanide

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A number of 2-aryl-2*H*-chromene-4-carbonitriles were synthesised by cyanation of 2-aryl-3-nitro-2*H*-chromenes using trimethylsilyl cyanide (TMSCN) in the presence of tetrabutylammonium fluoride (TBAF) in moderate yields *via* a Michael addition/elimination pathway. The structures of all the products were characterised thoroughly by NMR, IR and HRMS spectroscopy and X-ray crystallographic analysis.

Keywords: 3-nitro-chromene, Michael addition, trimethylsilyl cyanide, tetrabutylammonium fluoride

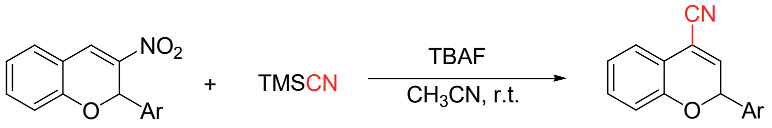
The chromene ring structure is an important structural component in numerous natural products that have diverse biological activities, such as antimicrobial,[1] antifungal,[2] antioxidant[3] and anticancer.[4] Furthermore, chromene derivatives are also used as photochromic materials and as precursors of flavylium dyes.[5,6] Thus the synthesis of chromene derivatives has attracted wide interest.[7]

Nitriles are a useful building block in organic synthesis and they can be converted to other important functional groups such as esters, aldehydes, carboxylic acids, ketones, amides, amines and heterocycles.[8] Transition-metal-catalysed cyanation of halides with metal cyanide is the conventional method for the synthesis of nitriles,[9] but it requires harsh reaction conditions and the use of a toxic reagent. Trimethylsilyl cyanide (TMSCN) is a better cyanide source than alkali metal salts of cyanide, with the advantages of being readily available, easy to handle and high activity.[10]

In continuation of our work on the synthesis of nitrile derivatives[11–13] and chromenes derivatives,[14] here we report the synthesis of 2-aryl-2*H*-chromene-4-carbonitrile derivatives by the reaction of 2-aryl-3-nitro-2*H*-chromene with trimethylsilyl cyanide in the presence of TBAF *via* a Michael addition/elimination pathway (Scheme 1).

Results and discussion

The structures of all compounds **2a–j** were established by spectroscopic techniques (NMR, IR and HRMS). The HRMS spectrum of **2e** gave a molecular ion peak at *m*/*z* 292.0965, which indicates the addition of one molecule of CN and elimination of $-NO_2$ from **1**. The IR spectrum of **2e** showed a



1a-j **2a-j**

Ar: **a**, 4-Cl-C_6H_4; **b**, 4-Br-C_6H_4; **c**, 4-F-C_6H_4; **d**, 2,4-Cl_2-C_6H_3; **e**, 4-CH_3O_2C-C_6H_4; **f**, C_6H_5; **g**, 4-CH_3S-C_6H_4; **h**, 3,4,5-$(CH_3O)_3$-C_6H_2; **i**, 4-CH_3O-C_6H_4; **j**, 4-CH_3-C_6H_4

Scheme 1 Synthesis of 2-aryl-2*H*-chromene-4-carbonitrile derivatives.

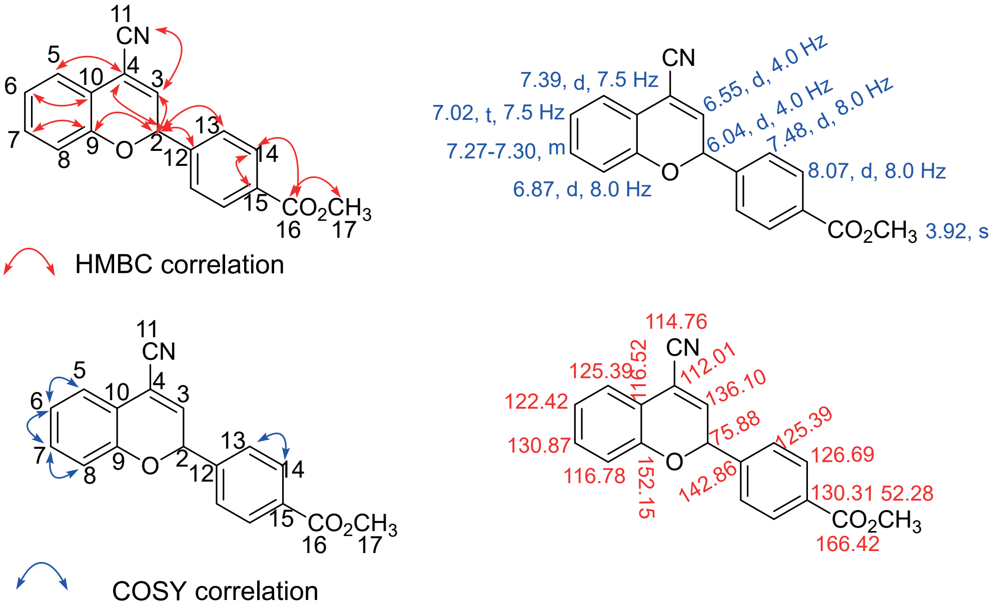


Fig. 1 HMBC correlations and ^1H and ^{13}C NMR chemical shifts of **2e**.

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Hydrothermal Synthesis and Electrochemical Properties of MoS_2/C Nanocomposite

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A molybdenum disulfide/carbon (MoS_2/C) nanocomposite was synthesized by a simple hydrothermal method using glucose as a carbon source followed by carbonization. The sample was systematically investigated by using X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) and high-resolution transmission electron microscopy (HRTEM). Electrochemical performances were evaluated in two-electrode cells versus metallic sodium. The synthesized MoS_2/C composite exhibits an initial capacity of 475.1 mAh g^{-1} at a current density of 100 mA g^{-1}, and a capacity retention of 71% is obtained after 100 cycles at a current density of 250 mA g^{-1}. The material shows enhanced electrochemical performances compared with pristine MoS_2 due to incorporation of the conductive carbon, which suppressed significant volumetric change in MoS_2 during the charge/discharge process and increased the electrical conductivity of MoS_2.

Keywords: MoS_2/C composite; hydrothermal synthesis; anode material; sodium-ion battery

1. INTRODUCTION

Due to the wide availability and low cost of sodium, sodium-ion batteries (SIBs) have attracted considerable attention in recent years as promising alternatives to lithium ion batteries[1-4]. Although the intercalation mechanism of sodium is very similar to that of lithium, the larger ion radius and transport barrier restrict the choice of electrode materials for SIBs[5,6]. Therefore, it is of great importance to explore a suitable host for SIBs.

Transition metal dichalcogenides (MX_2) with a similar feature of layered structure as graphite have great potential as alternative anode materials for sodium ion storage[7-10]. Over the past few years, great attention has been paid to molybdenum disulfide (MoS_2) due to its high theoretical specific

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One-step Convenient Hydrothermal Synthesis of MoS_2/RGO as a High-performance Anode for Sodium-ion Batteries

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A molybdenum disulfide (MoS_2) nanosheet was grown directly on a surface of reduced graphene oxide (RGO) by using a one-step hydrothermal growth technique. The samples were systematically characterized by using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and high-resolution transmission electron microscopy (HRTEM). The electrochemical properties were evaluated by cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy tests in two-electrode cells. The results indicate that the synthesized MoS_2/RGO composites show excellent electrochemical performance as anode materials for Na-ion batteries. The MoS_2/RGO composites exhibit an initial discharge capacity of 715.5 mAh g^{-1} and an initial charge capacity of 440.5 mAh g^{-1} at a current density of 100 mA g^{-1}. The composites also exhibit excellent cycling stability with almost no capacity fading after 100 cycles at a current density of 250 mA g^{-1} compared with only 39.6% of that for pure MoS_2, and the electrode shows stable high-rate performance. The superior electrochemical performance of the MoS_2/RGO composites as Na-ion battery anodes may be attributed to their loose structure and the excellent conductivity of reduced graphene oxide in MoS_2/RGO.

Keywords: MoS_2/RGO composites; hydrothermal synthesis; anode material; sodium-ion battery

1. INTRODUCTION

Due to the scarcity of lithium, there are clear and compelling economic and practical drivers to explore alternatives to lithium ions in charge storage devices[1,2,3]. Sodium-ion batteries (SIBs) have many advantages due to the intrinsic advantages of sodium, for example, they are environmentally benign, easy to recover, inexpensive and relatively abundant[4,5,6]. However, the larger ion radius and

Synthesis of cholestan-3-one derivatives possessing a C-2 spiro-oxindole substituent

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A series of C-2 cholestan-3-one spiro-oxindole derivatives were prepared by the 1:3 dipolar cycloaddition reaction between the cholestan-3-one substituted by a C-2 arylidene and the azomethine ylid derived from isatin and sarcosine. The dipolarophiles were efficiently obtained by a Claisen-Schmidt reaction of cholestan-3-one and aromatic aldehydes. The structures of the products were established by a combination of NMR, high-resolution mass spectrometry (HRMS) and X-ray data analysis.

Keywords: 1:3 dipolar cycloaddition, azomethine ylid, cholestan-3-one, steroidal spiro-oxindole

Chemical modification of the steroidal nucleus and side chain often gives products with increased structural diversity and biological activity.[1] In particular, the introduction of a heterocycle onto the steroid skeleton has been a focus for pharmaceutical chemists.[2]

Among the nitrogen heterocycles, spiro-oxindoles have attracted wide attention because of their unique structure and significant bioactivity.[3] The introduction of a spiro-oxindole moiety onto the steroid core has been attempted previously and has led to novel structures with potential activities (Fig. 1).[4–6] Yu Bin *et al.* obtained two groups of anti-proliferative steroidal derivatives by creating a spiro-oxindole structure on ring D and the C-17 side chain (II and III in Fig. 1).

All of these achievements stimulate our interest in constructing more novel steroidal heterocyclic structures, and in this paper we report the synthesis of steroidal spiro-oxindole derivatives obtained by modifying the A-ring of cholestan-3-one (Scheme 1).

Results and discussion

The arylidene-substituted cholestan-3-one (**1**) was efficiently obtained by a Claisen–Schmidt reaction of cholestan-3-one and an aromatic aldehyde.[7] The 1:3 dipolar cycloaddition reaction of the dipolarophile **1** to the azomethine ylid generated *in situ* from isatin and sarcosine yielded steroidal spiro-oxindole derivative **2**.

The structures of **1a–g** were established by examination of their NMR and HRMS data. The positive ESI-HRMS of **1a** gave a quasi-molecular ion peak at *m/z* 505.4039 ([M+H]$^+$), which indicated the addition of 4-methoxyphenyl methylene to cholestan-3-one. The characteristic arylidene proton was found as a singlet at δ 7.54 in the ^{1}H NMR. The protons of the aromatic ring and the 4-methoxyl group were clearly identified as two doublets at δ 7.38, 6.92 and a singlet at δ 3.84, respectively.

The related structures of **2a–g** were established by a combination of HRMS and 1D and 2D NMR data. The positive ESI-HRMS of **2a** exhibited a quasi-molecular ion peak at *m/z* 679.4836 ([M+H]$^+$), implying a molecular formula of $C_{45}H_{62}N_2O_3$. The ^{1}H NMR spectrum of **2a** showed seven methyl proton signals at δ 3.83 ($-OCH_3$), 2.13 ($-NCH_3$), 0.86 (CH_3-21), 0.85 × 2 (CH_3-26 and CH_3-27), 0.49 (CH_3-18) and –0.06 (CH_3-19). The upfield shift of CH_3-19 protons probably arose because of the anisotropic effect of the aromatic ring in the spiro-heterocycle moiety. The –NH proton of the oxindole

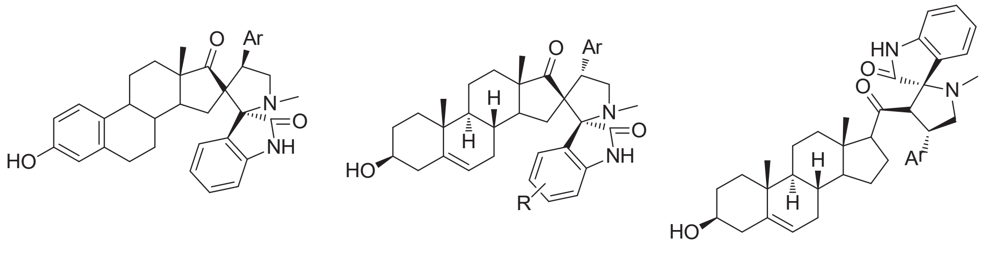
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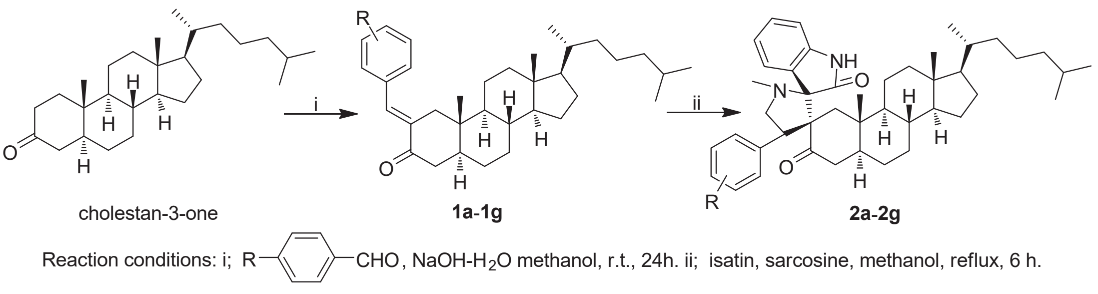
Fig. 1 Steroidal spiro-oxindole derivatives.


cholestan-3-one **1a-1g** **2a-2g**

Reaction conditions: i; R CHO, NaOH-H$_2$O methanol, r.t., 24h. ii; isatin, sarcosine, methanol, reflux, 6 h.

R: a, 4-OCH$_3$; b, 4-SCH$_3$; c, 4-CH$_3$; d, 4-H; e, 4-F; f, 4-Cl; g, 4-Br

Scheme 1 Synthesis of cholestan-3-one spiro-oxindole derivatives.

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Article

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Hydrothermal Synthesis of PAA-Coated $NaYF_4$:Yb^{3+}, Er^{3+} Nanophosphors with Predicted Morphology, Phase and Enhanced Upconversion Luminescence Properties

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In this study, well-defined PAA-coated $NaYF_4$:Yb^{3+}, Er^{3+} nanophosphors were synthesized via a poly(acrylic acid) (PAA) mediated hydrothermal process. The rational control of initial reaction conditions, such as hydrothermal temperature, pH value of precursor-solution, added amount of PAA, and molecular weight of PAA ligand, resulted in upconversion of $NaYF_4$:Yb^{3+}, Er^{3+} phosphors with varying crystal phases (α and β) and morphologies (e.g., nanosphere, submicrorod, microrod, microtube, and microprism). By assessing the upconversion luminescent properties of the synthesized $NaYF_4$:Yb^{3+}, Er^{3+} phosphors upon excitation by 980 nm infrared light, it was demonstrated that the β-phase $NaYF_4$:Yb^{3+}, Er^{3+} phosphors generally presented stronger upconversion luminescent than α-phase $NaYF_4$:Yb^{3+}, Er^{3+} phosphors and orthorhombic phase of YF_3:Yb^{3+}, Er^{3+} sample. Additionally, the β-phase $NaYF_4$:Yb^{3+}, Er^{3+} phosphors with hollow microtube morphology presented higher upconversion luminescent intensity than phosphors of other morphologies. This may be due to microtubes having larger surface area (inner and outer surfaces), which promoted the absorption efficiency under similar excitation conditions, therefore generating higher luminescent intensity. Findings form this study suggest for precisely controlled growth of other complex rare earth fluoride compounds and provide a reference for exploration of component-, phase- and morphology-dependent upconversion luminescence properties.

Keywords: Hydrothermal, Rare Earth Ion-Doped $NaYF_4$, Poly(Acrylic Acid), Upconversion Luminescence.

1. INTRODUCTION

Currently, materials with excellent properties plays an important role in the rapid development of modern technology.[1–3] Lanthanide ion-doped upconversion (UC) inorganic luminescent materials have become the focus of interest, due to their unique optical capability for absorbing and converting lower energy excitations with near-infrared long wavelength to higher energy emissions with short wavelength.[4–5] This unique property makes UC materials have a wide application in various fields, such as solar-energy conversion,[6] flat panel display,[7] biological imaging,[8] anti-counterfeiting,[9,10] etc. For these applications, the enhanced conversion efficiency and detection signals are highly demanded. Thus, synthesis of lanthanide ion-doped UC materials with superior luminescent properties (e.g., fluorescence intensity and lifetime) has attracted increasing research interests. It is generally accepted that, the precise control of component, morphology and phase for UC inorganic luminescent materials is crucial for obtaining excellent luminescent properties.[11–13] Understanding how the luminescent properties change with component, morphology and phase are of great significance in the design of upconversion materials.

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Original Research

Visible Light-Driven Photocatalytic Degradation of 1,2,4-trichlorobenzene with Synthesized Co_3O_4 Photocatalyst

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Abstract

A cubic crystal form Co_3O_4 was synthesized using the sol-gel method and applied as catalyst in the visible light-driven photocatalytic degradation of 1,2,4-trichlorobenzene (1,2,,4-TCB). 1,2,4-TCB removal efficiency initially increased and was followed by a gentle decrease as the Co_3O_4 dosage increased, with the optimal dosage of 2.0 g/L. The degradation rate changed positively with light intensity and reaction temperature. However, pH exerted only a slight effect on 1,2,4-TCB degradation. Strong acidic and basic conditions were conducive to the photocatalytic degradation of 1,2,4-TCB. The optimal parameters for the photocatalytic degradation of 1,2,4-TCB were found at a Co_3O_4 dosage of 2.0 g/L, 350 W of illumination intensity, initial 1,2,4-TCB concentration of 7.5 mg/L at 30ºC, with 1,2,4-TCB removal efficiency of 90.13% after 6.0 hours photocatalytic degradation. The Co_3O_4 synthesized in the study with high-purity and stable properties guaranteed its high catalytic activity and stability. The possible mechanisms of visible light-driven photocatalytic degradation of 1,2,4-TCB with synthesized Co_3O_4 photocatalyst were also proposed.

Keywords: visible light-driven photocatalyst, Co_3O_4, photocatalytic degradation, 1,2,4-TCB

Introduction

As persistent organic pollutants (POPs), chlorobenzenes (CBs) have been widely used in industrial and agricultural production of pharmaceuticals, petrochemicals, and pesticides and in the process have become common pollutants [1] found in air, soils [2-3], sludge [4], lake and coastal sediments [5], groundwater, and river entrances [6-7]. Trichlorobenzene is a common type of CB, with 3 isomers, including 1,2,4-TCB, which is the most widely used for industrial purposes and once was made widely available in the electrochemical industry as a substitute of

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Preparation and properties of BMPLGA/NBAG-β-TCP composite scaffold materials

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ABSTRACT
Biodegradable polymer/bioceramic composite scaffolds can overcome the limitations of conventional ceramic bone substitutes such as brittleness and difficulty in shaping. A novel degradable scaffold material for bone tissue repairing was developed by combining 1,4-butanediamin-modified poly(lactide-co-glycolide) (BMPLGA) with nano-biaoactive glass and nano-β-tricalcium phosphate (NBAG-β-TCP) . The effects of the inorganic filler content on the morphology, water adsorption, and compressive strength of the nanocomposite scaffolds were investigated. The nanocomposite scaffolds showed an interconnected pore structure with the pore size ranging from 50 to 200 μm. The compressive strength and the water adsorption ability were enhanced with increasing content of the inorganic fillers. The cell proliferation of fibroblast was significantly improved after three and seven days of culture on BMPLGA/NBAG-β-TCP films in comparison with BMPLGA films. The BMPLGA/NBAG-β-TCP composites have a wide application as a potential biomaterial in medical field.

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Composite scaffold; poly(lactide-co-glycolide); maleic anhydride; 1,4-butanediamin; nano-β-tricalcium phosphate; nano-bioactive glass

Introduction

Scaffolds for bone tissue engineering have become a very hot research field because the scaffold lies at the heart of all new tissue engineering approaches. Scaffolds play a key role as they serve as a three-dimensional template for cell differentiation, adhesion, proliferation and formation of an extracellular matrix, as well as a carrier of the growth factors or other biomolecular signals.[1–3] Various synthetic alternatives such as ceramics, polymers, and composites have been tried as scaffolds for many years.[4–7]

Biodegradable polymers are used in an increasingly large number of biomedical applications such as drug-releasing implants, bioresorbable surgical sutures, short-term fixation devices, and tissue engineering.[8–13] Biodegradable synthesized polymers, such as polylactide (PLA) and poly(-lactide-co-glycolide) (PLGA), have been widely studied for biomedical applications because they demonstrate favorable cell adhesion and proliferation properties.[14–17] PLGA degrades rapidly in the body compared to other biodegradable polyesters; however, acidic by-products which result

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Influence of substituent effects on the coordination ability of salicylaldehyde Schiff bases

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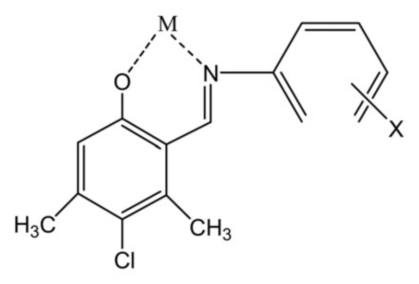
ABSTRACT

The logK_1 was quantified by four parameters, metal ion radii R, metal ion charge Q, metal atom polarizability P, and Hammett constants σ of substituent, where logK_1 was the stability constant of complexes (179) involving 10 Schiff bases Sal-A-X (N-(5-chloro-4-6-dimethyl-benzylidene)-anilines) reacting with 18 metal ions. The effect of substituents on the coordination ability of Sal-A-X was systematically investigated, and an expression with good correlation was obtained. The result shows that the electronic effect of substituent X on the aniline ring has an important influence on the stability of the complex; its electron-donating effect enhances the stability of the complex, whereas its electron-withdrawing effect lowers the stability of the complex. The theoretical results provide a potential value for the design of coordination compounds with unique function and reactivity. Moreover, their coordination selectivity to specific metal-ions can also be evaluated according to Equation (2).



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Synthesis and Characterization of Terpolymers of poly(L-lactide-glycolide-ε-caprolactone)

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ABSTRACT

Random terpolymers of poly(L-lactide-glycolide-ε-caprolactone) (PLLGC) was prepared by ring-opening polymerization of L-lactide, glycolide and ε-caprolactone monomers initiated with stannous octanoate. Fourier transform infrared spectra, nuclear magnetic resonance and gel permeation chromatography were employed to characterize the obtained PLLGC terpolymers. The effects of polymerization temperature, reaction time, the amount of initiator and the polymerization pressure on the weight average molecular mass and polydispersity index of the PLLGC were investigated. In addition, the water contact angle of the PLLGC was also tested. The characterization of chemical structure showed that the PLLGC was successfully synthesized. For instance, a PLLGC terpolymer with a weight average molecular mass of about 12.435×10^4 Da and a polydispersity index of 1.28 was obtained when the polymerization was conducted with a molar ratio of monomer to initiator ([M]/[I]) of 2000, polymerization temperature of 140 °C, polymerization pressure of 5.0 Pa and reaction time of 24 h. The random incorporation of ε-CL monomer units decreased the wettability of the PLGA copolymers.

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biodegradable polymer; glycolide; L-lactide; poly(L-lactide-glycolide-ε-caprolactone); terpolymer; ε-caprolactone

Introduction

Biodegradable polymers are widely used for biomedical applications such as surgical sutures, internal bone fixation, drug carriers and scaffolds for tissue engineering.[1–3] L-lactide (LLA) and glycolide (GA) are the most widely used monomers for syntheses of biodegradable polyesters.[4–6] Their homopolymers (poly-L-lactide (PLLA) and polyglycolide (PGA)) and the copolymer (poly(lactide-golycolide) (PLGA)) have been used in a wide variety of biomedical applications, including controlled drug release,[7,8] tissue scaffolds[9,10] and bone fixation,[11–13] due to their controlled degradability and excellent biocompatibility. However, their homopolyesters and copolymer are too brittle for most applications.

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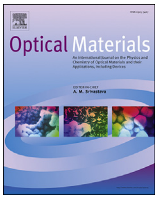

Rational design of $Bi^{3+}/Ln^{3+}:GdVO_4$ (Ln = Eu, Sm, Dy, Ho) nanophosphor: Synthesis, characterization and color-tunable property

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ABSTRACT

Novel rod-like $Bi^{3+}/Ln^{3+}:GdVO_4$ phosphor have been successfully fabricated via a mixed solvothermal route. X-ray diffraction, transmission electron microscopy, inductively coupled plasma and spectrofluorimeter equipments are used to characterize the samples. By introducing Bi^{3+} into $Ln^{3+}:GdVO_4$, efficient energy transfer occurs from Bi^{3+}–V^{5+} charge transfer state to Ln^{3+}, these phosphors can efficiently absorb near-ultraviolet light through the Bi^{3+}–V^{5+} metal–metal couple charge transfer and exhibit intense multifarious luminescent colors by modulating the doping content of Ln^{3+} ions. Therefore they have potential applications in color display field.

1. Introduction

In recent years, great efforts have been devoted to the fabrication of optical materials with emitting multicolor property [1–5]. Among these optical materials, lanthanide (Ln^{3+}) ions activated phosphors have aroused tremendous attention due to their wide range of emission colors and outstanding luminescent performance [6–11]. In order to conquer the low absorptions of Ln^{3+} with parity forbidden 4f - 4f transitions, host sensitization via energy transfer (ET) offers a valid method to realize practical applications [12–15]. There are many reports concern sensitizing emissions in several Ln^{3+} ions - doped nanocrystals, e.g. CeO_2, In_2O_3, SnO_2 and ZnO [16–20]. However, because of the unmatched charge compensation and radius between Ln^{3+} ions and doping host cations, realization of high content Ln^{3+} ions doping is very tough.

Serving as a traditional doping host, the ABO_4 type oxides (A = alkaline earth, transition metal, Ln^{3+}, Main group metal; B = nd^0 ions such as Nb^{5+}, V^{5+}, Mo^{6+},W^{6+}) have been proved to have sufficient ET from BO_4 groups to the A sites activator ions when excited by ultraviolet light. Generally, the absorption bands could be extended to the near ultraviolet region by doping ns^2 electron metal ions (e.g. Pb^{2+}, Sn^{2+}, Bi^{3+} and Sb^{3+}) in the ABO_4 type oxide, owing to the metal–metal charge transfer (CT) from the ns^2 metal ions to the nd^0 ones [21,22].

As a member in the ABO_4 type family, gadolinium orthovanadate ($GdVO_4$) – based materials are promising candidates that possess good chemical stability, thermal properties and high photoluminescence quantum yield, which give rise to a lot of applications. (such as field emission displays, light emitting diodes, plasma display panels and so on). So far, a series of synthetic methods have been developed to prepare Ln^{3+} ions doped $GdVO_4$ [23–25]. For example, M. Dramićanin et al. reported the synthesis of $GdVO_4:Ln^{3+}/Yb^{3+}$ ($Ln^{3+} = Ho^{3+}$, Er^{3+}, Tm^{3+}, $Ho^{3+}/Er^{3+}/Tm^{3+}$) nanorods, (Eu^{3+},Er^{3+}/Yb^{3+}) doped $GdVO_4$ nanoparticles from chemical co-precipitation and reverse micelle methods respectively. All the synthetic methods can be devided into two broad categories: solid-state reaction method and liquid-state reaction method. Many traditional phosphors are prepared through the former method, but it has some drawbacks, e.g. uncontrollable synthetic processes, impurity and the inhomogenous size-distribution in the final product [26,27]; For the latter,

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Fabrication of $Bi^{3+}/Ln^{3+}:LuVO_4$ (Ln = Eu, Sm, Dy, Ho) nanophosphors and its color-tunable optical performance

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ABSTRACT

The novel $Bi^{3+}/Ln^{3+}:LuVO_4$ (Ln = Eu, Sm, Dy, Ho) nanocrystals are successfully fabricated by a facile and mixed hydrothermal method. With 10 mol% Bi^{3+} doping into the $LuVO_4$ nanocrystal, the Ln^{3+} excitation band could be diverted from 293 nm to 346 nm, attributing to the dominant of Bi^{3+} - V^{5+} metal–metal charge transfer instead of O^{2-} to V^{5+} within VO_4 group before doping. Under 346 nm excitation, the as-prepared nanophosphors yield intense multicolor emissions. The emission color of $Bi^{3+}/Ln^{3+}:LuVO_4$ nanophosphors can be tuned through adjusting the doping Ln^{3+} ions. They may find potential applications as white light-emitting diode materials in color display field.

1. Introduction

Recently, serve as a new source for illumination, the white light-emitting diodes (W-LED) is gradually to supersede conventional incandescent and fluorescent lamps as a result of its merit in energy saving. Generally, the W-LED is made of a near-ultraviolet (NUV) GaN-based LED chip (350–400 nm) equipped with the red, green, and blue phosphors [1,2]. However, the multiple phosphors are usually excited by deep ultraviolet light in traditionally fluorescent lamps, with wavelength of 185 nm or 254 nm [3,4]. Thus, one approach concerning the new category of solid-state lighting based upon the GaN LED chip depends on the development of novel phosphors families which are optimized for excitation at longer wavelengths range (350–400 nm).

Currently, lanthanide (Ln^{3+}) ions activated phosphors have attracted enormous attention due to their broad range of luminescent colors as well as excellent optical performance [5–10]. To overcome the low absorptions of parity forbidden $4f-4f$ transitions of Ln^{3+}, host sensitization via energy transfer (ET) from the excited host to the Ln^{3+} ions provides an effective way to achieve highly efficient luminescence of Ln^{3+} ions for practical applications [11–16]. Sensitizing emissions in several Ln^{3+} ions - doped nanocrystals, e.g. ZnO, In_2O_3, CeO_2 and SnO_2, have been reported [17–21]. However, due to the necessary charge compensation and the radius mismatch between Ln^{3+} ions and cations of the doping host, doping semiconductor nanocrystals with a high concentration of Ln^{3+} ions is very difficult [22].

The ABO_4 type oxides(A = alkaline, transition metal, Ln^{3+}, Main group metal;B = nd° ions Nb^{5+}, V^{5+}, Mo^{6+},W^{6+}), as a traditional host, have been proved to have sufficient ET from BO_4 groups to the activator ions at A sites after excited by the ultraviolet light, which can exhibit efficient emissions. Usually, the ABO_4 type oxide are doped with metal ions (such as Pb^{2+}, Sn^{2+}, Bi^{3+} and Sb^{3+}) which have ns^2 electronic configurations, the absorption bands could be extended to the NUV region on account of the metal–metal charge transfer (CT) in which the electrons are transferred from the ns^2 metal ions to the nd° ones [23,24].

Among the ABO_4 oxide family, rare earth orthovanadates $LnVO_4$ are excellent hosts for luminescence. Up to now, $LuVO_4:Ln^{3+}$ (Ln^{3+} = Eu^{3+}, Dy^{3+}, Sm^{3+}, Er^{3+}) hollow porous spheres, nanoleaves and octahedral have been successfully synthesized [25–27]. These phosphors all have perfect luminescence properties. Unfortunately, the reports about color tunable emission phosphors using high content of Bi^{3+} ions doping into $LuVO_4$ as the host are rare, the reason can be listed below: on one hand, The different crystal structures between $BiVO_4$ and $LuVO_4$ makes it hard to form a continuous solid solution [28]; on the other hand, bismuth salt is easy to hydrolyze and cause the impurity in one solvent [29]. Except the liquid state reaction, solid-state reaction is another common technique to synthesize the phosphors. However, because of the uncontrollable synthetic processes, the obtained

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Analytical Chemistry

A New Fluorescent Probe Based on Aggregation Induced Emission for Selective and Quantitative Determination of Copper(II) and its Further Application to Cysteine Detection

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A new fluorescent chemosensor 2,2′-((1E,1′E)-hydrazine-1,2-diylidenebis(methanylylidene))bis(4-(1,2,2-triphenylvinyl) phenol) **TPESAA** incorporated with salicylaldehyde azine motif was developed based on aggregation-induced emission (AIE). The probe **TPESAA** was prepared from 4-hydroxy tetraphenyl ethylene which underwent formylation followed by condensation with hydrazine hydrate. It showed ratiometric fluorescence quenching behavior to Cu^{2+}, which could induce naked-eye color changes from colorless to pale yellow. Moreover, it displayed excellent sensitivity and selectivity toward Cu^{2+} without interference from other metal ions. The extent of quenching is dependent on the concentration of Cu^{2+} in the range of 0.5–7.5 μM, and a remarkable detection limit (30.9 nM) can be achieved. Furthermore, the obtained Cu^{2+} complex could be applied to quantitative determination of cysteine in the range of 0.2–2 μM with a good linear relationship.

Introduction

Developing new fluorescent transition and heavy metal probes and sensors is an emerging research area of great importance because of the momentous roles and potential applications in biological, environmental and supramolecular sciences.[1] Among the various metals, copper(II) is of special biological importance in human body as the third most abundant essential trace element. It plays significant roles in various fundamental physiological processes such as enzyme functions, blood formation, respiration, and transcriptional events.[2] However, a higher concentration of intracellular Cu^{2+} may be highly toxic to organism, which may lead to many severe diseases, such as coronary heart disease, liver, anaemia, and neurodegenerative disease.[3] On the other hand, copper deficiency may also cause Menkes disease, colon cancer, and so on.[4] In addition, copper(II) ions may produce enormous quantities of pollution to our living environment because of its extensive use and the toxic impact of its excess on micro-organisms.[5] Therefore, in view of the significance of copper ions, a great deal of effort has been devoted to the development of highly sensitive and selective methodology for detection of Cu^{2+}.[6] Among them, fluorescent chemosensors are becoming a more and more important detection method for Cu^{2}+ due to their high sensitivity and selectivity, low cost, easy operation, and especially compatibility as diagnostic tools in biological system.[7]

Most reported fluorophores such as fluorescein or rhodamine dyes show much weaker emission in aggregate or solid states compared to that in solutions because of concentration- or aggregation-caused quenching (ACQ) effect,[8] which limits their application. Also, it is difficult to apply these probes for copper(II) detection in aqueous solution due to their ACQ characteristics. Recently, aggregation-induced emission (AIE) phenomenon, a strong fluorescence emission phenomenon of molecules in the aggregate or solid states, has attracted more and more interest.[9] The novel and sensitive fluorescence 'turn-on' feature of the AIE fluorophores makes them potential building blocks in fabrication of chemical sensors, anion sensors, as well as probes for detection transition metal ions.[10]

AIE fluorophore systems could be classified to three types: aryl substituted heterocyclic compounds, intramolecular charge transfer compounds, hydrogen- bonding compounds. TPESAA are a class of hydrogen-bonding compounds which are AIE-active.[11] The hydroxyl groups at the *ortho*-position on the benzene ring of these compounds are key factor for their AIE fluorescence because that intramolecular hydrogen bonds of salicylaldimine moieties and stacking of molecules in aggregate state inhibit the free intramolecular rotation resulting in the

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CdS/TiO_2 纳米晶薄膜的原位法制备及光电化学性能研究

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摘　要: CdS/TiO_2 异质结薄膜因其优异的可见光催化性能，在光催化领域引起了广泛关注。然而，目前传统方法制备的 CdS/TiO_2 薄膜可能存在交界面结合不紧密的问题，不利于光生载流子在交界面处的传输。因此，本研究基于原位转换的原理($TiO_2 \rightarrow CdTiO_3 \rightarrow CdS$)，将 TiO_2 纳米晶表层原位转换成 CdS，制备了 CdS/TiO_2 纳米晶薄膜。采用 X 射线衍射(XRD)、扫描电子显微镜(SEM)和透射电子显微镜(TEM)手段对样品薄膜的形貌和结构进行了表征。由表征结果可知，在 TiO_2 纳米晶表面形成了 CdS，构成了交界面结合紧密的 CdS/TiO_2 异质结薄膜。光电化学性能研究表明，与传统的连续离子层吸附反应法(SILAR)制备的薄膜相比，原位法制备的 CdS/TiO_2 薄膜的光电流密度更高，达到 $9.8\ mA\cdot cm^{-2}$(V=0.4 V (*vs*. RHE))；交流阻抗谱(EIS)结果表明，原位法制备的 CdS/TiO_2 薄膜具有更小的电荷传输电阻，说明原位法形成的 CdS/TiO_2 异质结结合更紧密，能减小光生载流子在 CdS/TiO_2 界面处的传输阻力，降低光生载流子在传输过程中的复合几率，进而提高 CdS/TiO_2 薄膜的光电化学性能。

关　键　词: CdS/TiO_2；光电化学性能；原位法；光阳极；异质结

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CdS/TiO_2 Nanocrystalline Films: *In-situ* Synthesis and Photoelectrochemical Performance

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Abstract: CdS/TiO_2 heterojunction films have attracted much attention in the field of photocatalysis due to their excellent photocatalytic performance under visible light irradiation. However, the CdS/TiO_2 films prepared by the conventional methods may exhibit loose interface, leading to poor transport of photogenerated carriers in the interface. In this study, CdS/TiO_2 heterojunction films were successfully prepared by *in-situ* transformation ($TiO_2 \rightarrow CdTiO_3 \rightarrow CdS$). Morphologies and structures of as-prepared films were characterized by XRD, SEM and TEM. Results show that CdS formed on the surface of TiO_2 nanoparticle, and the interface of CdS/TiO_2 heterojunction was compact. Their photoelectrochemical (PEC) performance was investigated by electrochemical working station. Results indicate that the CdS/TiO_2 films prepared by *in-situ* method, whose photocurrent density was as high as $9.8\ mA\cdot cm^{-2}$ at 0.4 V (*vs*. RHE), present higher PEC activity than those prepared by successive ionic layer adsorption and reaction (SILAR). The electrochemical impedance spectroscopy (EIS) results show that the *in-situ* synthesized CdS/TiO_2 films own lower

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Nanofiber-like mesoporous alumina supported palladium nanoparticles as a highly active catalyst for base-free oxidation of benzyl alcohol

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ABSTRACT

A nanofiber-like mesoporous alumina supported palladium catalyst, Pd/γ-Al_2O_3-fibr, was successfully prepared by a hydrothermal method and used in the aerobic oxidation of benzyl alcohol to benzaldehyde with molecular oxygen under base-free conditions. The material was characterized by N_2 physisorption, FT-IR, X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and X-ray photo-electron spectroscopy (XPS). XRD and TEM results revealed that the palladium nanoparticles were uniformly dispersed in the framework of nanofiber-like mesoporous γ-alumina. The higher activity of Pd/γ-Al_2O_3-fibr compared to Pd/γ-Al_2O_3 and Pd/SBA-15 in the aerobic oxidation of benzyl alcohol reaction suggested that the unique fibrous architecture of our material and synergic effect between Pd species and γ-Al_2O_3 are beneficial to enhance the reactivity of palladium NPs. Furthermore, the unique architecture of Pd/γ-Al_2O_3-fibr catalyst also offers it good mass-transfer property and accessibility, which make it an effective catalyst for aerobic oxidation of steric bulk alcohol substrate. The Pd NPs supported on nano-fibrous mesoporous alumina in this paper is demonstrated to be a recoverable noble metal-based nanocatalyst with easy accessibility and may be great potential as a promising candidate for numerous catalytic applications.

1. Introduction

Benzaldehyde is of important value due to its application as intermediate and raw material in perfumery, pharmaceuticals, dyestuff and agrochemical industry. The tradition production of benzaldehyde via the toluene chlorination and subsequent hydrolysis process requires complicated preparation procedures and generates large amount of toxic acidic wastes, leading to serious environmental contaminations and costly separation process [1–3]. As an alternative green route to produce chlorine-free benzaldehyde, the aerobic oxidation of benzyl alcohol with molecular oxygen or air has attracted significant attention in recent years, being water the only by-product of the reaction. In this regards, the active catalysts concerning transition metal and noble metal such as Cu [4,5], Cr [6], Mn [7,8], Ru [9], Pt [10], Au [11,12], Pd [13–15], bimetallic Au-Pd [16,17] have been reported, among them, the Pd-based catalysts displays interesting and promising catalytic performance in both activity and selectivity, especially under the mild conditions.

Due to the environmental friendly and safety property, aerobic oxidation of benzyl alcohol in water is more appreciable because it helps to reduce the amount of waste after reaction and avoid explosion and hazards associated with the application of other toxic and oxidisable organic solvent. Palladium nanoparticles supported on various supporting materials are attractive catalyst for aerobic oxidation of alcohols [18–21]. However, owing to the high surface energy of catalytically active Pd NPs, Pd NPs supported on numerous conventional supports usually suffered from the problems such as gradual growth of Pd NPs into inactive large particles and poor accessibility of active sites that entrapped in the pores and channels of supports. Thus, for the purpose of improving the accessibility of active sites to reactant and reduce the propensity of Pd NPs to coalesce, many heterogenized Pd NPs catalysts with well-designed nanocomposite structures were developed for catalytic applications, including hollow core-shell structured Pd NPs-based nanocatalysts [22–25], Pd NPs@ metal–organic frameworks [26–28], and Pd NPs/CNT nanohybrids [29,30]. These nanocatalysts show promising properties to suppress aggregation, leading to enhanced catalytic activity. However, the fabrication of these nanocomposites also suffers from problems such as difficult synthesis

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Synthesis of Potential Anticancer 1-(1*H*-Indol-3-yl)isoquinolines by Silver Nitrate Mediated Tandem Reactions of 2-Alkynylbenzaldehyde Azines and Indoles

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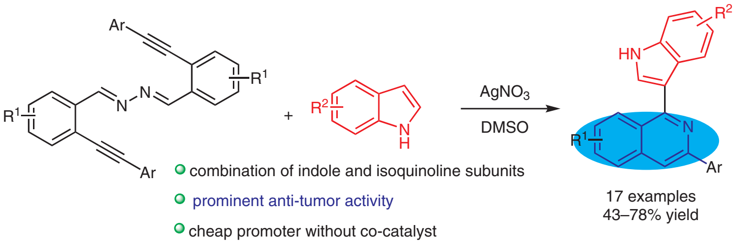

- combination of indole and isoquinoline subunits
- prominent anti-tumor activity
- cheap promoter without co-catalyst

17 examples
43–78% yield

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Abstract Novel antitumor compounds featuring isoquinoline and indole moieties were synthesized by a silver nitrate promoted domino reaction involving intramolecular cyclization, nucleophilic addition of indole, and subsequent N–N bond cleavage. The transformation from readily available starting materials into an interesting class of indole-substituted isoquinolines was completed under mild conditions and by simple operations in moderate to good yields. The antitumor activity of these compounds in vitro was significantly greater than that of a reference compound, 5-fluorouracil. The products might serve as new lead compounds for drugs for the treatment of cancer.

Key words bond cleavage, domino reaction, isoquinolines, indoles, silver nitrate, medicinal chemistry

Although there has been great progress in its diagnosis and treatment, cancer remains one of the three most common causes of human death, and results in considerable financial cost worldwide. Over the past few decades, tremendous efforts have been made in exploring novel antitumor lead compounds to improve cancer chemotherapy, and a great diversity of compounds have been discovered. Among the explored substances, derivatives of isoquinoline have attracted considerable attention for use as effective antitumor agents since the isolation of naphthyridinomycin in 1974.[1] Naphthyridinomycin,[2] trabectedin (ecteinascidin 743),[3] and quinocarcin[4] were later identified as three important antitumor isoquinolines alkaloids, and trabectedin has since been approved by the European Medicines Agency for the treatment of advanced soft-tissue sarcomas.[5] These compounds act on the farnesoid X receptor[6] and cell cycle,[7] function as redox cyclers,[8], and inhibit insulin growth factor (IGF) and IGF-binding proteins[9] by binding to the minor groove of DNA to form covalent adducts. In addition, isoquinolines alkaloids exhibit many other biological activities, including antidiabetic and antitubulin activities.[10]

As a result of the remarkable physiological properties of isoquinoline derivatives and their significant role in organic synthesis, the development of convenient, versatile, and efficient methods for the synthesis of isoquinoline derivatives has recently attracted considerable attention.[11] Among the wide range of strategies employed, transition-metal-catalyzed inter- or intramolecular cyclization/(hetero)annulation reactions have emerged as some of the most efficient, owing to their high selectivities and mild conditions.[12] For instance, isoquinoline derivatives can be obtained by silver(I)-catalyzed cyclization of *ortho*-alkynylaryl aldimines, because of the ability of silver cation to activate various π-systems when present at low catalytic loadings under mild conditions.[13] The Wu group reported a series of tandem reactions of 2-alkynylbenzaldehyde, sulfonohydrazides, and various aldehydes, α,β-unsaturated aldehyde, ketones, amines, nitriles, alkynes, or cyclopropenedicarboxylates catalyzed by silver salts for the synthesis of isoquinolines derivatives.[14]

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高灵敏磁分离荧光传感法检测黄曲酶毒素B1

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摘　要：以自组装方式制备了Au@Fe_3O_4/核酸适体/氨基-碳量子点磁性生物纳米复合物，并提出一种磁分离荧光传感法用于黄曲霉毒素B1的检测.当样品中有黄曲霉毒素B1时，磁性生物纳米复合物中核酸适体选择性地与黄曲霉毒素B1结合并释放出氨基-碳量子点，经磁性分离后，氨基-碳量子点留在溶液中，体系溶液荧光强度随黄曲霉毒素B1浓度的增大而增强.黄曲霉毒素B1浓度在0.001～1.0 ng/mL范围与溶液荧光强度成良好线性关系，线性相关系数为0.996 4，检测限为0.3 pg/mL.该方法利用磁性分离技术，有效地消除了背景荧光影响，改善了荧光传感性能.

关键词：荧光传感器；痕量分析；黄曲霉毒素B1测定；磁性分离；核酸核酸适体；氨基-碳量子点

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Magnetic Separation Fluorescent Sensor for Highly Sensitive Detection of Aflatoxin B1

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Abstract: A fluorescent aptasensor was developed and applied to detect aflatoxin B1 based on Au@Fe_3O_4/aptamers/aminofunctioned carbon quantum dots magnetic nanocomposites which were constructed self-assembly. The selective interactions between aflatoxin B1 and the aptamer in the samples cause release of the aminofunctioned carbon quantum dots which remains in the solution after magnetic separation. A linear fluorescence signal response to aflatoxin B1 concentration is obtained over a wide aflatoxin B1 concentration range of 0.001～1.00 ng/mL with a detection limit of 0.3 pg/mL, and the correlation coefficient is 0.996 4. The performances of the fluorescent sensor are significantly improved as the background fluorescence is effectively removed by magnetic separation.

Key words: Fluorescent sensor; Trace analysis; Detection of aflatoxin B1; Magnetic separation; Aptamers; Aminofunctioned carbon quantum dots

OCIS Codes: 280.1415; 230.0040; 230.0250; 260.2510; 300.6280

0　引言

碳量子点具有优异的光学特性和很好的生物相容性，同时还具有碳源来源广、制备方法简单、成本低廉、

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Synthesis and characterization of poly(D,L-lactide-*co*-glycolide) modified by maleic anhydride and 1,4-butanediamine

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ABSTRACT
Bone tissue engineering is sought to apply strategies for bone defects healing biodegradable porous scaffolds without limitations and shortcomings. In this work, we have developed a novel maleic anhydride (MAH) and 1,4-butanediamine modified poly(lactide-co-glycolide) polymer (BMPLGA). The synthesized polymer was characterized by Fourier transform infrared spectrometry (FTIR), Nuclear magnetic resonance spectra (^{1}H NMR), gel permeation chromatography (GPC) and contact angle measurements. In addition, cell morphologies in the extracts and cell cytotoxity were also studied. The results showed that the BMPLGA was successfully obtained by introducing MAH and 1,4-butanediamine into PLGA in bulk. The introduction of anhydride and amino groups improved the hydrophilicity of PLGA. Fibroblastic cells showed normal morphologies in BMPLGA extracts, and the BMPLGA materials showed no cell cytotoxicity. The synthetic BMPLGA material may have potentials for biomedical applications due to improving hydrophilicity.

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Poly(lactide-co-glycolide); maleic anhydride; 1,4-butanediamine; modification

Introduction

Tissue engineering applies methods from materials engineering and life science to create artificial constructs for regeneration of new tissue. With tissue engineering, we can create biological substitutes to repair or replace the failing organs or tissues.[1,2] Various controlled biodegradable polymers have been very attractive for tissue engineering scaffold materials due to their controllable biodegradability.[3–5]

Poly(lactide-*co*-glycolide) (PLGA) has received increased attention from biomedical researchers in recent decades, especially for bone repair and fixation, because of its advantageous properties, including its biodegradability, biocompatibility and processability.[6–9] In addition, PLGA have been used as scaffolds for cell adhesion and expansion both *in vitro* and *in vivo* and to guide tissue regeneration. However, the surface of the PLGA is not suitable for cell attachment because of its highly hydrophobic property and lack of chemically modifiable side-chain groups, especially the acidic products of its degradation which would lead to aseptic inflammation in the

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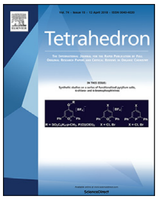

Air-stable μ^2-hydroxyl bridged cationic binuclear complexes of zirconocene perfluorooctanesulfonates: their structures, characterization and application

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ABSTRACT

Three air-stable zirconocene perfluoro-octanesulfonates were successfully synthesized by treatment of $C_8F_{17}SO_3Ag$ with $(RCp)_2ZrCl_2$ [R = H, *n*-Bu, *t*-Bu]. According to X-ray analysis, they have μ^2-hydroxyl bridged cationic binuclear structures: (*i*) $[CpZr(OH_2)_3]_2(\mu^2\text{-}OH)_2(OSO_2C_8F_{17})_4\cdot 2THF\cdot 4H_2O$ (**1a**$\cdot 2THF\cdot 4H_2O$), (*ii*) $[n\text{-}BuCpZr(OH_2)_3]_2(\mu^2\text{-}OH)_2(OSO_2C_8F_{17})_4\cdot 6H_2O$ (**2a**$\cdot 6H_2O$), and (*iii*) $[t\text{-}BuCpZr(OH_2)_3]_2(\mu^2\text{-}OH)_2(OSO_2C_8F_{17})_4\cdot 2C_3H_6O\cdot 8H_2O$ (**3a**$\cdot 2C_3H_6O\cdot 8H_2O$). The ligands of water and organic molecules in the complexes originated from the moist air and solvent during their recrystallization. These complexes were characterized with different techniques, and found to show water tolerance, air/thermal stability as well as strong Lewis acidity. Moreover, the complexes showed highly catalytic activity in various reactions of C–C bond formation. With good recyclability, they should find wide applications in organic chemistry.

1. Introduction

Cationic zirconium compounds have wide applications in organic chemistry[1] since the synthesis of Cp_2ZrCl_2 in 1961.[2] Among them, zirconocene derivatives were often used in olefin allylation and polymerization.[3] Initially, researches were mainly focussed on the preparation of various zirconocene compounds such as $Cp_2Zr(OR)Cl$,[4] $Cp_2Zr(keotone)Cl$,[5] $Cp_2Zr(CO_2Me)\text{–}Cl$,[6] $Cp_2ZrMe(THF)]^+[BPh_4]^-$,[7] and $[Cp_2ZrR]^+$ cation.[8] Subsequently, zirconocene complexes were developed to serve as efficient catalyst.[9] For example, ansa-zirconocene ester enolates were used to catalyze the polymerization of methacrylates.[10] Cationic zirconocene hydrides were also reported to posses highly catalytic ability.[11] The zirconocene-catalyzed asymmetric methylalumination of terminal alkenes in the presence of water was developed by Wipf and Ribe.[12] Scott and coworkers investigated the synthesis of zirconium salicyloxazoline complexes and the catalytic mechanism for cyclohydro-amination reactions.[13] Xi et al. reported the zirconocene-mediated intermolecular coupling of aromatic ketones and alkynes to give multiply substituted indene derivatives.[14] Miller et al. found that diynes underwent coupling reaction with $Cp_2Zr(\eta^2\text{-}Me_3SiC)_2(py)$ to give dimeric macrocycles in moderate yields.[15] It is obvious that zirconocene complexes have an important role in organometallic chemistry. However, their potential utilization as Lewis acid catalysts in organic reactions is rarely reported, plausibly due to the weak lewis acidity of Cp_2ZrCl_2 and their derivatives.[16]

To address this problem, Thewalt and Lasser[17] synthesized $Cp_2Zr(OTf)_2$ from the reaction of Cp_2ZrCl_2 with AgOTf in 1983, which was later employed by Hollis's group as an efficient Lewis acid catalyst for the construction of C–C bonds. [18] Unfortunately, the hygroscopic nature of $Cp_2Zr(OTf)_2$ limited its practical application.[18a] Therefore, it is highly desirable to lower the hygroscopic nature while enhancing the Lewis acidity. In 2006, Otera

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· 快递论文 ·

5-(4-羟基-3-硝基苯基)-10,15,20-三苯基卟啉结构高选择性苯硫酚荧光探针的研究

付秀芳[1a], 陈冠凡[1a,1b,1c*], 成奋明[1a,1b,1c], 李媛媛[1a], 时统昊[1a], 曾荣今[1a,1b,1c*]

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摘要: 基于卟啉为荧光发色团,以 2,4-二硝基苯磺酰氯为识别部分,设计并合成了一种具有较高选择性、高灵敏度的近红外苯硫酚荧光探针,其结构经^{1}H NMR, IR 和 HR-MS(ESI) 表征。并研究了其荧光性能。结果表明: 该探针可快速(90 s)、高选择性地检测苯硫酚,在 $5 \times 10^{-6} \sim 13 \times 10^{-6}$ mol·L^{-1}呈良好的线性关系,检出限为 61 nm。

关 键 词: 卟啉化合物; 合成; 荧光探针; PET; 苯硫酚

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Study of Highly Selective Thiophenol Fluorescent Probe Based on 5-(4-Hydroxyl-3-nitrophenenyl)-10,15,20-triphenyl-porphyrin

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Abstract: A kind of near infrared thiophenol fluorescent probe with high selectivity and sensitivity was synthesized, based on the excellent performance of porphyrins fluorescence chromophore, with 2,4-dinitrobenzesulfonyl chloride as recognition part. The structure was characterized by ^{1}H NMR, IR and HR-MS(ESI). The fluorescence property was investigated. The results showed that this fluorescent probe exhibited efficent, and sensitive detection for thiophenol, with a good linear relationship in the concentration range of $5 \times 10^{-6} \sim 13 \times 10^{-6}$ mol·L^{-1}, and the detection limit was 61 nm.

Keywords: porphyrin compound; synthesis; fluorescent sensor; PET; thiophenol

苯硫酚(PhSH)在室温条件下是一种带有恶臭味的透明液体,在有机合成中发挥着重要作用[1-3],被广泛应用于农药、医药及多种工业品的制备,是重要的有机合成中间体[4-5]。然而,苯硫酚对呼吸道、眼睛、皮肤及粘膜有强烈刺激性,吸入后容易发生中毒,严重者甚至可导致死亡。长

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重金属废水吸附处理的研究进展*

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摘　要　由于重金属对人、动植物和微生物具有显著的毒性，不能被微生物降解，重金属废水已成为全球性重大环境问题.本文综述了重金属废水的来源、特点、危害及常见的处理方法.与其他方法比较，吸附法具有操作简单、效率高和成本低等特点，已在重金属废水处理中获得广泛应用.本文重点分析了重金属吸附剂的研究进展与存在问题，提出了重金属吸附剂的研究重点和发展方向.

关键词　重金属，吸附法，吸附剂，研究进展.

Research progress on treatment of heavy metal wastewater by adsorption

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Abstract: The presence of heavy metals in wastewater has led to major global environmental problem, because heavy metals have significant toxicity to humans, animals and plants and microorganisms even at low levels, and cannot be degraded by microorganisms. In this paper, the origin, characteristics, hazards and common treatment methods of heavy metal wastewater are summarized. Compared with other methods, adsorption is widely applied in the treatment of heavy metals because of its simple operation, high efficiency, and low cost. The research progress and existing problems of heavy metal adsorbents are discussed emphatically. The research emphasis and development direction of heavy metal adsorbents are also put forward.

Keywords: heavy metal ions, adsorption, adsorbent, research progress.

重金属废水主要源于采矿、冶金、机械制造、化工、电子、农药、油漆、燃料和仪表等行业.铅、镉、汞、铬和类金属砷等非生命活动所必需的重金属对人、动植物和微生物具有显著的毒性，不能被微生物降解，易在生物体内特别是人体内富集而产生显著毒性效应，是一类对环境污染最严重、对人类危害最大的污染物之一[1-2].锌、铜、锰和镍等微量元素是人体必需元素，但长时间饮用被重金属污染的水，即使浓度低也可能引起心血管、肺、神经和内分泌障碍与癌症，较高量的摄入会使人的中枢神经系统受到刺激，

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特约专栏

重金属吸附材料的研究进展

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摘　要：重金属不能被微生物降解，微量即可产生显著毒性，并易在生物体内特别是人体内富集而产生累积性中毒，是一类对人类危害极大的污染物。重金属废水是对环境污染最严重，对人类危害最大的废水之一。迄今，已研发了多种重金属废水处理方法，主要有化学沉淀法、铁氧体法、离子交换法、膜分离、浮选法、电化学方法和吸附法等。其中，吸附法因其操作简单、效率较高、成本较低等优点，在重金属废水处理中获得日益广泛的应用。吸附法处理重金属废水的关键在于吸附材料的性能。用于重金属废水处理的吸附材料按来源可分为天然吸附材料、合成吸附材料和生物吸附材料。综述了重金属吸附材料的研究进展，分析了存在的问题与不足，提出了发展趋势和方向。

关键词：重金属；吸附法；天然吸附材料；合成吸附材料；生物吸附材料

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Research Progress in Adsorption Materials for Heavy Metals

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Abstract: Heavy metal is a type of hazardous pollutants to human beings because it is non-biodegradable, high toxic even at microsacle, and easily accumulate in organisms, especially in human body, ultimately leading to cumulative poisoning. Heavy metal wastewater is one of the most serious pollution to the environment and the most harmful pollution to humans. Many heavy metal wastewater treatment methods have been developed so far, including chemical precipitation, ferrite method, ion exchange, membrane separation, electrochemical method, and adsorption. Among these methods, adsorption is widely applied in the treatment of heavy metals because of its simple operation, high efficiency, and low cost. The key to heavy metal wastewater treatment by adsorption is the performance of the adsorbent. According to the sources, the adsorption materials applied in the heavy metal wastewater treatment can be divided into natural adsorption material, synthetic adsorption material and biosorption material. In this paper, the research advances in adsorption materials for heavy metal are reviewed, the existing problems and deficiencies are analyzed, and the development trend and direction are put forward.

Key words: heavy metal; adsorption method; natural adsorption material; synthetic adsorption material; biosorption material

1　前　言

重金属一般指的是密度大于 5.0 g/cm^{3}的金属，约有 45 种，一般都属于过渡元素，原子序数在 24 以上，不包括放射性元素[1]。典型的重金属有 Cu，Pb，Zn，Fe，Co，Ni，Mn，Cd，Hg，Cr，As，W，Mo，Au 和 Ag 等，其中 Mn，Cu，Zn 等是生命活动所需要的微量元素，但大部分重金属如 Hg，Pb，Cd 等并非生命活动所必需。所有重金属超过一定浓度都对人体有毒。Pb，Cd，Hg，Cr 和类金属 As 等对人、动植物和微生物具有显著的毒性，被称为“五毒”。在重金属潜在毒性分类中，Hg，Cd，Pb 被划分为第一类的第一、二、四位。职业暴露或长期低水平接触重金属都会产生疾病，影响巨大的重金属疾病有水俣病(Hg)、痛痛病(Cd)、乌脚病(As)等。

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10 – 羟基苯并喹啉激发态分子内质子转移取代基效应的理论研究

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摘　要： 运用密度泛函（DFT）和含时密度泛函（TDDFT）计算方法研究了 10 – 羟基苯并喹啉（HBQ）及其衍生物分子内质子转移过程，探究了取代基效应对质子转移过程的影响，研究发现，HBQ 及其衍生物可以形成分子内氢键，且激发态时氢键增强．基态时各分子以醇式构型稳定存在，激发态时酮式构型为优势构象．各化合物的最大吸收峰和发射峰主要是电子从 HOMO 到 LUMO 之间的跃迁引起的．基态分子内质子转移（醇式→酮式）需要跃过较高的能垒因而难以发生，而激发态时只需跃过较低能垒就很容易发生分子内质子转移，吸电子基的引入可以使该过程的能垒降低，因此吸电子基有利于激发态质子转移．取代基效应影响化合物的光谱性质．

关键词： 10 – 羟基苯并喹啉；氢键；激发态分子内质子转移；前线分子轨道；势能曲线

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Theoretical study on substituent effects in excited state intramolecular proton transfer processes of 10 – hydroxybenzo [h] quinoline

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Abstract: The intramolecular proton transfer processes of 10 – Hydroxybenzo [h] quinoline (HBQ) compounds have been studied by using DFT and TDDFT methods, and the substituent effects existed in the intramolecular proton transfer reactions have been explored. The calculated results show that HBQ compounds can form intramolecular hydrogen bonds, which can be significantly strengthened in the excited state. In the ground state, the enol form is the normal form, but the keto form is the normal form in the excited state. The maximum absorption peaks and emission peaks of each compound are mainly caused by the transition of electrons from HOMO to LUMO. Because the GSIPT (enol form→keto form) barrier is very high, the proton transfer process is hard to occur. However, in the excited state, there is only a low – barrier ESIPT curve for HBQ compounds, and the barrier decreases when the substituent is electron withdrawing, so the electron withdrawing substituent is in favor of ESIPT. Substituent effects affect the spectral properties of HBQ compounds.

Key words: HBQ; ESIPT; Hydrogen bond; Frontier molecular orbitals; Potential energy curves

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危险化学品监管信息系统的建设

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摘　要: 近年来，我国危险化学品事故频发，海关作为危险化学品进出口的重要监管部门，对口岸危险化学品安全监管负有重要职责.随着信息化建设与新科技应用在口岸建设经营中发挥着日益重要的作用，海关应加强危险化学品监管信息化建设.通过加强基础设施配置建设、加强危险化学品监管专业人才队伍建设、加强信息资源共享，建立海关监管信息化体系，实现海关监管的高效科学，保障口岸安全运营发展.本文提出的海关危险化学品信息系统建设思路，还可以为矿业工程中危险化学品的管理和监控提供有益的参考.

关键词: 危险化学品; 监管; 海关; 信息系统

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Construction of Supervision Information System for Hazardous Chemicals

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Abstract: In recent years, accidents of hazardous chemicals have occurred frequently in China. Customs, as an important regulatory department of import and export of hazardous chemicals, have important responsibilities for the supervision of hazardous chemicals at ports. Both the construction of information technology and the application of new technology in the port construction and management have played an increasingly important role, thus customs shall strengthen the construction of the supervision information system for the hazardous chemicals. To realize the efficient and scientific customs supervision and ensure the safe operation of ports, we shall strengthen the infrastructure construction, the construction of the contingent of professionals in the supervision of hazardous chemicals and the sharing of information resources, and establish the customs supervision information system. The idea of building hazardous chemicals information system proposed by this paper can provide a useful reference for managing and monitoring the hazardous chemicals in the mining industry.

Keywords: hazardous chemicals; supervision; customs; information system

危险化学品是指“具有易燃、易爆、有毒、有害及有腐蚀特性，对人员、设备、环境造成伤害或损害的化学品”[1].因而，在运输装卸和储存保管过程中需要对其进行特别保护.随着全球经济一体化进程加速，各种危险化学品在全球范围内的流动和共享同步加快，使得危险化学品的监管比以往更加复杂和困难，处理

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大豆秸秆生物炭对铅锌尾矿污染土壤的修复作用

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摘要：采用盆栽空心菜的方法，研究了大豆秸秆生物炭对铅锌尾矿污染土壤的修复作用。污染土壤中 Cu、Zn、Pb 和 Cd 含量分别为 50，400，1 119，3.4 mg/kg。结果表明：土壤无论是否受到铅锌尾矿污染，添加 3% 生物炭（*w/w*）均能显著提高土壤 pH；3% 生物炭能够抑制铅锌尾矿污染导致的土壤 pH 降低。大豆秸秆生物炭对尾矿污染土壤和未污染土壤中重金属有效态的影响不同，与未污染土壤相比，3% 生物炭的钝化作用不能抵消铅锌尾矿污染导致的重金属有效态含量的增加。铅锌尾矿污染抑制空心菜生长；施加 3% 生物炭可以消除铅锌尾矿污染对空心菜生长的抑制作用。生物炭显著降低污染土壤空心菜根部重金属含量，而对地上部分的影响，不同元素表现出不同的特点；3% 生物炭能够阻控铅锌尾矿污染土壤中 Cu、Zn、Pb 和 Cd 向空心菜地上部迁移富集。大豆秸秆生物炭对空心菜吸收重金属的影响，在铅锌尾矿污染土壤和未污染土壤上表现不同，存在元素之间的拮抗作用以及由于生物炭提高空心菜生物量所产生的稀释作用。在研究设置条件下，与未污染土壤相比，从空心菜生物量和可食部分吸收重金属含量来评价，施加 3% 大豆秸秆生物炭可以修复铅锌尾矿导致的土壤污染。

关键词：重金属；铅锌尾矿；空心菜；大豆秸秆；生物炭

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Remediation of Soil Polluted by Lead-Zinc Tailings Using Soybean Straw Biochar

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Abstract：The method of potted swamp cabbage was adopted to research the remediation effects of soybean straw biochar on soil contaminated by lead-zinc tailings. In the contaminated soil，the concentration of Cu，Zn，Pb and Cd was 50，400，1 119 and 3.4 mg/kg，respectively. The results showed that whether the soil contaminated by lead-zinc tailings or not，adding 3% biochar could significantly improve soil pH and inhibit the soil pH value reduction leaded by lead-zinc tailings pollution. Soybean straw biochar had different effects on effective state of heavy metals in soil contaminated by tailings and uncontaminated soil；compared with the uncontaminated soil，the passivation of 3% biochar could not offset the increase of bioavailability of heavy metal caused by lead-zinc tailings pollution. The pollution of lead-zinc tailings inhibited the growth of water spinach，and the application of 3% biochar could eliminate the inhibitory effect. Biochar significantly reduced heavy metal content of swamp cabbage roots in pollution soil，but in the aboveground part of swamp cabbage，biochar had different effects on different heavy metals；adding 3% biochar could prevent the migration of Cu，Zn，Pb and Cd from lead-zinc tailings contaminated soil to shoot of swamp cabbage. The effect of soybean straw biochar on the absorption of heavy metals in swamp cabbage was different in lead-zinc tailings contaminated soil and uncontaminated soil，there were interaction between elements，and dilution effect caused by biomass increase of swamp cabbage after adding biochar. Under the experimental conditions，evaluating from the biomass and heavy metal content in the edible parts of swamp cabbage，applying 3% soybean

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三氟化硼乙醚催化合成1-(氨基甲酰基甲基)-2-烃基-3,1-苯并噁嗪类化合物

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摘 要 研究了三氟化硼乙醚($BF_3 \cdot OEt_2$)催化2-(*N*-取代氨基甲酰基甲基氨基)苯甲醇与醛的反应,发展了合成取代3,1-苯并噁嗪类化合物的方法,通过该方法合成了一系列新型结构的1-(氨基甲酰基甲基)-2-烃基-3,1-苯并噁嗪类化合物。对于这类反应$BF_3 \cdot OEt_2$比三甲基氯硅烷(TMSCl)和四氯化锡($SnCl_4$)的普适性更广,它能有效催化这类反应,而后二者却不能。探讨了TMSCl和$SnCl_4$不能催化2-(*N*-取代氨基甲酰甲基氨基)苯甲醇与醛反应的原因。

关键词 氮杂环化合物;取代3,1-苯并噁嗪;合成;$BF_3 \cdot OEt_2$;催化剂

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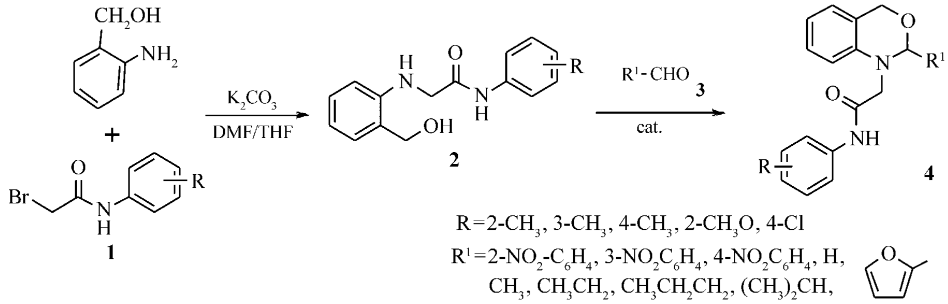
3,1-苯并噁嗪类化合物具有广泛的生物活性,如抗惊厥[1]、杀菌[2]、除草[3]、抗高血压[4]以及抗癌活性[5]等,其中有些可作为潜在的孕激素受体(PR)激动剂[6-8]、DNA结合抗肿瘤剂[9]、抗HIV-1逆转录酶抑制剂[10-12]、丝氨酸蛋白酶抑制剂[13-15]、人类白细胞弹性蛋白酶抑制剂[16]、长链脂肪酸延长酶6抑制剂[17]、神经激肽1(NK1)/神经激肽3(NK3)受体拮抗剂[18]、α-胰凝乳蛋白酶抑制剂[19]等。含3,1-苯并噁嗪-2-酮核心结构的依法韦仑是美国FDA批准的第一个抗艾滋病毒药物[10]。因此,3,1-苯并噁嗪类化合物的合成受到越来越多的关注。使用较多的方法是利用邻氨基苯甲醇与醛或酮在乙酸或对甲苯磺酸(TsOH)的催化作用下经缩合反应来制备的[7,20-22]。硅胶也可以用来催化邻氨基苯甲醇与醛的缩合反应[23]。最近,Zhang等[24]报道了一种利用高价碘催化叔胺氧化合成二氢-3,1-苯并噁嗪的新方法。Saá等[25]报道了一种基于Ru-H/Bronsted酸协同催化2-(*N*-取代氨基)苯甲醇反应合成3,1-苯并恶嗪类化合物的新途径。然而,这些方法仍存在一些不足,如2-氨基苯甲醇与羰基化合物的缩合反应局限于制备二氢-3,1-苯并噁嗪类化合物,且催化剂种类不多,而其它一些方法则往往针对某些特殊的反应物,普适性不广。因此,发展合成3,1-苯并噁嗪类化合物的新方法和催化剂仍然非常必要。其次,合成新的3,1-苯并噁嗪类化合物对药物化学和农药来说也非常重要。为了寻找新型高效杀菌剂,我们设计了一类新



Scheme 1 Synthesis of disubstituted 3,1-benzoxazines **4**

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浅析初中历史问题教学法的内涵与特点

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【摘　要】问题探究教学法，围绕“问题探究”这一中心，根据学习目标和学习者发展需要，通过创设历史情境启发学生思维，使学生在生成问题、呈现问题过程中通过自主、合作、探究等方式探讨问题、研究问题、解决问题，以提高能力和促进学习者健康成长。这一方法注重培养学生自学能力、语言表达、辨析能力、逻辑思维能力和创造能力等等，突出学生的主体地位，有利于构建师生互动、生生互动的历史课堂。同时教师也会在设计、探究和拓展问题的动态中不断成长和提高。进入21世纪，新一轮课程改革提倡问题探究教学法，问题探究教学法在初中的应用也在逐步探索的过程中前进，本文通过对问题探究教学的内涵和特点进行浅析，从而加深对问题探究教学法的认识，更好的应用到教学之中。

【关键词】历史；教学

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一、问题探究教学法的内涵

“问题”的概念含义很广，也有不同的定义。美国学者纽厄尔（Newell．A）和西蒙（Simon）对问题下的定义是：“问题是这样一种情境，个体想做一件事，但不是即刻知道对这件事所需采取的一系列行动，就构成问题”。这一定义目前受到大多数心理学家和教育学家的认同，所以问题实际上是一种等待处理的“情境”，“探究”就是求索知识的过程，通过不断的搜集资料，调查研究，检验等不同方式，追寻其答案，其本质是为了求真而质疑。

探究始于问题，问题激发探究。然而，并不是所有问题都能引发探究，人们一般把问题分为呈现型、发现型和创造型三类。呈现型问题是指由他人提出，有现成的答案，解题思路和方法，问题解决者只需通过回忆就能回答问题；发现型问题是指自己发现或由自己提出某种疑难或疑点，自己无法得出结论，需要通过一定的学习才能得出结论的问题；创造型的问题是指人类没有发现的问题，对于初中生来说，发现自己不懂得问题就是一种创造。问题探究教学就是指在教师的指导下，学生自己发现问题，但目前没有现成的答案，通过自己的学习寻找解决疑难的过程，这是一种新的教学方法，也是一种学习方法。

二、问题探究教学法的特点

1.问题性。问题是学习的动力并且贯穿学习过程的始终。问题是学习的动力，教师应在教学伊始有意识的设置疑问，使学生在头脑中产生悬念，在困惑、疑难中激发求知的愿望，引发起积极的思考，问题设置由浅入深，循序渐进，在学习的过程中不断的发现问题，问题贯穿于教学过程的始终。开放性的探究问题可以激发学生求知的兴趣和探究的欲望，这有助于培养学生的发散性思维和创造性思维，培养创造能力；以问题引导学生的思维，可以帮助学生吸收消化知识，培养思维能力，教学的最终结果不应该消灭问题，而是应该在问题初步解决的基础上发现新的问题，从而培养学生良好的学习习惯，真正转变学生的学习方式。在初中历史课中，教师设计了许多值得思考的问题，但是许多学生不愿意回答问题，或者只有少数学生起来回答，更不要提去思考问题、发现问题和提出问题。其中一个重要原因是学生缺乏学习的动力和求知的欲望，缺乏思考的兴趣。正如夸美纽斯所说：“应该用一切可能的方式把孩子们的求知与求学的欲望激发起来”。这就要求教师要精心设计教学过程，问有疑问之处，问题难度适中，而且问题应该具有启发性。

2.探究性。探究也称发现学习，是指学生在学习情景中通过观察、阅读，发现问题，搜集资料，形成解释，获得答案进行交流、检验和探究的学习。问题探究教学法具有探究性，学生对所学的问题提出质疑，教师要尽可能的给学生时间和空间，让他们进行充分的自主探究和独立思考，鼓励学生在了解基本知识的基础上另辟蹊径，提出自己独到的见解；教师应该尊重学生的多样性和差异性，能够做到因材施教，提供良好的问题探究的条件，鼓励他们积极提问，勇于探究。

3.开放性。传统教学注重教师的讲解，而问题探究教学法强调学生的主动参与、自主探究，要求教师不能过多的干预学生的探究过程，充分发挥学生的主体作用。所以问题探究教学法与传统的教学方式有很大的区别，在新课改的要求下，要转变教学观念，采用问题探究式教学法，在这种方式下，学生处于一种发现的状态，开放性可以激发学生求知的兴趣和探究的欲望，这有助于培养学生的发散性思维和创造性思维，促进学生更主动，深入的学习和探究。

4.交互性。在问题探究的过程中，讨论是一种很重要的方式，师生之间、生生之间相互交流、相互沟通、相互启发和相互补充。在这个过程中，师生之间、生生之间不仅分享彼此的思考经验和知识，还进行情感交流，从而了丰富教学内容，他们之间达到共识、共享、共建，实现了教学相长和长期发展。教师对学生的思考给予充分的鼓励和肯定，理性的引导学生树立科学的历史观，正确的人生观和价值观，让学生尽情的发挥想象力，更近距离地关注现实、体验人生、了解社会。

新一轮基础教育改革的潮流不可阻挡，我们必须适应时代的潮流，积极推进教育改革，把问题探究教学法运用到实践教学中，唤醒学生的问题意识，养成主动积极探究的习惯。但由于教师自身的专业素养，教学技能和教学视野的束缚，学生学习习惯、探究意识、探究能力的制约，问题探究教学在实际应用中存在很多问题。当下教师选择自主、探究、合作等方式来转变学生的学习方式，教学有法，但无定法，贵在得法，希望广大教师灵活应用不同的教学方式，达到真正转变学生学习的方式，体现学生的主体地位，学会学习，学会做人。

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关于制药工程专业英语课程教学现状的思考

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【摘　要】《制药工程专业英语》是学生在掌握了一定的专业知识的基础上开设的一门课程，对于培养学生在专业科技论文的阅读和写作方面的能力至关重要，且可开拓学生在制药工程领域的国际化视角和思维。笔者讲授专业英语两年多，对该课程的教学经验进行了总结思考，为专业英语课程教学效果的提高提供一定参考。

【关键词】制药工程；专业英语；教学思考

【中图分类号】G642.0　　【文献标识码】A　　【文章编号】2095－3089(2018)12－0030－02

制药工程虽然一门年轻的学科，但发展迅速，各种新的研究成果和专业信息层出不穷，而这些前沿知识均是以英语为载体进行传播的。同时该专业的人才往往从事药品研发、医药工业设计、药品生产管理和销售等工作，都离不开英文资料的收集、整理和分析。在学习完基础英语后，专业英语作为大学英语教学的重要组成部分，是培养学生具备将理论学习过渡到实际应用能力的有效途径。[1]但是，纵观我国高校开设制药工程专业英语的现状，存在诸多不合理现象，笔者仅就此进行思考和探讨，并简单提出改进的方向，以望为专业英语的教学改革提供一定的参考。

一、主客观上不重视

专业英语作为基础英语的延续和延伸，受重视的程度远不及基础英语，一方面来自高校客观上不重视，另一方面也存在学生主观上不重视。大部分的高校普遍对基础英语相当重视，甚至与学位证学历证息息相关。[2]然而专业英语仅定位为专业选修课，相当一部分高校并未开设专业英语这一课程。然而，对于该专业的学生来说，基础英语是专业英语学习的前提和基础，而专业英语的学习才是最终的目的和将为之所用的手段。某种程度上来说，直接从基础英语过渡到专业英语的跨度大，各高校并未开设将两者自然衔接的基础专业英语，造成学生学习中产生疲惫感。长此以往，专业英语学习的优势无法得以体现，反馈给高校与学生的信息是专业英语复杂且无用，更造成了高校与学生主客观上的双重懈怠。

二、教材匮乏、教学资源有限

目前，基本上大部分高校沿用的专业英语材料是吴俊达主编的《制药工程专业英语》。该书包括药物化学、生物制药、工业药剂、制药工程和前沿知识五个部分，知识的广度和深度比较适合本科生学习。然而，该教材自2000年出版以来，现今已第18次印刷，版本却仍停留在第1版。书中存在一些简单的重复、拼写等低级错误，且内容均是上个世纪的旧知识，新颖性、时效性和实践性方面已跟不上时代。尤其是第五部分前沿，随着二三十年的时间推移，已不再前沿，急需更新。另外，目前国内可供参考的制药工程专业英语教学大纲、教案、多媒体课件、教学视频等教学资源稀少[3]，教师们难以提高自身的教学水平。

三、课程设置不合理

在现阶段的高等教育中，重心偏向于通识教育，出现了重公共基础科目而轻专业教育的现象。可笑的是，历年来培养方案的修订不是由专业教师探讨决定，而是在规定总专业课学时减少的前提下，由教师们自行分配各门专业学科所应减少的课时，而这还建立在公共基础课程的学时不减反增的基础上。在这种情况下，专业英语作为专业中的选修课地位也略显尴尬。制药工程专业的词汇相当庞杂，难于掌握，且涵盖的范围较广[4]，在有限的课时内，只能尽可能让学生全面掌握词汇，理解句子，融贯全文，至于在此基础上教会学生学以致用的能力往往难以达到。当然，这其中的另一个缘由前面已经提到，就是公共英语与制药工程专业之间缺乏有效的桥梁。这中间必须要开设一门化学与药学交叉的基础专业英语，使学生具备进一步深入学习专业英语的基础。

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农药及中间体

$BF_3 \cdot OEt_2$ 催化合成1-(酰胺苄基)-2-芳基-3,1-苯并噁嗪类化合物

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摘　要：在 $BF_3 \cdot OEt_2$ 的催化作用下，*N*-苄基-2-(2-羟甲基苯基氨基）乙酰胺与硝基苯甲醛反应合成了1-酰胺基苄基-2-芳基-3,1-苯并噁嗪。研究了催化剂对反应的影响，实验结果表明 $BF_3 \cdot OEt_2$ 比TMSCl，*p*-TsOH，$ZnCl_2$ 和 $FeCl_3$ 对反应的催化活性高。

关键词：3,1-苯并噁嗪；合成；催化剂；$BF_3 \cdot OEt_2$

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$BF_3 \cdot OEt_2$-Catalyzed Synthesis of 1-Amidobenzyl-2-aryl-3,1-benzoxazines

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Abstract: Using $BF_3 \cdot OEt_2$ as catalyst, *N*-benzyl-2-(2-hydroxymethylphenylamino)acetamide was reacted with nitrobenzaldehyde to obtain 1-amidobenzyl-2-aryl-3,1-benzoxazines. The effects of catalyst on the reaction were studied and the experimental results showed that $BF_3 \cdot OEt_2$ was of better catalytic activity than catalysts including TMSCl, p-TsOH, $ZnCl_2$ and $FeCl_3$.

Key words: 3,1-benzoxazine; synthesis; catalyst; $BF_3 \cdot OEt_2$

1　前　言

近年来，3,1-苯并噁嗪由于具有广泛的生物活性而日益受到关注，其活性有杀真菌剂[1]、除草剂[2]、抗炎剂[3]、人类白细胞弹性蛋白酶抑制剂[4]，胰凝乳蛋白酶和胰弹性蛋白酶抑制剂[5]，抗高血压[6]和作为DNA结合抗肿瘤药物等[7]。3,1-苯并噁嗪类化合物的合成方法大多是利用邻氨基苯甲醇与醛或酮在乙酸或对甲苯磺酸（TsOH）等的催化作用下经缩合反应来制备[8-10]。最近，Miura等[11]报道了通过Cu/Mn促进的分子内反应将苄胺氧化重排成2-取代-4*H*-3,1-苯并恶嗪的新方法。Ren等[12]报道了通过酰化/催化Aza-Wittig反应合成3,1-苯并恶嗪类化合物的途径。然而，这些方法往往存在一定的局限性，如Ren等使用的简便方法只适用于合成4*H*-3,1-苯并恶嗪类化合物。因此，合成3,1-苯并噁嗪类化合物的新方法仍然值得探索。笔者设计了1-酰胺基苄基-2-芳基-3,1-苯并噁嗪类新化合物，但是当利用TMSCl[10]，

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