ANNUAL REPORT 2017

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
(2017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），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。

通过近8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，其中教授 27 人，副高职称人员 17 人，博士 66 人，博士生导师 4 人，硕士生导师 48 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，湖南省跨世纪学术和技术带头人 1 人，湖南省 121 人才工程入选者 3 人，湖南省普通高校学科带头人 2 人。外聘湖南科技大学“湘江学者计划”特聘教授 2 人。

8年来实验室新增科研项目 223 项，其中国家级项目 69 项（国家自科基金项目 67 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 67 项、横向项目 38 项，累计科研经费累计 8800 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 716 篇，其中被 SCI、EI、ISTP等收录的论文 457 篇，出版专著 4 部、教材 6 部。获发明专利 104 项（授权），省部级科研奖励 24 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，拥有液质联用仪、核磁共振波谱仪(500 MHz)、X-射线单晶衍射仪、扫描电镜、微量热仪、原子力显微镜、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 5100 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，8 年来共招收硕士研究生 384 人，309 人获得硕士学位。同时还与厦门大学、中南大学、湘潭大学等联合培养研究生，共招收博士生 7 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 4 个研究方向构成，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	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)	副教授/硕士导师
	袁华	1976	2007.07(博士)	副教授/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)	副教授/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)	副教授/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：曹晨忠

实验室常务副主任：唐子龙

学术秘书：于贤勇，周再春

室务会成员：曹晨忠，易平贵，唐子龙，曾荣今，易清风，曾云龙，于贤勇

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，杨新玲，易平贵，易清风，朱晓晴。

4．实验室2017年取得成绩

4.1 获得的科研项目

新增各类科研项目 30 项，其中国家自科基金课题 16 项、省部级课题 7 项、横向课题 6 项；累计经费 975.5 万元，学校配套经费 406.6 万元，合计 1382.1 万元。

序号	项目下达编号	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	21675049	基于碳点及复合物模拟酶构建食品中金黄色葡萄球菌及肠毒素的现场、快速检测方法研究	国家自然科学基金面上项目	2017.01-2020.12	65（+32）	黄昊文
2	21672058	纳米银-二芳基希夫碱超分子体系中紫外和荧光谱的取代基效应	国家自然科学基金面上项目	2017.01-2020.12	65（+32）	曹晨忠
3	21671063	反芳香 norcorrole 衍生物的合成及其在锂离子电池正极材料中的应用	国家自然科学基金面上项目	2017.01-2020.12	65（+32）	李筱芳
4	31671635	微生物-改性生物炭联合阻控玉米、大豆累积重金属锰的效应及机理研究	国家自然科学基金面上项目	2017.01-2020.12	65（+32）	冯涛
5	41673070	细粒富 Ca, Al 包体 W-L 边氧同位素和稀土元素组成特征研究	国家自然科学基金面上项目	2017.01-2020.12	71（+33.2）	戴德求
6	61674056	基于稀土掺杂介孔 ZnO 的薄膜光电传感器的关键技术研究	国家自然科学基金面上项目	2017.01-2020.12	65（+32）	胡仕刚
7	61675067	基于上转换纳米颗粒的荧光生物传感器的关键技术研究	国家自然科学基金面上项目	2017.01-2020.12	67（+32.4）	吴笑峰
8	41672350	Fe(III)改性耐锑芽孢杆菌吸附处理含锑废水的影响机制及其机理研究	国家自然科学基金面上项目	2017.01-2020.12	60（+31）	邓仁健
9	21601210	线粒体靶向磷光铱氮杂环卡宾配合物的细胞内催化活性及抗癌机制研究	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	李毅
10	51605404	基于电场调制的金属辅助刻蚀技术及其机理研究	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	张杰

11	21605047	基于改性3D石墨烯的在体电化学方法研究及其在活体分析	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	谷慧
12	51603067	甲基乙二醛高选择性比率型荧光聚合物点的设计、合成及其细胞成像	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	张培盛
13	21604021	轴对称稠环内酰胺类D-A共聚物的设计合成及光伏性能研究	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	曹佳民
14	21601058	芳香多羧酸稀土簇基配合物类线性荧光探针的合成及其识别农药残留的研究	国家自然科学基金青年项目	2017.01-2019.12	19（+16.6）	张少伟
15	21602054	大环变形对卟啉中心钴(II)离子电子结构的调控	国家自然科学基金青年项目	2017.01-2019.12	20（+17）	彭丽芬
16	51604113	三维氧化石墨烯/海藻酸钠双网络复合凝胶球处理锑矿废水的机理研究	国家自然科学基金青年项目	2017.01-2019.12	21（+17.4）	杨秀贞
17	2017JJ2095	高性能储气多孔配位聚合物的设计、合成与构-效关系研究	湖南省自然科学基金项目	2017.01-2019.12	5（+2）	汪朝旭
18	2017JJ3081	基于过渡金属催化C-O键活化的炔烃加成反应研究	湖南省自然科学基金项目	2017.01-2019.12	5（+2）	肖晶
19	2017JJ3079	$BiVO_4$-WO_3纳米复合电极光电化学法处理含Cr和Cd废水的应用基础研究	湖南省自然科学基金项目	2017.01-2019.12	5（+2）	刘灿军
20	2017JJ3080	改性3D石墨烯复合材料的设计及其在生物电化学传感器中的应用	湖南省自然科学基金项目	2017.01-2019.12	5（+2）	谷慧
21	17A066	新型咪唑并苯并噁嗪/酮类化合物的合成及其抗菌活性研究	湖南省教育厅重点项目	2017.01-2020.12	6（+2）	唐子龙
22	17A065	ESPT-FRET的耦合与调控机制及其在构建荧光识别体系中的应用	湖南省教育厅重点项目	2017.01-2020.12	6（+2）	易平贵
23	17B091	Pt-SnOx纳米簇负载氮化碳复合材料的构建及其光电催化性能研究	湖南省教育厅优秀青年项目	2017.09-2019.12	5（+2）	陈述
24	17K032	以G-quadruplex为靶的吲哚-2,3-二酮新型衍生物的合成和抗癌作用	湖南教育厅创新平台开放基金项目	2017.01-2020.12	6	谢文林
25	D117A6	3-羟基苯胺的合成工艺开发	长沙麓兴生物科技有限公司	2017.12-2018.12	60	于贤勇
26	D11804	废旧线路板有价组分的绿色、高效分离提取工艺技术开发研究	上海臻九翔环保科技有限公司	2017.12-2018.12	100	伍泽广

27	D11789	锂离子电池新型正极材料表面结构特性和稳定性研究	湖南升华科技有限公司	2017.12-2018.12	6	张杰
28	D11779	高纯硫酸锰精制技术开发	邵阳市新华材料科技有限公司	2017.12-2019.12	65	郑柏树
29	D117B5	具有杀菌活性的 3,4(6)-二取代-1,3-苯并噁嗪-2-酮类化合物	长沙麓兴生物科技有限公司	2017.08-2035.11	5	唐子龙
30	D11770	安乡县地下水资源保护区划技术支持	北京南科大蓝色科技有限公司	2017.06-2018.03	13.5	易平贵

4.2 发表论文

2015年本实验室共发表论文 85 篇，其中被SCI、EI收录 69 篇。

4.3 专利授权

2017年本实验室共获 32 项发明专利。

序号	专利名称	专利号	专利类型	授权时间	第一完成人
1	5-取代-3-[5-羟基-4-吡喃酮-2-基-甲硫基]-4-羟基苯甲氨基-1,2,4-三唑类化合物及其用途	ZL201510414130.4	发明专利	2017-12-19	谢文林
2	一种醇/Fe(III)液流燃料电池及其制造方法	ZL201510364531.3	发明专利	2017-11-14	易清风
3	新型水溶性八羟基卟啉的一步合成方法	ZL201510945703.6	发明专利	2017-11-10	刘秋华
4	一种基于乙二胺四乙酸模拟酶试剂盒的制备方法及其应用	ZL201510545849.1	发明专利	2017-11-07	黄昊文
5	一种胶原纤维/氯化银杂化材料的制备方法	ZL201510944237.X	发明专利	2017-09-26	周虎
6	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	ZL201510947214.4	发明专利	2017-09-15	唐子龙
7	一种无离子膜的紧凑型醇-空气燃料电池及其制造方法	ZL201510810885.6	发明专利	2017-09-12	易清风
8	一种 3-氰基-N-错位卟啉吡咯环氰基化合成方法	ZL201510652818.6	发明专利	2017-09-08	杨雷雷

9	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	ZL201610309985.5	发明专利	2017-08-25	谢文林
10	一种强散射强度的银纳米粒子合成及检测硫离子的方法	ZL201610170396.3	发明专利	2017-08-25	龙云飞
11	电压梯度法检测气体中痕量组分的方法	ZL201510945811.3	发明专利	2017-07-04	周再春
12	一种荧光银纳米簇同时检测溶液中的 I-和 Br-的方法及运用	ZL201510322759.2	发明专利	2017-06-16	龙云飞
13	一种卟啉型近红外硫离子荧光探针的合成方法及应用	ZL201510413666.4	发明专利	2017-06-06	曾荣今
14	一种基于羟基卟啉的高选择性近红外硫离子荧光探针的制备方法及应用	ZL201510873704.4	发明专利	2017-05-24	曾荣今
15	一种除氨氮固体絮凝剂的制备方法	ZL201510309820.3	发明专利	2017-05-17	朱国成
16	一种具有催化性能碳点的制备及基于此碳点试剂盒的应用	ZL201510545769.6	发明专利	2017-04-05	黄昊文
17	一种基于聚乙二醇的硫离子传感器及其制备方法和应用	ZL201510413193.8	发明专利	2017-04-05	陈建
18	一种液流型醇-过氧化氢燃料电池及其制造方法	ZL201510323198.1	发明专利	2017-04-05	易清风
19	负载纳米氧化铁的网状多孔重金属吸附材料及制备方法	ZL201410781433.5	发明专利	2017-04-05	刘立华
20	一种四取代吡唑并异喹啉化合物及其合成方法	ZL201510900085.3	发明专利	2017-03-22	赵云辉
21	一种具有多识别功能的荧光聚合物及其制备方法和应用	ZL201510425158.8	发明专利	2017-03-15	陈建
22	一种可视化检测水溶液中 Ag+的方法	ZL201410759571.3	发明专利	2017-03-15	龙云飞
23	一种熔盐法制备锂离子电池正极材料 LiMnBO3 的方法	ZL201510066404.5	发明专利	2017-02-22	唐安平
24	溴化 N，N-二烯丙基哌啶鎓盐阳离子单体的制备方法	ZL201410784342.7	发明专利	2017-02-22	刘立华
25	基于罗丹明衍生物的比色汞离子传感器的制备方法及应用	ZL201410776232.6	发明专利	2017-02-22	陈建
26	以羟基尼罗红为母体的硫离子荧光探针的合成方法及应用	ZL201410756555.9	发明专利	2017-02-22	曾荣今
27	一种光/温度双响应的共聚物修饰的荧光碳纳米颗粒	ZL201410774657.3	发明专利	2017-02-22	廖博

28	一种可控单分散聚苯乙烯微球接枝石墨烯的制备方法及其产品	ZL201410741428.1	发明专利	2017-02-08	欧宝立
29	一种温度/光双响应的金纳米簇杂化微凝胶及其制备方法	ZL201410775106.9	发明专利	2017-02-01	廖博
30	一种温度响应的荧光碳纳米颗粒杂化微凝胶及其制备方法	ZL201410762873.6	发明专利	2017-02-01	廖博
31	一种高效重金属离子吸附材料及其制备方法	ZL201410782577.2	发明专利	2017-01-18	刘立华
32	一种 pH 响应的共聚物修饰的荧光碳纳米颗粒	ZL201410774515.7	发明专利	2017-01-11	廖博

4.4 学科建设与人才培养

2017年本实验室共招收 48 名硕士研究生，34 名研究生获得硕士学位。

4.5 获奖情况

2017获省部级以上科研成果奖1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	PCB钻孔用覆膜铝基盖板的研制与应用	罗小阳、周虎、秦先志、唐甲林、杨柳	湖南科技大学	2017.12	中国电子学会科学技术三等奖	中国电子学会

二、学术交流情况

2017 年主办学术会议 2 次。

学术会议名称	时间	参加总人数
第十二届全国物理有机化学学术会议	2017-10-16	150
2017 年青年物理有机化学学术研讨会	2017-07-31	100

2017 年实验室人员参加国内外学术会议统计情况如下

参会人	时间	地点	会议名称	主（承）办单位
张少伟	2017-04-28	陕西西安	2017 年中西部地区无机化学化工学术研讨会	中国化学会、国家自然科学基金委员会

唐子龙	2017-07-31	湖南科技大学	2017 年青年物理有机化学学术研讨会	湖南省化学化工学会
周再春	2017-08-03	湖南科技大学	2017 青年物理有机化学学术研讨会	湖南省化学化工学会
周再春	2017-08-22	四川省绵阳	全国第三届化学键及应用学术研讨会	中国化学会
唐子龙	2017-08-27	北京	2017 年中国药物化学学术会议暨中欧药物化学研讨会	中国药学会、清华大学
万义超	2017-08-27	北京	2017 年中国药物化学学术会议暨中欧药物化学研讨会	中国药学会，清华大学
曹佳民	2017-09-20	湖南长沙	中国新能源材料与器件第一届学术会议	中国有色金属学会
黄昊文	2017-10-08	北京	第十七届北京分析测试学术报告会暨展览会	中国分析测试协会
陈建	2017-10-10	四川成都	2017 年全国高分子学术论文报告会	中国化学会高分子学科委员会
张培盛	2017-10-10	四川成都	2017 年全国高分子学术论文报告会	中国化学会高分子学科委员会
彭丽芬	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
曹晨忠	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
李筱芳	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
于贤勇	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
唐子龙	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
曹佳民	2017-10-16	湖北武汉	第十二届全国物理有机化学学术会议	中国化学会、武汉大学
周再春	2017-10-16	湖北武汉	全国第十二届物理有机化学学术会议	中国化学会、武汉大学
黄昊文	2017-10-17	上海	the 14th International Conference on Plasma Based Ion Implantation & Deposition, PBII&D 2017	中国科学院上海硅酸盐研究所

陈建	2017-10-23	北京	第二届亚洲化学传感与成像会议	中国科学院化学研究所
张培盛	2017-10-23	北京	第二届亚洲化学传感与成像会议	中国科学院化学研究所
李筱芳	2017-10-27	上海	第二届先进分子材料合成方法学及应用研讨会	上海师范大学
邓克勤	2017-11-05	广西桂林	第十三届全国化学传感器学术会议	中国仪器仪表学会分析仪器分会化学传感器专业委员会
黄昊文	2017-11-05	广西桂林	第十三届全国化学传感器学术会议	中国仪器仪表学会分析仪器分会化学传感器专业委员会
陈建	2017-11-05	广西桂林	第十三届全国化学传感器学术会议	中国仪器仪表学会分析仪器分会化学传感器专业委员会
张培盛	2017-11-05	广西桂林	第十三届全国化学传感器学术会议	中国仪器仪表学会分析仪器分会化学传感器专业委员会

2017 年来访人员学术报告情况

姓名	**职称**	**单位**	**报告题目**	**时间**
刘育	教授	南开大学	超分子可控组装及其功能	2017-05-12
韩立彪 许新华	教授 教授	日本产业技术综合研究所 新型超强酸与无机超强碱在有机合成中应用研究	The next-generation manufacturing process for organophosphorus compounds 新型超强酸与无机超强碱在有机合成中应用研究	2017-05-25
巢晖	教授	中山大学	抗肿瘤研究与金属配合物的生物识别的研究切入点	2017-06-06
李毅	博士	中山大学	线粒体靶向金属配合物的抗肿瘤诊疗研究	2017-06-16
Patrik Bjoorn	教授	比利时鲁汶大学	In situ real-time nanoplasmonic sensing for molecular processes and nanomaterials at surfaces	2017-06-18

毛宗万	教授	中山大学	金属配合物及无机有机杂化材料的抗肿瘤研究	2017-06-22
王长崴	博士	中国石油大学	非共价相互作用的理论研究	2017-09-12
万跃华	教授	浙江工业大学	化学 ESI 学科建设和如何进入前 1%	2017-11-02
洪学传	教授	武汉大学	有机小分子近红外二区荧光探针的挑战和机遇	2017-11-06
郭灿城	教授	湖南大学	烃类仿生催化氧化研究与应用	2017-11-13
赵刚	研究员	中国科学院上海有机化学研究所	氨基酸衍生的手性离子对催化反应研究	2017-11-17
沈建良	研究员	中科院温州生物材料与工程研究所	Engineering Functional Inorganic-Organic Hybrid System Advances in Anticancer Therapeutics	2017-11-21
刘宣勇	教授	中国科学院上海硅酸盐研究所	骨植入材料表面修饰及其生物学性能研究	2017-11-23
张献明	教授	山西师范大学	金属簇及其配位框架	2017-11-28
陈旭东	教授	中山大学	材料表征方法及应用	2017-12-18
袁林	教授	湖南大学	“激活型”荧光探针设计及成像应用	2017-12-19
程鹏	教授	南开大学	金属–有机框架的制备和性能调控	2017-12-22

三、开放基金评审

2017年度共评审开放基金课题 8 项，累计经费 10 万元。

2017年度理论化学与功能分子教育部重点实验室开放基金

序号	姓名	题　　目	经费/万元	申报人所在单位
1	韩新亚	基于糖尿病靶标 FBPase 底物位点新型抑制剂虚拟筛选	1.5	安徽工业大学
2	石德清	可见光催化在具有潜在生物活性的有机磷化合物合成中的应用	1.5	华中师范大学
3	唐瑞仁	烯丙位羰基化催化剂的制备及催化性能研究	2	中南大学
4	肖晶	过渡金属催化 N，N-二甲基苄胺衍生物邻位 C-H 键磷酰化的反应研究	1	湖南科技大学

5	张培盛	聚合物基比率型荧光探针在活性氧检测中的应用探讨	1	湖南科技大学
6	万义超	新型 1,3,4-恶二唑衍生物的设计、合成及抗肿瘤活性研究	1	湖南科技大学
7	于俊婷	供体-受体型双极传输环金属铱(III)配合物近红外发光材料的合成及其光电性能研究	1	湖南科技大学
8	赵云辉	钐促进的稠环氮杂化合物的合成	1	湖南科技大学

四、科普传播

2017.06.05 - 2017.06.07 (3天) 和 2017.10.10-2017.10.12 (3天) 作为实验室科普固定开放日，共接收 100 余人来实验室参观学习。2017年7月承办了湖南省教育厅主办的大学生实验技能竞赛、化工设计竞赛和大学生课外创新作品竞赛，师生共计 150 余人。本年度科普宣讲，累计参与公众 250 余人次；发表科普文章 1 篇。

五、2017年发表的主要研究论文

理论化学与功能分子教育部重点实验室2017年所发代表性论文目录

1. Xiaofang Li, Yankui Meng, Pinggui Yi, Marcin Stępień, Piotr J. Chmielewski. Pyridine-Fused Bis(Norcorrole) Through Hantzsch-Type Cyclization, Enhancement of Antiaromaticity by An Aromatic Bridge. ***Angewandte Chemie International Edition***, 2017, 56, 10810-10814.

2. Haowen Huang, Lanfang Liu, Lingyang, Zhang, Qian Zhao, Yuan Zhou, Shishan Yuan, Zilong Tang, Xuanyong Liu. Peroxidase-Like Activity of Ethylene Diamine Tetraacetic Acid and Its Application for Ultrasensitive Detection of Tumor Biomarkers and Circular Tumor Cells. ***Analytical Chemistry***, 2017, 89, 666-672.

3. Shu Chen, Yangfang Kuang, Pingping Zhang, Yuanzhi Huang, Aoli Wen, Xuyao Zeng, Ruihong Feng, Huidong Nie, Xiaochun Jiang, Yunfei Long. A Dual-Functional Spectroscopic Probe for Simultaneous Monitoring Cu^{2+} and Hg^{2+} Ions by Two Different Sensing Nature Based on Novel Fluorescent Gold Nanoclusters. ***Sensors and Actuators B-Chemical***, 2017, 253, 283-291

4. Jian Chen, Adam W. Ziegler, Baoming Zhao, Wei Wan, Alexander D. Q. Li. Chemomechanical-Force-induced Folding-Unfolding Directly Controls Distinct Fluorescence Dual-Color Switching. ***Chemical Communications***, 2017, 53, 4993-4996.
5. Haowen Huang, Yuan Zhou, Qian Zhao, Lingyang Zhang, Lanfang Liu, Xiaodong Xia, Shoujun Yi. A Highly Sensitive EDTA-Based Senor for Detection of Disease Biomarker and Drug. ***Sensors and Actuators B-Chemical,*** 2017, 249, 478-485.
6. Canjun Liu, Yahui Yang, Jie Li, Shu Chen, Wenzhang Li, Xinde Tang. An in Situ Transformation Approach for Fabrication of $BiVO_4$ /WO_3 Heterojunction Photoanode With High Photoelectrochemical Activity. ***Chemical Engineering Journal***, 2017, 326, 603-611.
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8. Jian Chen, Chonghua Zhang, Kun Lv, Hong Wang, Peisheng Zhang, Pinggui Yi, Jianhui Jiang. A Silica Nanoparticle-Based Dual-Responsive Ratiometric Probe for Visualizing Hypochlorite and Temperature with Distinct Fluorescence Signals. ***Sensors and Actuators B-Chemical***, 2017, 251, 533-541.
9. Hong Wang, Peisheng Zhang, Jian Chen, Ya Li, Maolin Yu, Yunfei Long, Pinggui Yi. Polymer Nanoparticle-Based Ratiometric Fluorescent Probe for Imaging Hg^{2+} Ions in Living Cells. ***Sensors and Actuators B-Chemical***, 2017, 242, 818-824.
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11. Keqin Deng, Chunxiang Li, Haowen Huang, Xiaofang Li. Rolling, Circle Amplification Based on Signal-Enhanced Electrochemical DNA Sensor for Ultrasensitive Transcription Factor Detection. ***Sensors and Actuators B-Chemical***, 2017, 238, 1302-1308.
12. Keqin Deng, Xinyan Liu, Chunxiang Li, Zhaohui Hou, Haowen Huang. An Electrochemical Omeprazole Sensor Based On Shortened Multi-Walled Carbon Nanotubes-Fe_3O_4 Nanoparticles and Poly(2, 6-Pyridinedicarboxylic Acid). ***Sensors and Actuators B-Chemical***, 2017, 253, 1-9.

13. Keqin Deng, Xinyan Liu, Chunxiang Li, Zhaohui Hou, Haowen Huang. A Comparative Study of Different Fe_3O_4-Functionalized Carbon-Based Nanomaterials for The Development of Electrochemical Sensors for Bisphenol A. ***Analytical Methods***, 2017, 9, 5509-5517.

14. Qingquan Liu, Gen Li, Zhe Tang, Lijuan Chen, Bo Liao, Baoli Ou, Zhihua Zhou, Hu Zhou. Design and Synthesis of Conjugated Polymers of Tunable Pore Size Distribution. ***Materials Chemistry and Physics***, 2017, 186, 11-18.

15. Demin ren, Guoqiang Kuang, Xiaolian Hu, Xiaofang Li. Synthesis of Novel Dispiro[indazole-5, 3’-Pyrrolidine-2’, 3’’-indole] Derivatives Via 1, 3-Dipolar Cycloaddition of Azomethine Ylide. ***Journal of Chemical Research***,2017, 7, 427-429.

16. Haomin Liu, Gang mei, Shu Chen, Yunfei Long. High sensitivity cysteine detection using novel fluorescent Ag nanoclusters. ***Analytical Methods,*** 2017, 9, 3249-3254.

17. Jian Chen, Weibang Zhong, Mingju xue, Hong Wang, Maolin Yu, Peisheng Zhang, Pinggui Yi. Photochromic RAFT Reagent Helps Constructing Superior Photoswitchable Fluorescent Polymer Nanoparticles for Rewritable Fluorescence Patterning and intracellular Dual-Color Imaging. ***Polymer Chemistry***, 2017, 8, 6520-6526.

18. Min Tang, Yan Yang, Shaowei Zhang, Jiafu Chen, Jian Zhang, Zaichun Zhou, Qiuhua Liu. Electron Transfer and Geometric Conversion of Co−NO Moiety in Saddled Porphyrins, Implications for Trigger Role of Tetrapyrrole Distortion. ***Inorganic Chemistry***, 2017, 57, 277-287.

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Core for Solution Processed Organic Photovoltaic Cells. ***Chemical Physics Letters***, 2017, 667, 254-259.

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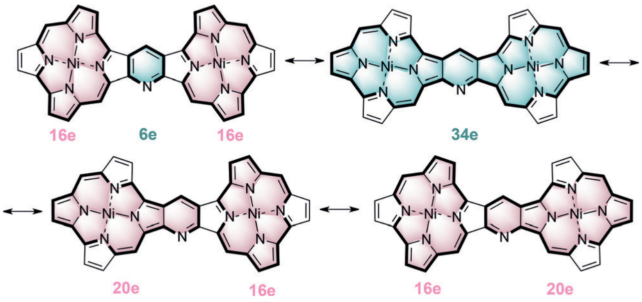
Porphyrinoids

International Edition: DOI: 10.1002/anie.201705715
German Edition: DOI: 10.1002/ange.201705715

Pyridine-Fused Bis(Norcorrole) through Hantzsch-Type Cyclization: Enhancement of Antiaromaticity by an Aromatic Bridge

Xiaofang Li, Yankui Meng, Pinggui Yi, Marcin Stępień, and Piotr J. Chmielewski**

Abstract: *A non-catalytic condensation of Ni^{II} β-aminonorcorrole with aryl aldehydes is shown to produce a family of pyrromethane dimers that undergo deaminative cyclization to yield pyridine-fused bis(norcorrole)s comprising two antiaromatic macrocycles communicating by an aromatic moiety. The new compounds were characterized by spectroscopic, structural, and electrochemical methods supported by DFT calculations, all of which revealed unexpected antiaromaticity enhancement in the fused system.*



Scheme 1. Resonance forms of pyridine-fused bis(norcorrolatonickel(II)). Antiaromatic and aromatic circuits are shaded in pink and blue, respectively.

Antiaromatic compounds have attracted considerable attention owing to the theoretical and experimental significance of these systems[1] and their potential applications in molecular electronics.[2] Compounds exhibiting paratropicity appear to be better electricity conductors when compared with their aromatic congeners.[2b,c,3,4] Effective control over the stability of antiaromatic systems as well as of their electronic and redox properties can be achieved by their fusion with aromatic substructures.[2d–f,5] Such fused systems can be obtained via direct annulation of properly activated aromatic precursors.[6] In the special case of porphyrinoid-based aromatic–antiaromatic hybrids, the nominally antiaromatic ring is either a part of the macrocyclic system[7] or acts as a bridge between two macrocycles.[6] The latter bridged systems can be seen as complementary to the numerous oligoporphyrinoids fused to aromatic junctures that have been synthesized over the last decade.[6,8,9] The properties of these systems have led us to the expectation that fusion of two antiaromatic macrocycles via an aromatic ring, may considerably perturb π conjugation in the constituent subunits.

Herein we report the first example of such an architecture, a system comprising two antiaromatic norcorrole macrocycles fused to an aromatic pyridine ring. Linear fusion of three π-electron units with alternating aromatic characteristics leads to a dichotomous conjugation pattern, described by a complex set of valence structures (Scheme 1). Along with the [16+6+16] pathway pattern, echoing the conjugation of individual subunits, the π system can be partitioned into two antiaromatic circuits [20+16], or it can be described with a single [34]annulene pathway, formally aromatic, encompassing both norcorrole moieties and the pyridine ring. The superposition of these distinct conjugation modes was expected to have a marked, yet unobvious, influence on the optical, magnetic, and redox properties of the system.

It has been shown that norcorrolatonickel(II) **1**, a readily obtainable air-stable antiaromatic 16-π-electron tetrapyrrolic porphyrinoid,[10–12] can be effectively functionalized by means of diverse substitution,[1e,13–15] addition,[16] insertion,[15,17] or dimerization[15,16] reactions. Amination of the macrocycle followed by oxidative annulation has been recently shown to be an effective way to fuse aromatic rings.[18] We thus decided to explore this reactivity for the purpose of construction of fused bis(norcorrole) systems. While direct amination of the norcorrole ring is a feasible reaction,[15] it is insufficiently selective to be used for large-scale preparation of aminonorcorrole **3**. In contrast, regioselective nitration of **1** with amyl nitrite[14] followed by an efficient reduction of NO_2 group with tin chloride, turned out to be an efficient path to the monoaminated norcorrolatonickel(II).

In the next step, we reacted **3** with variously substituted aryl aldehydes in refluxing toluene under anaerobic conditions. Such condensations yielded dipyrromethane-type products **4a**–**e** in yields of 60 to 80% (Scheme 2). Remarkably, treatment of **4a**–**e** with *p*-chloranil induced a Hantzsch-like oxidative cyclization to produce the pyridine-fused dimers **5a**–**e** quantitatively.

High-resolution mass spectrometry revealed the presence of two norcorrole units in each of the above complexes, and the observed *m*/*z* ratios were consistent with the proposed formal loss of NH_3 and H_2 molecules upon conversion of **4a**–**e** into **5a**–**e**. In the ^1H NMR of **4a**–**e**, the numbers of pyrrole as well as *meso*-mesityl signals indicated the twofold symmetry (C_s) of the dimers and their non-planarity. The norcorrole rings in **4a**–**e** retained the antiaromatic character of the

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Supporting information for this article can be found under: https://doi.org/10.1002/anie.201705715.

analytical chemistry

Article

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Peroxidase-Like Activity of Ethylene Diamine Tetraacetic Acid and Its Application for Ultrasensitive Detection of Tumor Biomarkers and Circular Tumor Cells

Haowen Huang,*[†] Lanfang Liu,[†] Lingyang Zhang,[†] Qian Zhao,[†] Yuan Zhou,[†] Shishan Yuan,[‡] Zilong Tang,[†] and Xuanyong Liu*[§]

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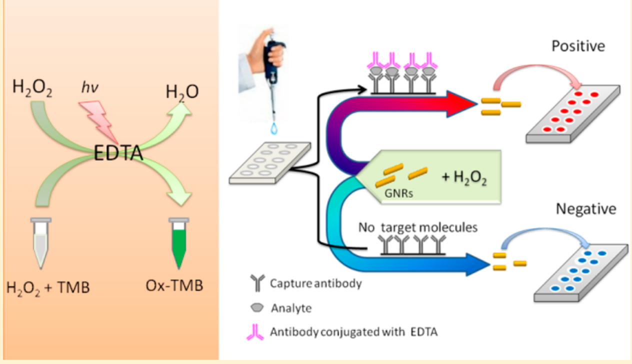
Supporting Information

ABSTRACT: Ethylene diamine tetraacetic acid (EDTA) is such a powerful chelating agent that it may form stable complexes with most metal ions, which has wide applications in industry, agriculture, environment, and pharmaceutical technology. Recently, EDTA was found to enhance the photocatalytic property of some materials. Inspired by this fact of EDTA in the photocatalytic role, we further investigated the photocatalytic property of EDTA and found much the same as that of natural horseradish peroxidase (HRP). This significant discovery of peroxidase-like property may extend the applications of conventional EDTA in life science. A novel and colorimetric sensor based on the peroxidase-like EDTA and unique gold nanorods (GNRs) was designed. Under light irradiation, EDTA may catalyze decomposition of hydrogen peroxide and in situ regulate the longitudinal plasmon wavelength (LPW) of GNRs, displaying various color solution as a read-out means. This colorimetric nanosensor has a great potential to develop into a platform to quantitatively determine analytes as long as the specific antibodies against them were available. Biomarkers of different diseases, such as breast cancer and prostate cancer, were detected with high accuracy. Moreover, combined with immunomagnetic separation of circulating tumor cells (CTCs) from blood, a visual read-out for detection of CTCs was established, which has promising applications in clinical diagnosis, environmental monitoring, and food quality control only using naked eyes.



EDTA is such a powerful chelating agent that it may form stable complexes with most metal ions. As an additive, EDTA can preserve color, flavor and prevent deterioration in the food because it deactivates the oxidation reactions catalyzed by metal ions.[1−5] EDTA is also recognized to directly inhibit the growth of bacteria in food through disruption of the integrity of bacterial membrane by its chelation with metal ions.[6,7] In addition, EDTA facilitates to generate hydroxyl radical in the Fenton reaction.[8] The specific structure of EDTA favors the activation of H_2O_2 and the generation of hydroxyl radicals. It has widely industrial applications such as pulp, paper, metal, textile production and pharmaceutical technology.[9−14] Recently, EDTA was introduced to semiconductor materials to attend the photocatalytic process, leading to significantly enhancing degradation rate of these particles to some organic dyes and organic pollutions.[15−20] There are six lone-pair electrons attributed to six atoms of EDTA not only facilitate to coordinate with most of metal ions but also serve as a hole scavenger in the photocatalytic process. Inspired by the fact of EDTA in the photocatalytic role, we further investigated the photocatalytic property of EDTA with the special structure. Interestingly, our exploration demonstrated that the conventional EDTA exhibits a fascinating photocatalytic property under light irradiation, much the same as that of natural horseradish peroxidase (HRP). The significant discovery of peroxidase-like EDTA suggests a cost-effective and easy storage mimic enzyme with small molecules will provide promising applications in life science.

Enzyme-linked immunosorbent assay (ELISA) is often extensively used in clinical diagnosis, environmental monitor-

Received: August 1, 2016
Accepted: December 5, 2016
Published: December 5, 2016

DOI: 10.1021/acs.analchem.6b02966
Anal. Chem. 2017, 89, 666−672

Sensors and Actuators B 253 (2017) 283–291

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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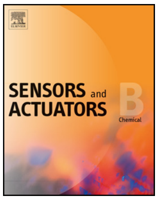

A dual-functional spectroscopic probe for simultaneous monitoring Cu^{2+} and Hg^{2+} ions by two different sensing nature based on novel fluorescent gold nanoclusters

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ARTICLE INFO

Article history:
Received 28 December 2016
Received in revised form 17 June 2017
Accepted 19 June 2017
Available online 21 June 2017

Keywords:
Gold nanoclusters
Dual-functional probe
Fluorescence quenching
Resonance light scattering (RLS)
Copper ions (Cu^{2+})
Mercury ions (Hg^{2+})

ABSTRACT

Here a dual-functional spectroscopic probe was developed based on novel gold nanoclusters (Au NCs) for highly selective and sensitive detection of heavy metal ions targeting copper ions (Cu^{2+}) and mercury ions (Hg^{2+}). Small sized Au NCs (3.9 nm) with highly orange emitting fluorescent were synthesized via an one-pot reaction by using citrate-stabilized stannous ions (Sn(II)-citrate) as reducing and capping agent. The dual spectroscopic probe was conceived in such a way to utilize both the fluorescence (FL) quenched by Cu^{2+} and resonance light scattering (RLS) enhanced by Hg^{2+}. Two different ions in the corresponding discrete spectral response appeared completely independent of each other by different mechanism. The intensity of fluorescence decreasing at 575 nm in FL spectra and the scattering increasing at 520 nm in RLS spectra, show linear relationships with Cu^{2+} and Hg^{2+} ion concentrations in the ranges of 0.5–70 and 0.25–10 $\mu mol\,L^{-1}$, respectively. The detection limits are as low as 0.38 $\mu mol\,L^{-1}$ and 0.05 $\mu mol\,L^{-1}$ for Cu^{2+} and Hg^{2+} ions, respectively. Furthermore, these Au NCs could be readily applied to Cu^{2+} and Hg^{2+} detection in environmental water samples, indicating it is promising to serve as a convenient, dual-functional, and label-free probe for related ions monitoring.

1. Introduction

The detection of various metal ions with selective and sensitive probes are of considerable interest due to their vital role in the human body even in trace amounts [1]. Among these, copper is the third most abundant essential trace element. The alternations of copper ions (Cu^{2+}) in cellular homeostasis are connected to serious neurodegenerative diseases, including Alzheimer's disease, amyotrophic lateral sclerosis (ALS), Menkes and Wilson's diseases and prion diseases [2–4]. On other hand, mercury is one of the most ubiquitous non-biodegradable toxic element that easily contaminates foods and natural environments. Mercury ions (Hg^{2+}) can be transformed into the human body through food chain due to their water solubility, and its excessive accumulation can cause Minamata disease, cognitive disorder and kidney damage [5–7]. Accordingly, many traditional techniques are readily available to quantify these two ions (Cu^{2+} and Hg^{2+}) independently by sophisticated analytical equipment [8–10]. The fluorescent, scattering and colorimetric spectrum for the monitoring have been rapidly developed in recent years, due to their simplicity in approach, fast response time and cost effectiveness [11–15]. However, challenges still exist in using single probes for simultaneous detection of Cu^{2+} and Hg^{2+} in multi-ion systems [16–21].

Recently, various spectroscopic probes including small organic molecules [22], polymer particles [23], quantum dots [24] and fluorescent metal nanoclusters (FM NCs) [25] have been developed and attracted tremendous attention for sensing metal ions. FM NCs

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http://dx.doi.org/10.1016/j.snb.2017.06.140
0925-4005/

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Cite this: *Chem. Commun.*, 2017, 53, 4993

Received 2nd March 2017,
Accepted 12th April 2017

DOI: 10.1039/c7cc01643c

rsc.li/chemcomm

Chemomechanical-force-induced folding–unfolding directly controls distinct fluorescence dual-color switching†

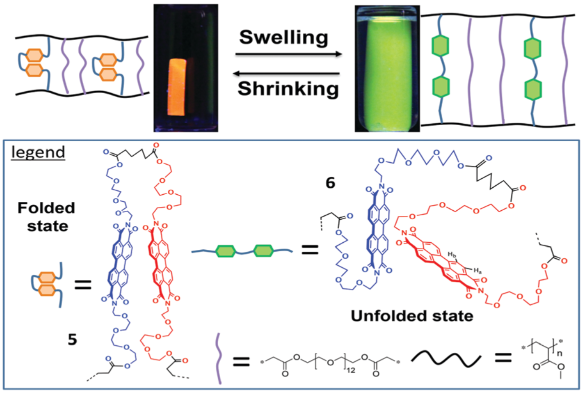
Jian Chen,[ab] Adam W. Ziegler,[b] Baoming Zhao,[b] Wei Wan[b] and Alexander D. Q. Li*[b]

Folding–unfolding imparts fluorescence dual color switching, thus a novel concept to switch fluorescence between two distinct colors while avoiding traditional bond rupturing and bond forming in photoswitching. Because folding and unfolding minimize the wear and tear on molecular structures, the new systems have excellent reversibility and fatigue resistance.

Photoswitching has created a wealth of innovative technologies for molecular imaging and chemical analyses using bond formation and bond rupture to realize switching between two states. However, photochemical reaction yields and molecular fatigue effects remain as unsolved problems. To replace photo-induced molecular switching, herein we introduce force-induced fluorescence dual-color switching. Rather than forming and rupturing bonds, force-induced dual-fluorescence-color switching is enabled by folding and unfolding of chromophoric dimer, here after defined as foldamers. The design of foldamer consists of a hinge of flexible oligo ethylene glycol chain pivoting two rigid chromophores terminated with telechelic polymerizable groups. The telechelic groups crosslink vinyl polymers, which form a gel that can change its volume as much as ≥800% of its original size upon exposure to organic solvents, thus a lipogel as a contrast to the popular hydrogels. Interestingly, the as-prepared lipogel (**5**) emits orange photoluminescence, but the gel swollen by a halogenated solvent fluoresces bright green (**6**). The presence or absence of a halogenated solvent thus either imparts or removes the chemomechanical stretching forces that induce reversible fluorescence dual-color switching *via* folding and unfolding.

Reversible molecular switching imparting distinct changes in luminescence has attracted great interest recently, because it not only enriches fundamental research, but also has potential applications in information technologies, frequency-domain imaging, data storage, super-resolution nanoscopy, dual-color correlation, and biosensors.[1] Although many external stimuli such as light,[2] electricity,[3] heat,[4] pH[5] or others,[6] can elicit molecular switching, the performance of mostly current fluorescence switchable materials is far from satisfactory because of the lack of reliable reversibility, photo-stability, fatigue resistance, and thermo-stability.[2a–6] Moreover, using chemomechanical forces to fold and unfold and hence switch between two distinct fluorescence colors has not yet been reported. To prove this novel concept, we report the first foldamer-based lipogel of crosslinked polymer that exhibits high contrast of dual-color fluorescence. Because folding and unfolding of chromophoric dimers does not degrade molecular structure in the manner of photochemical reactions, the foldamer-based lipogels have excellent reversibility and superb fatigue-resistance during fluorescence dual-color chemomechanical switching (Scheme 1).

The novel aspect of the lipogel is the introduction of the foldable chromophoric dimer. The strategy to construct such a



Scheme 1 Chemomechanical forces exerted on the lipogel cause it to expand and the expansion unfolds chromophoric foldamers, thus inducing a reversible fluorescence color switching from orange (folded state) to green (unfolded state).

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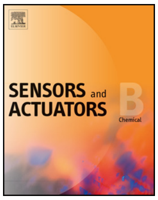
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7cc01643c

Sensors and Actuators B 249 (2017) 478–485

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



A highly sensitive EDTA-based senor for detection of disease biomarker and drug

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ARTICLE INFO

Article history:
Received 9 December 2016
Received in revised form 18 April 2017
Accepted 20 April 2017
Available online 23 April 2017

Keywords:
EDTA
Peroxidase-like
Colorimetric nanosensor
Cancer antigen 15-3
Methamphetamine

ABSTRACT

In this study, a fascinating photocatalytic property of EDTA under light irradiation was observed, much the same as that of natural horseradish peroxidase. The small EDTA molecules enable it easily attaches to amine terminal on antibody surface, an ELISA-like assay may be fabricated through combining with gold nanoparticles (AuNPs) in suspensions can exhibit various colors. The labeled EDTA on the proteins which may catalyze decomposition of hydrogen peroxide and in situ mediate the growth of hydrogen peroxide-induced formation of AuNPs, displaying various color nanoparticle dispersion as a read-out means. A straightforward plasmonic sensor was accordingly designed to enable naked-eye observation and quantitative determination of ultra-trace target analytes based on peroxidase-like EDTA. The highly sensitive assay was utilized to determine cancer antigen 15-3 (CA15-3, a breast cancer biomarker) and methamphetamine, and their limit of detection CA15-3 and methamphetamine are 7.5×10^{-15} U/mL and 2.8×10^{-20} mg/mL by naked eyes, respectively. Furthermore, practical applications for detection of CA15-3 and MA in human blood samples were also carried out. The results of detecting CA15-3 of breast cancer serum samples are close agreement with those given by hospital, implying this sensor with high accuracy. This assay has a great potential to be developed into a platform to quantitatively determine analytes as long as the specific antibodies against them were available. Its versatile features will broaden the applicability toward the ultrasensitive detection of target molecules in clinical diagnosis, environmental monitoring, and food quality control only using naked eyes.

1. Introduction

Enzyme-linked immunosorbent assay (ELISA) is often used nowadays for qualitative and quantitative determinations of target molecules, which is extensively used in clinical diagnosis, environmental monitoring and food quality control [1–5]. ELISA works on the natural enzymatic reactions which require additional introduction and conjugation of enzyme(s). However, natural enzymes have some intrinsic drawbacks, such as low stability, high costs in preparation and purification as well as catalytic activity subjected to environmental conditions. Thereby, the use of mimetic enzyme substitutes for natural enzymes has markedly increased in recent years [6–9]. Metal and semiconductor nanoparticles, especially noble metal nanoparticles, have attracted great interests [10–14]. These enzyme-like particles might also be used to fabricate ELISA-like sensors [15–18]. Whereas, some uncertain factors resulted from the size of nanoparticles are not neglectable. The size of enzyme-like nanoparticle is close to or larger than that of conjugated proteins, which maybe affect the conformation and function of the protein conjugated. Thus, small enzyme-like molecules are expected to develop more effective ELISA-like immunoassay.

Ethylene diamine tetraacetic acid (EDTA) is such a powerful chelating agent that it can form stable complexes with most metal ions [19,20]. The six lone-pair electrons attributed to six atoms of EDTA not only facilitate to coordinate with most of metal ions but also serve as hole scavenger in the photocatalytic process [21,22]. The specific structure of EDTA favors the activation of H_2O_2 to produce hydroxyl radicals. For example, EDTA facilitates to generate hydroxyl radical in the Fenton reaction [23]. Recently, EDTA was introduced to semiconductor materials to attend the photocatalytic process, leading to significantly enhancing degradation rate of these particles to some organic dyes and organic pollutions [24–26]. Our further exploration on EDTA shows it exhibits a fas-

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http://dx.doi.org/10.1016/j.snb.2017.04.122
0925-4005/

Chemical Engineering Journal 326 (2017) 603–611

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

An in situ transformation approach for fabrication of $BiVO_4/WO_3$ heterojunction photoanode with high photoelectrochemical activity

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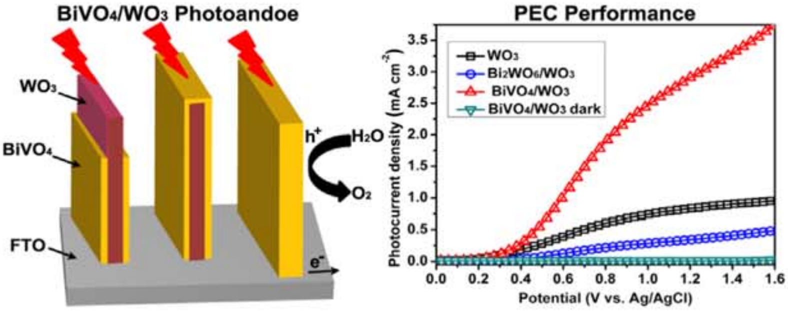
HIGHLIGHTS

- $BiVO_4/WO_3$ heterojunction film was fabricated by an in situ transformation method.
- The prepared films show a high photoelectrochemical activity.
- Our method is potential to be applied to obtain other heterojunction films.

GRAPHICAL ABSTRACT

A high quality $BiVO_4/WO_3$ heterojunction film was prepared by using an in situ transformation approach, exhibited an excellent photoelectrochemical activity.



ARTICLE INFO

Article history:
Received 22 February 2017
Received in revised form 16 May 2017
Accepted 31 May 2017
Available online 31 May 2017

Keywords:
Photoelectrochemical water splitting
Heterojunction film
Tungsten trioxide
Bismuth vanadate
Photoanode

ABSTRACT

$BiVO_4/WO_3$ heterojunction film is considered as a very promising candidate for photoelectrochemical water splitting. However, the $BiVO_4/WO_3$ films prepared by a conventional method exhibit numerous grain boundaries in the $BiVO_4$ layer and a weak contact at the heterojunction interface. In this paper, we found that $BiVO_4$ could be formed from hydrothermal Bi_2WO_6 in the weak acid solution dissolving V_2O_5 and successfully developed an in situ transformation method to prepare $BiVO_4/WO_3$ heterojunction films. The prepared $BiVO_4/WO_3$ heterojunction films were characterized in detail and showed a high quality core/shell $WO_3/BiVO_4$ structure. The formation mechanism of the $BiVO_4$ layer on the surface of WO_3 film has been put forward. In particular, the prepared $BiVO_4/WO_3$ films were used as photoanodes and showed an excellent visible light response, a good photostability and high photoelectrochemical activity. The photocurrent density for $BiVO_4/WO_3$ photoanode was up to 2.92 mA cm^{-2} at 1.81 V_{RHE} without additional electrocatalyst or doping under visible light illumination.

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http://dx.doi.org/10.1016/j.cej.2017.05.179
1385-8947/

analytical chemistry
Letter
Cite This: Anal. Chem. 2017, 89, 11173-11177
pubs.acs.org/ac

Discovery of a Turn-On Fluorescent Probe for Myeloid Cell Leukemia-1 Protein

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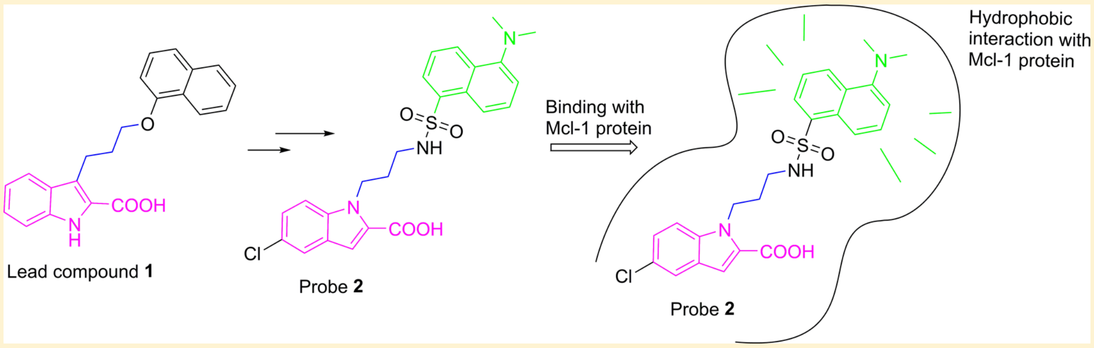
Supporting Information



ABSTRACT: The environment-sensitive probe **2** with turn-on switch for Mcl-1 protein was developed herein. After careful evaluation, this small molecule fluorescent probe revealed a selective binding affinity with Mcl-1 protein with a K_i value of 2.6 μM and can be well applied to imaging Mcl-1 protein or detecting the cellular distribution of Mcl-1 protein inhibitors. Compared with other imaging approaches, such as the immunofluorescence and fluorescent protein-based techniques, this fluorescent method is rapid, convenient, and affordable, especially since a washing procedure is no longer needed. This environment-sensitive "off-on" design strategy may present a case in point for developing small-molecule fluorescent probe of Bcl-2 family proteins.

Generally speaking, apoptosis (programmed cell death) characterized by some morphological changes is a conserved cellular process that is critical for embryonic development and tissue homeostasis.[1] Aberrant function of apoptosis contributes to numbers of human pathologies including neurodegeneration, autoimmunity, and cancer.[2−4] Therefore, modulating apoptosis by regulating the balance of the key proteins in apoptotic pathways may be an effective approach to cancer therapy.

In mitochondria-mediated (intrinsic) apoptotic pathway, B-cell lymphoma (Bcl-2) family proteins can govern apoptosis by targeting on the outer mitochondrial membrane to change its permeabilization and then releasing cytochrome c, activating caspase, and ultimately leading to cell death.[5] The Bcl-2 family is comprised of pro- and antiapoptotic proteins. For the pro-apoptotic subgroup, it can be further divided into the multidomains proteins (e.g., BAX, Bok, Bcl-Xs, and BAK) and BH3-only proteins (e.g., BIM, BID, BAD, PUMA, and NOXA). BAK and BAX are essential mediators and once activated can lead to cytochrome c released. The BH3-only proteins act upstream in response to various cellular stimuli to promote the dynamic activation of BAX and BAK. The antiapoptotic members, such as Bcl-2, Bcl-xL, Bcl-w, and Mcl-1, usually share up to four BH domains (BH1−4). They bind to their pro-apoptotic counterparts and sequester them, thus preventing the binding interactions between BAX and BAK and promoting cell survival. By abnormal overexpressing one or more of pro-survival (antiapoptotic) proteins, tumor cells can evade being removed by normal physiological processes and subsequently gain a survival advantage.[6,7]

As a prominent member of pro-survival proteins family, the overexpression of Mcl-1 protein could lead to that cancerous cells can avoid death, and the normal fate for cells may exhibit abnormal and deregulated growth.[8,9] Indeed, overexpressed Mcl-1 is a very common genetic aberration observed in many human cancer,[10,11] including breast, lung, prostate, ovarian, pancreatic, and cervical cancers as well as leukemia and

Received: March 28, 2017
Accepted: October 12, 2017
Published: October 12, 2017

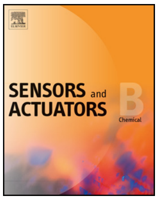
DOI: 10.1021/acs.analchem.7b01148
Anal. Chem. 2017, 89, 11173−11177

Sensors and Actuators B 251 (2017) 533–541

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb



A silica nanoparticle-based dual-responsive ratiometric probe for visualizing hypochlorite and temperature with distinct fluorescence signals

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ARTICLE INFO

Article history:
Received 15 February 2017
Received in revised form 11 May 2017
Accepted 14 May 2017
Available online 19 May 2017

Keywords:
Silica nanoparticle
Ratiometric fluorescent sensor
Dual-response
Hypochlorite
Temperature

ABSTRACT

Hypochlorite (ClO^-) and temperature play crucial roles in a wide range of physiological processes, and they are also implicated in various diseases, including cancer, inflammation of tissues and so on. Therefore, it is of great importance to explore a novel method to detect ClO^- and temperature instantly. In this study, we developed a silica nanoparticle-based dual-responsive ratiometric fluorescent sensor (DRFS), whose correlative dual emissions can response to ClO^- and temperature independently and sensitively. The detection limit of DRFS can reach to as low as 26 nM for the detection of ClO^-. And further research demonstrates that DRFS possesses excellent anti-interference feature when other possible interferents exist, and has been successfully applied in ClO^- detection in human serum and recognition of exogenous/endogenous ClO^- in HeLa cells and macrophages by fluorescence microscopic imaging. Moreover, DRFS can also be used as a ratiometric temperature sensor, and the fluorescence intensity ratio (I_{576}/I_{445}) exhibits a linear temperature response in the range from 20 to 60 °C with a change ratio as large as a factor of 5. Based on the above research, the DRFS can be used as versatile fluorescence sensor in various physiological and environmental systems.

1. Introduction

Hypochlorite (ClO^-) is widely existed in the biological and environmental systems [1–3], which plays an important role in our daily life. For example, ClO^- is usually selected as a domestic detergent or a disinfectant for dealing with drinking water, treating wastewater, swimming pool water and others [4–7]. ClO^- is also recognized as natural defense in living organisms due to its prominent antimicrobial properties [8,9] and involved with a wide variety of biological behaviors. However, excessive generation of ClO^- conceals huge health threat to human and animals [10–13]. Experimental investigation has ascertained that superabundant intake ClO^- can result in tissue damage and diseases like lung injury [14], atherosclerosis [15], arthritis [16], neuron degeneration [17] and even cancers [18,19]. On the other hand, temperature, which is one of pivotal physical parameters, plays an important role in chemical and biological systems, such as cellular behaviors and chemical equilibrium [20,21]. The normal metabolism of all cells requires a proper temperature to regulate. However, acatastatic temperature is tightly associated with various pathological cellular dysfunctions [22], which may lead to many diseases such as inflammation of tissues, and cancer [23]. Therefore, it is extremely vital to explore novel strategies to effectively and accurately detect ClO^- and temperature instantly.

Nowadays, a large number of fluorescent sensors for ClO^- or temperature with single emission have been reported [24–31]. Among these traditional sensors [32], they usually suffer from a severe limitation. For example, the change of emission peak

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http://dx.doi.org/10.1016/j.snb.2017.05.072
0925-4005/

Sensors and Actuators B 242 (2017) 818–824

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Polymer nanoparticle-based ratiometric fluorescent probe for imaging Hg^{2+} ions in living cells

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A R T I C L E   I N F O

Article history:
Received 4 June 2016
Received in revised form 30 August 2016
Accepted 28 September 2016
Available online 29 September 2016

Keyword:
Polymer nanoparticle
Ratiometric fluorescent probe
Photoinduced electron transfer (PET)
Hg^{2+}
Living cell imaging

A B S T R A C T

Mercury pollutant brings huge threat to human health and the environment because of its bioaccumulation and permanent damage. Thus, highly selective and ratiometric detection and imaging of Hg^{2+} in organisms is quite important. Herein, we report on a polymer nanoparticle-based ratiometric fluorescent probe (**NP3**) for highly selective recognition of Hg^{2+} in totally aqueous solution and imaging in living cells. This probe comprises the reference fluorescent dye (4-ethoxy-9-allyl-1,8-naphthalimide: EANI), which resides in the core of nanoparticle, and the Hg^{2+}-recognition group (fluorescein derivative: AEMH-FITC) on the surface of nanoparticle. It displays distinct dual emissions at 432 nm and 528 nm under a single-wavelength excitation. The fluorescence of the FITC moieties can be effectively quenched by Hg^{2+} due to photoinduced electron transfer (PET) mechanism, while that of the EANI remains constant, resulting in a ratiometric fluorescent detection of Hg^{2+}. The as-prepared **NP3** not only shows favorable water dispersibility, excellent long-term photostability, but also exhibits highly selective ratiometric detection of Hg^{2+} over other interfering ions (such as Cu^{2+}, Na^+, Mg^{2+}, Zn^{2+}, Co^{2+}, Mn^{2+}, K^+, Ca^{2+}, Fe^{3+}, Cd^{2+}, Ag^+, Fe^{2+}), and quite low detection limit (~75 nM). Furthermore, intracellular fluorescence imaging experiments demonstrate that **NP3** has good permeability of cell-membrane, and is able to facilitate visualization of Hg^{2+} changes in living cells.

1. Introduction

Mercury (Hg) pollutant brings a great threat to human health and the environment due to its bioaccumulation and permanent damage in central nervous and endocrine systems [1,2]. As its general ion form, Hg^{2+} can easily pass through biological membranes and lead to prenatal brain damage, serious cognitive and motion disorders, and Minamata disease [3,4]. In view of many common diseases related to Hg^{2+}, it is of significant interest to develop a simple and rapid method for Hg^{2+} detection in environment and biological samples [5].

So far, several traditional analytical techniques including atomic absorption spectroscopy (AAS) [6], inductively coupled plasma mass spectrometry (ICPMS) [7], X-ray absorption spectroscopy [8], surface enhanced Raman scattering (SERS) [9], electrochemical [10] and colorimetric [11] have been established to determine Hg^{2+} concentration, Despite of these methods (AAS, ICPMS, X-ray absorption spectroscopy, SERS and electrochemical) provide sensitive and selective analysis, they require sophisticated instrumentation and complicated sample preparation. The colorimetric method is free of the above problems and it requires minimal instrumentations, making on-site real-time sensing even easier. However, it is still not suitable for in situ detection for living biosystems (live cells and tissues). Compared to traditional analytical techniques, fluorescence spectroscopy has become a powerful tool for sensing metal ions because of its non-ionizing radiation damage, simple operation and high sensitivity and selectivity [12–58]. To date, a variety of fluorescent sensors based on a single emission signal ("turn-on" or "turn-off") for sensing Hg^{2+} have been reported [24–35]. However, one fluorescence emission signal-based measurements are readily perturbed by some limitations, such as microenvironment, sensor concentration, photobleaching and excitation intensity, etc [36–38]. By contrast, the ratiometric fluorescent sensors based on two emission signals at two distinct wavelengths can greatly alleviate the above limitations of one emission signal-based measurements [36–38].

In recent years, various ratiometric fluorescent sensors including small organic molecules [39–46], quantum dots (QDs) [47–49] and polymer particles [50–57] have been developed and attracted

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http://dx.doi.org/10.1016/j.snb.2016.09.177
0925-4005/

Sensors and Actuators B 240 (2017) 315–321

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Simultaneous determination of iodide and bromide using a novel LSPR fluorescent Ag nanocluster probe

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ARTICLE INFO

Article history:
Received 2 June 2016
Received in revised form 18 August 2016
Accepted 25 August 2016
Available online 26 August 2016

Keywords:
Ag nanoclusters
Iodide ions
Bromide ions
Carboxymethyl dextran
Fluorescenct probe

ABSTRACT

A novel fluorescent Ag nanocluster (AgNCs) stabilized with carboxymethyl dextran (CMD) was prepared by the photochemical reduction of a CMD-$[Ag(NH_3)_2]^+$ mixture under ultraviolet C (UVC) light irradiation. Interestingly, the as-prepared Ag NCs showed the maximum fluorescence near the localized surface plasmon resonance (LSPR) wavelength of AgNCs; therefore, we defined this Ag NCs as LSPR-AgNCs. This was developed as a fluorescent probe for the simultaneous determination of iodide and bromide ions (I^- and Br^-) in different media. The sensing mechanism is based on the unique reactions between I^-/Br^- and silver atom on the surface of AgNCs, which results in their fluorescence quenching. Specifically, I^- was detected selectively in the presence of Br^- in a 4.5×10^{-4} M ammonia solution. At the same time, the total concentration of Br^- and I^- was obtained by detecting the fluorescence change in Britton–Robinson buffer (pH 6.8). This medium-selective fluorescent probe provides the highly selectively detection of I^- in the range from 1.0×10^{-10} M to 1.0×10^{-7} M. Moreover, this sensing system could be applied to the detection of I^- in kelp samples.

1. Introduction

The selective and sensitive detection of iodide and bromide ions (I^- and Br^-) in aqueous media is important because they are related to environmental monitoring, medical diagnostics, and the analysis of biological samples [1–3]. I^- is a typical halide ion; also it is a critical micronutrient and utilized by the thyroid gland to biosynthesize the thyroid hormones, fundamental for neurological activity, metabolism, and thyroid function in the body [4–6]. Iodine deficiency causes several diseases such as goiter, hypothyroidism, and cretinism. However, excessive ingestion of iodine contributes to certain thyroid diseases including hyperthyroidism and hypothyroidism [6–10]. On the other hand, the toxicity of Br^- is well known; it causes bromism and bromoderma [11]. Hence, the quantitative determination of I^- and Br^- is important for human health.

Considerable researches have been recently carried out for the specific detection of I^- ion, such as ion chromatography [12,13], capillary electrophoresis [14], atomic emission spectroscopy [15,16], electrochemical analysis [17,18], inductively coupled plasma mass spectrometry (ICP-MS) [19], radiochemical neutron activation analysis [20], spectrophotometric methods[21], and fluorescent sensors [22].

Nowadays, fluorescent sensors, especially Ag nanoclusters (AgNCs), have been reported to exhibit high sensitivity and selectivity for chemical sensing. AgNCs have exceptional properties including catalytic, optical, electrical, chemical, antibacterial, and antifungal properties [23–31], significantly depending on their shape, structure, size, and surface-to-volume ratio. Therefore, AgNCs have been applied extensively. Several methods have been developed for the syntheses of fluorescent AgNCs, including chemical reduction [32], sonochemical reduction [33,34], radiolytic methods [35], and photochemical synthesis [36–38]. However, it is difficult to develop a green method for the synthesis of AgNCs in aqueous solutions under common conditions because of small interparticle distances and unavoidable van der Waals forces, resulting in their aggregation. Some methods have been developed to solve the above problem by using various stabilizers such as polymers (including PAA, PMAA, and PEI) [21,35,37], saccharides [30,32], DNA [39–41], peptide, and protein [42–44].

Here, we propose an effective and facile method for the synthesis of water-soluble fluorescent AgNCs by the reduction

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http://dx.doi.org/10.1016/j.snb.2016.08.151
0925-4005/

Sensors and Actuators B 238 (2017) 1302–1308

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Rolling circle amplification based on signal-enhanced electrochemical DNA sensor for ultrasensitive transcription factor detection

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ARTICLE INFO

Article history:
Received 26 May 2016
Received in revised form 27 August 2016
Accepted 17 September 2016
Available online 19 September 2016

Keywords:
Electrochemical DNA sensor
Transcription factor detection
Rolling circle amplification
Nuclear factor kappa B

ABSTRACT

An electrochemical biosensor based on specific protein-DNA binding and rolling circle amplification (RCA) signal enlargement was developed for transcription factor (TF) detection. The TF biosensor was constructed by three oligo-DNA probes. Probe 1 (P1) was immobilized on gold electrode. Probe 2 (P2) hybridized with P1 to form a partially complementary double-stranded DNA. The complementary part contained a TF binding sequence, while the non-complementary part of P2 integrated a RCA primer sequence. Probe 3 (P3) can displace P2 by hybridizing with P1 to produce a completely complementary double-stranded DNA. When TF protein was introduced, a stable TF-DNA complex would form and the displacement reaction mentioned above was hindered, which made the RCA possible. Finally, the electrochemical redox probe methylene blue (MB) was bound to the RCA product and offered the available detection signal. Using nuclear factor kappa B (NF-κB) p65 as a model target, the fabricated electrochemical biosensor exhibited a wide linear region and a low detection limit.

1. Introduction

Transcription factor is a class of sequence-specific DNA-binding proteins. It can regulate the rate of transcription of genetic information from DNA to messenger RNA [1], thereby control cell development, differentiation and growth through [2]. Due to its crucial role in gene transcriptional regulation, the dynamic changes in expression or DNA-binding activity of TF proteins have been confirmed to closely connect with various diseases such as cancer, autoimmunity, diabetes, cardiovascular disease, neurological disorders, developmental syndromes, and obesity [3]. Therefore, quantitative detection of TF proteins is of great importance in biomedical research and clinical diagnosis.

Some effective traditional methods have been established to detect TF, such as Western blot, electrophoretic mobility shift assay (EMSA) [4], DNase footprinting assay [5], and enzyme-linked immunosorbent assay (ELISA) [6,7]. Nevertheless, these methods suffer from some obvious flaws. For example, EMSA and DNase footprinting assay can only be used to qualitatively study the interaction of transcription factors with specific DNA sequences. Western blot is a universal solution for protein detection, but it is really costly and need sophisticated operation skills, actually it is only a semi-quantitative method. ELISA is a convenient and effective quantitative technique for the detection of proteins and other analytes. In order to get the best specificity, the expensive monoclonal antibodies are needed in ELISA kits, thus the test fee is elevated.

For the last decade, several alternative approaches have been developed for TF detection, including the fluorescence techniques [8–10], electrochemiluminescence sensor [11], electrochemical biosensor technique [12–15], colorimetric assay [16,17]. microarray chip technology [18], surface plasma resonance chip [19], and surface-enhanced resonance Raman scattering [20], Among these relatively new methods, the electrochemical biosensors display many attractive merits such as simplicity, specificity, high sensitivity [21]. They perform well in cellular extracts [22], serum [23], and other complex media. Moreover, the electrochemical biosensors are easy to be miniaturized to meet the portability requirements of on-site detection or decentralized testing [24].

The reported electrochemical biosensors for TF detection can be categorized into three major classifications. One is based upon a change of DNA-mediated electrochemistry associated with protein binding [13,15]. Another employs redox-tagged probes. In this class, the detection signal is linked to binding-induced changes in the charge transfer efficiency between an attached redox-tag and the electrode surface [12,25,26]. Signal enlargement strategy is adopted in the third class, for instance, Au nanoparticle-catalyzed silver enhancement for TF detection [27].

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http://dx.doi.org/10.1016/j.snb.2016.09.107

Sensors and Actuators B 253 (2017) 1–9

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

An electrochemical omeprazole sensor based on shortened multi-walled carbon nanotubes-Fe_3O_4 nanoparticles and poly(2,6-pyridinedicarboxylic acid)

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ARTICLE INFO

Article history:
Received 14 February 2017
Received in revised form 5 June 2017
Accepted 17 June 2017
Available online 19 June 2017

Keywords:
Omeprazole
Shortened multi-walled carbon nanotube
Fe_3O_4 nanoparticles
Poly (2,6-pyridinedicarboxylic acid)

ABSTRACT

Three types of shortened and acidified multi-walled carbon nanotubes (S-MWCNTs) were synthesized by ultrasonication of the raw long carbon nanotubes in H_2SO_4/HNO_3 mixed acids. A comparative electrochemical investigation was performed in 5 μM omeprazole (OMZ) solution. It demonstrated that S-MWCNTs with specific length and acidity showed higher electrocatalysis to the oxidation of OMZ. Magnetite nanoparticles Fe_3O_4 were hybridized with S-MWCNTs to form a nanohybrid (S-MWCNTs-Fe_3O_4) through a simple, effective and reproducible chemical co-precipitation method. The nanohybrid was characterized by transmission electron microscope (TEM), X-ray diffractometer (XRD), thermogravimetric analyses (TGA), and field emission scanning electron microscopy (FESEM). The electrochemical response characteristic of S-MWCNTs-Fe_3O_4 modified GCE toward OMZ was investigated by cyclic voltammetry. It showed that the nanohybrid enhanced the electrocatalytic oxidation to OMZ. Linear sweep voltametry (LSV) was applied to determine low concentrations of OMZ on S-MWCNTs-Fe_3O_4/poly (2,6-pyridinedicarboxylic acid) modified electrode. A linear relationship was found between peak currents ($i_{p,a}$) and the concentration of OMZ within 0.05–9.0 μM with an estimated detection limit of 15 nM.

1. Introduction

Omeprazole (OMZ), that is 5-methoxy-2-[[(4-methoxy-3,5-dimetyl-2-pyridinyl) methyl] sulfinyl]-1*H*-benzimidazole, is a benzimidazole derivative. As a gastric H^+-, K^+- ATPase inhibitor, it can effectively control the gastric acid production and thus is applied for the treatment of duodenal ulcer, gastroesophageal reflux disease (GERD), Zollinger-Ellison syndrome ulcers, and erosive esophagitis. Furthermore, it is used to combine with antibiotics for killing helicobacter pylori [1–3]. So far, a few techniques, including high performance liquid chromatography (HPLC) [4,5], spectrophotometry [6–8], electrochemical methods [9–11], electrochemiluminescence [12], capillary electrophoresis [13], and capillary chromatography [14], have been used for the determination of OMZ in pharmaceutical preparations and biological samples. Among these techniques, electrochemical methods are suitable for quantitative determination of OMZ. They possess the advantages of easy operation, fastness, low cost, sensitivity, and reliability [10,11]. Despite some efforts have launched for the detection of OMZ in the area of analytical chemistry, it is still a challenge to develop some novel materials to further achieve sensitive and facile detection.

Carbon nanotubes (CNTs) have been widely employed in the construction of electrochemical sensors to improve their analytical performance owing to their many unique structural and desirable electronic properties, such as large surface area, good biocompatibility, ease of preparation as well as the ability to form a three-dimensional conducting matrix [15,16]. Commonly, although long multi-walled carbon nanotubes (MWCNTs) have both ends, the surface utilization is still mainly limited to their outer surface [17,18]. Their inner surface is less utilized because of the poor ion penetrability into the inner pores to access the inner surface [19]. Furthermore, researchers consider the catalysis of MWCNTs is influenced by defects [20]. It is believed that defects can not only change the physical properties but also tune

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http://dx.doi.org/10.1016/j.snb.2017.06.117
0925-4005/

Analytical Methods

PAPER

Cite this: *Anal. Methods*, 2017, **9**, 5509

A comparative study of different Fe_3O_4-functionalized carbon-based nanomaterials for the development of electrochemical sensors for bisphenol A†

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No work studied and compared Fe_3O_4-functionalized carbon-based nanomaterials. Also, no work investigated their application for detecting bisphenol A (BPA), an important organic chemical raw material, which had been proved to cause malformation, cancers, sexual precocity, and neural and behavioral changes in infants and children. In this work, Fe_3O_4 magnetite nanoparticles were stably anchored on carbon materials to synthesize three types of nanohybrids, *i.e.* hybrids of graphene oxide with Fe_3O_4 (GO–Fe_3O_4), carbon nanotubes with Fe_3O_4 (CNTs–Fe_3O_4), and graphene oxide and carbon nanotubes with Fe_3O_4 (GO–CNTs–Fe_3O_4). These nanohybrids were characterized using a transmission electron microscope (TEM), X-ray diffractometer (XRD), and Fourier transform infrared spectrometer (FT-IR). GO–Fe_3O_4, CNTs–Fe_3O_4, and GO–CNTs–Fe_3O_4 were immobilized on the surface of a GCE using electro-poly(glutamic acid). The electrochemical response characteristic of bisphenol A (BPA) on different modified electrodes was investigated by cyclic voltammetry. It showed that these three types of nanohybrids greatly enhanced the anodic peak current of BPA. Then, these hybrids were applied to determine BPA by differential pulse voltammetry. Their determination performance was compared with each other. Among them, the GO–CNTs–Fe_3O_4 modified electrode exhibited wider linear ranges of 0.003–0.2 and 0.2–30.0 μmol L^{-1} with a lower estimated detection limit of 1.0 nmol L^{-1}.

Received 26th June 2017
Accepted 21st August 2017

DOI: 10.1039/c7ay01573a

rsc.li/methods

1. Introduction

Bisphenol A (BPA), an important organic chemical raw material, is mainly used for the preparation of epoxy resin, polycarbonate, polysulfone resin, polyphenylene oxide resin and other polymer materials. It is also used as a plasticizer, flame retardant, antioxidant, and heat stabilizer, and in paints and other fine chemicals. From mineral water bottles, medical devices to food packages, BPA exists everywhere. Due to the leakage or hydrolysates from polycarbonate plastics, epoxy resins, or PVC products, BPA will be released and migrates to the environment or food. For the reason that BPA has been proved to cause malformation, cancers, sexual precocity, neural and behavioral changes in infants and children,[1] it is therefore very important to establish a reliable method for highly effective determination and monitoring of the trace amounts of BPA.

Various analytical techniques, including high performance liquid chromatography,[2,3] gas chromatography-mass spectrometry,[4] chemiluminescence immunoassay,[5,6] enzyme-linked immunosorbent assay,[7] and electrochemical detection,[8–10] have been used for the determination of BPA. Among these techniques, electrochemical methods are suitable for the determination of BPA. They possess the advantages of easy operation, low cost, rapidity, sensitivity, and reliability.[11,12] Despite some efforts being made for BPA detection in the area of analytical chemistry, it is still a challenge to develop some novel materials to further improve the detection performance.

Iron oxide (Fe_3O_4) nanoparticles, a half-metallic metal oxide with an inverse spinel structure,[13] may improve electrode conductivity and facilitate electron transfer.[14–17] However, pure Fe_3O_4 nanoparticles tend to aggregate and oxidize on account of their large ratio of surface area to volume and high chemical activities, resulting in their poor dispersibility and limited application.[18] Thus, hybridization or surface modification is significant to prevent Fe_3O_4 nanoparticles from aggregation and improve their stability.[19] Also, hybrids may exhibit a synergistic effect and enhance the performance of constructed sensors.[15–17]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ay01573a

Materials Chemistry and Physics 186 (2017) 11–18

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Design and synthesis of conjugated polymers of tunable pore size distribution

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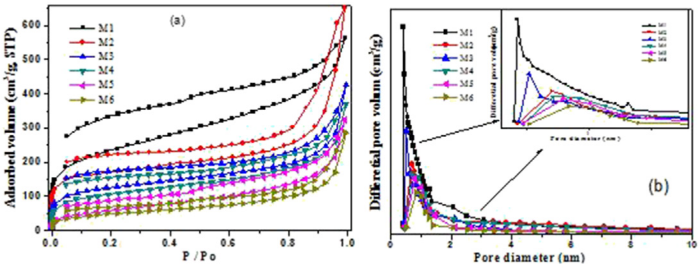
HIGHLIGHTS

- Microporous conjugated polymers were prepared by Yamamoto coupling.
- Pore structure of microporous polymers could be tuned by chaining monomers.
- H_2 and CO_2 storage properties of microporous polymers were investigated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 December 2015
Received in revised form
27 May 2016
Accepted 2 June 2016
Available online 9 November 2016

Keywords:
Microporous materials
Polymers
Microstructure
Chemical synthesis

ABSTRACT

Conjugated microporous polymers of tunable pore size distribution were synthesized by Yamamoto homo-coupling or co-coupling of 1,3,5-tris(4-bromophenyl)benzene with five chaining monomers of different strut length, respectively. Conjugated microporous polymers with apparent BET surface area in the range from 172 to 820 $m^2\ g^{-1}$ were prepared. The materials were found to have excellent microporosity, which could be accurately tuned by changing the strut length of chaining monomers. It was revealed that copolymerization of the core monomer and several chaining monomers with different strut length was an effective strategy to fine-tuning properties of the materials. Moreover, the incorporation of "flexible" double bonds into the chaining monomers could further promote this strategy. H_2 and CO_2 adsorption capacity of conjugated microporous polymers were also systematically investigated.

1. Introduction

Porous organic polymers (POPs) have drawn considerable attentions owing to their potential applications in the fields such as in catalysis, sensing, optoelectronics, light harvesting as well as gas storage and separation [1–10]. According to the IUPAC classification [11], microporous polymers are defined as polymeric materials with pore diameter smaller than 2 nm. Up to now, various porous polymer materials such as covalent organic frameworks (COFs) [12,13], covalent trianzine frameworks (CTFs) [14,15], conjugated microporous polymer networks (CMPs) [16,17], porous aromatic frameworks (PAFs) [18,19], polymers of intrinsic microporosity (PIMs) [20,21], porous polymer networks (PPNs) [22] and hypercrosslinked porous polymers (HCPs) [23,24] were successfully prepared in the past decade years. Yaghi and co-workers [12] successfully synthesized COF-103 with BET surface area of 4210 m^2/g. Based on tetraphenylmethane subunits, Zhu group [22] designed and prepared microporous polymers with BET surface areas of

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http://dx.doi.org/10.1016/j.matchemphys.2016.06.004

Synthesis of novel dispiro[indazole-5,3'-pyrrolidine-2',3''-indole] derivatives *via* 1,3-dipolar cycloaddition of azomethine ylide

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The 1,3-dipolar cycloaddition of azomethine ylide, generated *in situ* from isatin and sarcosine, to 5-arylmethylidene-1-phenyl-6,7-dihydro-1*H*-indazol-4(5*H*)-ones afforded novel 1'-methyl-4'-aryl-1-phenyl-6,7-dihydrodispiro[indazole-5,3'-pyrrolidine-2',3''-indole]-2'',4(1*H*,1''*H*)-diones in moderate yields. The structures of all the products were characterised thoroughly by NMR, IR, HRMS, together with X-ray crystallographic analysis.

Keywords: 1,3-dipolar cycloaddition, azomethine ylide, isatin, sarcosine

The 1,3-dipolar cycloaddition reaction has attracted considerable attention from many synthetic organic chemists as it is considered one of the most powerful processes for the construction of five-membered pyrrolidine heterocycles,[1] which have different biological activities and find medical uses in the treatment of several serious diseases (*e.g.* (−)-codonopsinine, tosufloxacin, (*R*)-crispine A (Fig. 1)).[2–6] A series of natural products containing the pyrrolidine structural unit possess significant potential for use in medicine and agriculture.[7] Isatin has been used as a precursor for an azomethine ylide cycloaddition followed by reaction with sarcosine.[8]

Recently, much attention has been given to the synthesis of spiro compounds due to their important antibacterial activity.[9] Numerous novel spiro pyrrolidine heterocycles have been synthesised, and the majority of them have been reported to exhibit effective *in vitro* antibiotic activity.[10]

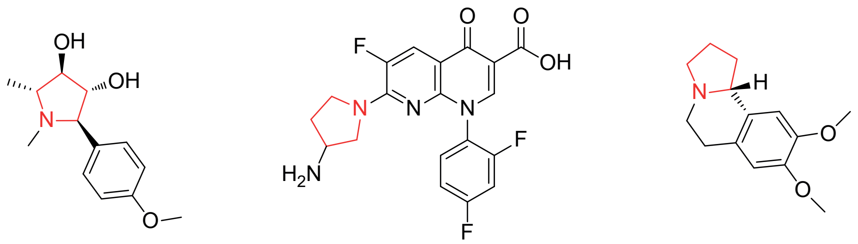
In this study we report the results of synthesising further novel heterocyclic systems (Scheme 1).

Results and discussion

The 1,3-dipolar cycloaddition reaction of 5-arylmethylidene-1-phenyl-6,7-dihydro-1*H*-indazol-4(5*H*)-ones **1** to the azomethine ylide generated *in situ* from isatin and sarcosine yields 4'-aryl-1'-methyl-1-phenyl-6,7-dihydrodispiro[indazole-5,3'-pyrrolidine-2',3''-indole]-2'',4(1*H*,1''*H*)-diones **2**.

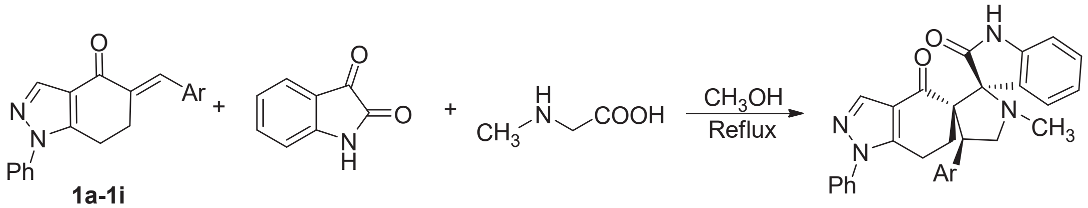
The structures of all compounds **2a–i** were established by spectroscopic techniques (NMR, IR) and HRMS. The IR spectrum of **2f** displayed $\nu_{C=O}$ at 1723.9 and 1702.8 cm^{-1}. The ^{1}H NMR spectrum of **2f** revealed multiplet signals at δ 1.34–1.41 (H6), at δ 2.38–2.43 (H6, H7), at δ 2.75–2.82 (H7) and singlets at δ 2.13 for NMe (H1'), at δ 2.44 for SMe, at δ 7.94 resulting from N=CH (H3), two triplets at δ 3.51 (*J* =*J* = 8.5) and 3.97 (*J* =*J* = 9.5) assignable to the methylene protons (H5') and one triplet at δ 4.98 (*J* =*J* = 8.5) corresponding to the CH (H4') proton in the pyrrolidine ring. The presence of signals at δ 6.78–7.44 ppm corresponded to the aromatic protons. The singlet at δ 8.70 is in accord with the NH proton in the indole ring.

The ^{13}C NMR spectrum of the product **2f** exhibited the presence of an N-CH_3 carbon (C1') at δ 34.75 and carbonyl carbons at δ 178.29 (C2'') and 193.43 (C4). The signals at δ 45.92 and 57.57 are assignable to the CH (C4') and CH_2 (C5') carbon atoms, respectively, which exist in the pyrrolidine ring (based on heteronuclear multiple quantum coherence (HMQC)). The signals at δ 60.91 and 76.64 represent the spiro carbon atoms



(-)-Codonopsinine Tosufloxacin (*R*)-Crispine A

Fig. 1 Some biologically active compounds bearing a pyrrolidine ring.



1a-1i

2a-2i

Ar: a, C_6H_5; b, 2-ClC_6H_4; c, 2,4-$Cl_2C_6H_3$; d, 4-$CH_3OC_6H_4$; e, 4-FC_6H_4;
f, 4-$CH_3SC_6H_4$; g, 4-$CH_3C_6H_4$; h, 3,4,5-$(OCH_3)_3C_6H_2$; i, 4-ClC_6H_4

Scheme 1 Synthesis of dispiro derivatives.

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Analytical Methods

PAPER

View Article Online
View Journal | View Issue

Cite this: *Anal. Methods*, 2017, **9**, 3249

High sensitivity cysteine detection using novel fluorescent Ag nanoclusters†

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Received 5th February 2017
Accepted 30th April 2017

DOI: 10.1039/c7ay00310b

rsc.li/methods

Fluorescent Ag nanoclusters (AgNCs) stabilized by carboxymethyl dextran (CMD) were prepared by the photochemical reduction of a mixture of CMD and $[Ag(NH_3)_2]^+$ under ultraviolet C (UVC) light irradiation. Further study showed that the as-prepared AgNCs had the maximum fluorescence emission peak near the located surface plasmon resonance (LSPR) wavelength of AgNCs. Thus, these AgNCs are defined as LSPR-AgNCs. The maximum excitation wavelength of AgNCs is 250 nm and the maximum emission wavelength is 425 nm. In solution, the fluorescence of AgNCs could be quenched in the presence of cysteine. Based on this phenomenon, AgNCs were developed as a fluorescent probe for the detection of cysteine. The fluorescence intensity quenching value (ΔI) has a linear relationship with the concentration of cysteine, which follows a linear equation of $\Delta I = 4.25 \times 10^9 c + 36.84$ with the correlation coefficient of $r = 0.9967$ in the linear range of 5.0×10^{-10} to 1.0×10^{-7} mol L^{-1}. The detection limit ($3\sigma/k$) was 3.2×10^{-10} mol L^{-1}. It has been applied to the cysteine concentration detection with the accepted results in the synthesized samples and compound amino acids injection sample.

1. Introduction

Cysteine (Cys) is a natural, thiol-containing amino acid, which is one of the most critical components among the bio-relevant proteins.[1] Owing to the high reactivity of the sulfhydryl group, Cys plays a critical role in many biological functions, *i.e.*, providing a disulfide for the intramolecular cross-linking of proteins through disulfide bonds to support their secondary structures and functions. Cys also maintains the intracellular redox activity, xenobiotic metabolism, intracellular signal transduction and gene regulation.[2] Abnormal levels of Cys are closely associated with certain diseases.[3] For instance, Cys deficiency is involved in numerous syndromes, including slowed growth, hair depigmentation, edema, lethargy, liver damage, muscle and fat loss, skin lesions, and weakness.[4–6] Therefore, the measurement of Cys becomes crucial and has attracted considerable interest in recent years. Several analytical techniques, such as high-performance liquid chromatography (HPLC),[7,8] capillary electrophoresis (CE),[9] electrochemical assay,[10,11] UV/vis spectroscopy,[12,13] mass spectrometry,[14] and colorimetric methods,[5,15–18] have been employed to detect Cys. However, most of these methods have some limitations, such as unsuitable rapid detection or poor sensitivity.

Recently, fluorescent probes, especially Ag nanoclusters (AgNCs), which are different from silver nanoparticles (AgNPs), have drawn more and more attention due to their high sensitivity, low detection limit and low cost.[19,20] The major difference between AgNCs and AgNPs is that the particle size of AgNPs is bigger than that of AgNCs.[21] Owing to the especial shape, structure, and size, AgNCs have various properties, including catalytic, optical, electrical, chemical, antibacterial and antifungal properties.[22–29] A number of reported methods, such as chemical reduction,[30] sonochemical reduction,[31,32] light irradiation methods,[33] photochemical synthesis, *etc.*[34] have been used to synthesize AgNCs. However, it is difficult to develop a green method for the synthesis of AgNCs in aqueous solutions under common conditions because of small interparticle distances and unavoidable van der Waals force, resulting in their aggregation easily.[35] This aggregation could be avoided by using stabilizers such as polymers,[33] saccharides,[29,30] DNA,[36,37] peptides and proteins.[38] In particular, PMAA has been proved to serve as a stabilizer to synthesize red emission fluorescent AgNCs under the irradiation of UV light (365 nm).[39–41]

In this paper, an effective and facile method was presented to synthesize the water-soluble fluorescent AgNCs using carboxymethyl dextran (CMD) as the reducing and stabilizing agent.[42] $[Ag(NH_3)_2]^+$ could be reduced to form AgNCs through ultraviolet C (UVC, 110 W cm^{-2}) light irradiation. The as prepared AgNCs showed the maximum fluorescence emission at the localized surface plasmon resonance (LSPR) wavelength,[35] which is distinct from the reported fluorescence properties of AgNCs. Thus, these AgNCs were defined as LSPR-AgNCs. The LSPR-AgNCs were aggregated after the addition of Cys, which resulted

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c7ay00310b

Polymer Chemistry

PAPER

View Article Online
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Cite this: *Polym. Chem.*, 2017, **8**, 6520

Photochromic RAFT reagent helps construct superior photoswitchable fluorescent polymer nanoparticles for rewritable fluorescence patterning and intracellular dual-color imaging†

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Received 21st August 2017,
Accepted 2nd October 2017

DOI: 10.1039/c7py01408b

rsc.li/polymers

Superior photoswitchable fluorescent polymer nanoparticles (PFPNs) are highly desirable for photo-rewritable data storage and ultrahigh-resolution bioimaging. Herein, 2-(3′,3′-dimethyl-6-nitrospiro[chromene-2,2′-indolin]-1′-yl)ethyl 2-(((dodecylthio)-carbonothioyl)thio)-2-methylpropanoate (SPTTC), a novel photochromic spiropyran-based reversible addition–fragmentation chain transfer (RAFT) reagent, and 5-dimethylaminonaphthalene-*N*-allyl-1-sulfonamide (DNS), the energy-level matched green fluorescent dye, were firstly synthesized. Then, they are used as donor and acceptor of the designed fluorescence resonance energy transfer (FRET) system to help fabricate superior dual-color PFPNs *via* a simple one-pot RAFT miniemulsion method. Thanks to its multiple merits such as the photochromic property, improved miscibility, and the ability to control polymerization rate, not only did the designed SPTTC provide the PFPNs with superior photoswitchable fluorescence properties such as high energy transfer efficiency (up to 91%), high dual-color contrast (green and red), rapid photoresponsiveness (2–4 min) and outstanding photoreversibility upon irradiation with UV and visible light, but it also endowed PFPNs with controllable molecular weight and narrow polydispersity index (PDI), excellent cell membrane permeability and long-term fluorescence stability. Moreover, the as-prepared PFPNs were successfully used for rewritable fluorescence patterning and intracellular dual-color imaging due to its prominent properties.

Introduction

Photoswitchable fluorescent polymer nanoparticles (PFPNs) have huge potential for applications in reversible optical switching, photo-rewritable data storage and ultrahigh-resolution bioimaging.[1–6] Generally, PFPNs are generated by integrating an energy-matched fluorescent dye with a corresponding photochromic compound, such as spiropyran,[3] diarylethene,[4] spirooxazine,[5] azobenzene[6] *etc.* into the polymer nanoparticles. In particular, the fluorescence of the as-prepared nanoparticles can be optically switched "on" and "off" by specific illumination wavelengths,[1–6] which is ascribed to the switchable fluorescence resonance energy transfer (FRET) process between the fluorescent dye (donor) and the corresponding photochromic compound (acceptor).[1–6]

To date, multifarious techniques such as self-assembly method,[7,8] reprecipitation,[4–6,9,10] and microemulsion[3,11–14] or miniemulsion polymerization,[15–18] *etc.*, have been utilized to fabricate various PFPNs. Among the synthetic strategies, miniemulsion polymerization has attracted greater attention due to its multiple advantages, such as facile preparation process, controllable ratio of incorporated fluorescence dyes and photochromic compounds, as well as endowing nanoparticles with excellent water dispersibility and colloidal stability.[15–18] Despite the great efforts, the polymer molecular weight and the polydispersity index (PDI) of the formed PFPNs cannot be effectively controlled by using the traditional miniemulsion polymerization method, which may lead to an undesirable result.[15–18,19] In order to eliminate the effect of uncontrollable polymerization rate, the more economical and environmentally friendly RAFT polymerization was adopted to work with miniemulsion polymerization in constructing novel PFPNs.

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra, absorption spectrum, fluorescence spectra, fluorescence lifetime, cell viability. See DOI: 10.1039/c7py01408b

Inorganic Chemistry
Article
Cite This: Inorg. Chem. 2018, 57, 277−287
pubs.acs.org/IC

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

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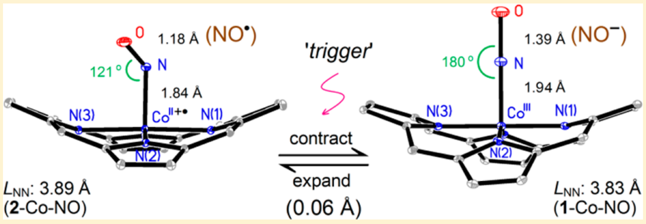
Supporting Information

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 (Co^{II})$^{+•}$−NO$^•$ to Co^{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$^•$ 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^{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^{III},[17−19] Co^{II},[20,21] Cu^{II},[22] and Zn^{II}.[23] For materials containing Fe^{III} and Co^{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.

Received: September 25, 2017
Published: December 19, 2017

DOI: 10.1021/acs.inorgchem.7b02455
Inorg. Chem. 2018, 57, 277−287

Inorganic Chemistry Communications 86 (2017) 87–89

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Short communication

A 3D supramolecular network constructed from {Ni_9} cluster and benzotriazole

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ARTICLE INFO

Article history:
Received 21 August 2017
Received in revised form 23 September 2017
Accepted 26 September 2017
Available online 28 September 2017

Keywords:
Cluster
Crystal structure
Benzotriazole
Magnetism
Nickel

ABSTRACT

The solvothermal reaction of Hbta (Hbta = benzotriazole) and $Ni(NO_3)_2 \cdot 6H_2O$ yielded a blue block crystal, $[Ni_9(bta)_{12}(NO_3)_6(DMA)_6] \cdot 3DMA$ (**1**), (DMA = *N,N*-dimethylacetamide), which has been characterized by various measurements including elemental analysis, thermogravimetric (TG) analysis, infrared (IR) spectrum, powder X-ray diffraction (PXRD), and X-ray single-crystal diffraction. In compound **1**, three crystallographic independent Ni^{2+} ions are connected by two types of Hbta ligands to generate a centrosymmetric nine-nuclear {Ni_9} cluster, which could further form a 3D supramolecular network through intra- and intermolecular hydrogen bonds. The TG curve of **1** exhibits a weight loss between 25 and 330 °C, being in accordance with the release of DMA. Furthermore, the variable-temperature magnetic susceptibility of **1** has studied, and the results indicate that antiferromagnetic interactions exist among Ni^{2+} ions.

Coordination compounds could be systematically designed and synthesized by the assembly of metal ions/clusters and organic ligands, have attracted increasing interests in different areas such as crystal engineering and material science. Especially in the past two decades, with the rapid development of X-ray single-crystal technology, numerous of coordination compounds with different dimensions have been well prepared to present variety of impressive structures and significant potentials in catalysis, magnetism, molecular recognition, gas storage and separation [1–8]. Multinuclear clusters as one type of important coordination compounds have provoked intense interests because of their aesthetically intriguing architectures and their possible applications especially in molecular magnets [9–12]. In recent years, lots of clusters including but not limited to transition-metal (TM)-, lanthanide (Ln)-, and TM-Ln-heterometallic based clusters have been documented sequentially [9–14]. Among the various metal clusters, nickel-clusters are fascinating due to their multiple applications especially magnetism and catalysis [15–19]. As a result, many Ni-based clusters including different nuclear have been reported such as {Ni_6} [15], {Ni_8} [16], {Ni_9} [17], {Ni_{12}} [18], and {Ni_{14}} [19]. In contrast with limited choice of metal centers, the various organic ligands could give more effective opportunities to construct different coordination clusters. The most used organic linkers are usually ligands with N and/or O coordination donors, which mainly derived from the groups such as —OH, —COOH, and *N*-heterocyclic groups including triazole, pyrazole, imidazole, pyridine, and so on [20]. According to the theory of hard and soft acids and bases (HSAB) [21], the strong oxyphilic Ln ions as hard acids tend to combine with O donors while the soft or borderline acid TM ions usually coordinate to N donors. Generally, the carboxylic group can bridge one, two, three, or even four metal ions through bridging/chelating modes, enhancing the uncertainty and unpredictability in the self-assembly of clusters. Whereas the *N*-heterocyclic groups have shown great potentials to form coordination compounds due to the strong and directional coordination ability. In the plenty of *N*-heterocyclic ligands, 1H-1,2,3-triazole (Htz) has been widely used to prepare numerous coordination cluster compounds since it can form the triangular rigid-jointed planar building units to exhibit interesting magnetic properties [22–23]. As one derivative of the Htz ligand, benzotriazole (Hbta) ligand possessing the tri-N-donors property of Htz could similar coordination sites to bridge metal ions to produce cluster compounds [24–30]. Moreover, the benzene is equal to the sterically bulky substituent, which can hinder the formation of interpenetration structures. Based on the above aforementioned points, a centrosymmetric nine-nuclear cluster compound, $[Ni_9(bta)_{12}(NO_3)_6(DMA)_6] \cdot 3DMA$ (**1**), (DMA = *N,N*-dimethylacetamide), was isolated by the solvothermal reaction of Hbta and $Ni(NO_3)_2 \cdot 6H_2O$ in the mixed solvent DMA/CH_3OH. Three independent Ni^{2+} ions in **1** are linked by two types of Hbta ligands to generate a nine-nuclear {Ni_9} cluster, further producing a 3D supramolecular network through hydrogen bonds. In addition, the magnetic property of **1** has been studied.

Compound **1** was obtained with 78% yield by the assembly of $Ni(NO_3)_2 \cdot 6H_2O$ and Hbta in the mixed solvent DMA/CH_3OH [31]. The high phase purity of bulky sample **1** was demonstrated by comparing the patterns between the experimental powder X-ray

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https://doi.org/10.1016/j.inoche.2017.09.029
1387-7003/

Polymer
Chemistry

PAPER

Cite this: *Polym. Chem.*, 2017, **8**, 4849

Photoswitchable fluorescent polymeric nanoparticles for rewritable fluorescence patterning and intracellular dual-color imaging with AIE-based fluorogens as FRET donors†

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Received 19th May 2017,
Accepted 24th July 2017

DOI: 10.1039/c7py00834a

rsc.li/polymers

Photoswitchable fluorescent polymer nanoparticles (PFPNs) were constructed from an aggregation-induced emission (AIE) based fluorogen and a photochromic spiropyran-linked amphiphilic copolymer *via* a simple co-precipitation method. Possessing the reversible photoisomerization property and high fluorescence resonance energy transfer (FRET) efficiency, not only did the designed spiropyran-linked amphiphilic copolymer provide the PFPNs with excellent long-term stability (~5 weeks) in aqueous media, but also it could both efficiently and reversibly switch on/off the fluorescence emission of the AIE-based fluorogen upon irradiation with UV and visible light. It is worth noting that the high contrast dual-color characteristics written with PFPNs as rewritable fluorescence patterning can be tuned by altering the wavelength of the irradiation light. Moreover, the resultant PFPNs were successfully applied for intracellular dual-color imaging due to their outstanding cell-membrane permeability and rapid photo-responsiveness, as well as excellent repeatability properties.

Introduction

Possessing high-contrast dual-color fluorescence properties, photoswitchable fluorescent materials have attracted a great deal of attention for use in various applications such as rewritable data storage, optical switches, smart labeling, and super-resolution fluorescence imaging.[1–5] In particular, the combination of photoswitchable fluorescent materials and fluorescence resonance energy transfer (FRET) strategy reveals some excellent advantages over conventional fluorescent materials containing single-molecule fluorophores as they are able to differentiate the fluorescence signals, eliminate the background noise or autofluorescence, and provide high-resolution images.[6–9]

To date, various classes of FRET-based photoswitchable fluorescent materials have been developed, including fluorescent proteins,[10,11] small organic dyes,[12] organic quantum dots (QDs),[13,14] polymer nanoparticles,[15–27] *etc*. Despite the fact that the encoded photoswitchable proteins do not need exogenous fluorescent probes for targeting proteins, their drawback of a low fluorescence signal severely limits their advanced biological applications.[28] The photoswitchable small organic dyes possess some advantages such as high brightness and good biocompatibility as well as a fast switching process,[29,30] but they still have some defects including poor photostability and a small Stokes shift.[7] Photoswitchable QDs show the merits of narrow and symmetric emission spectra, bright multiple colours and good photostability.[31,32] However, their applications are hampered by their photoblink, cytotoxicity and incompatibility in aqueous media.[33] Therefore, it is highly desirable to design novel photoswitchable fluorescent materials that not only possess the merits of small organic dyes and QDs, but also overcome these drawbacks.

The recently developed photoswitchable fluorescent polymer nanoparticles (PFPNs) can effectively solve the above issues due to their outstanding properties, such as good water solubility/dispersibility, improved biocompatibility, tunable structure and function, and excellent photostability, as well as other outstanding properties.[18,21,26] Nevertheless, conventional organic-dye-encapsulated PFPNs are facing a major challenge

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra, absorption spectra, AIE behaviour, fluorescence spectra, GPC curves, and cell viability. See DOI: 10.1039/c7py00834a

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Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2017, **8**, 7271

Selective visualization of endogenous hydrogen sulfide in lysosomes using aggregation induced emission dots†

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Received 6th October 2017,
Accepted 7th November 2017

DOI: 10.1039/c7py01696d

rsc.li/polymers

The development of novel fluorescent probes for selective detection of endogenous hydrogen sulfide (H_2S) in lysosomes is imperative for elucidating its functions associated with diseases. Nevertheless, the reported fluorescent probes for lysosomal H_2S detection usually undergo an aggregation caused quenching (ACQ) phenomenon in the aggregate state and cause the self-quenching of fluorescence due to the "self-absorption" effect with a small Stokes shift, which largely limited their sensing application. To solve this problem, we present the aggregation induced emission dots (**AIED**) for selective visualization of endogenous H_2S in lysosomes *via* a simple co-precipitation method. It is worth noting that **AIED** with excellent AIE properties and large Stokes shift (~150 nm) could effectively prevent the notorious ACQ phenomenon and the self-quenching of fluorescence. In addition, the as-prepared **AIED** exhibits favorable features including good water dispersibility, high sensitivity (~43.8 nM), outstanding selectivity toward H_2S over other thiols, long-term stability (>15 weeks) and good biocompatibility. Significantly, the resultant **AIED** with good membrane permeability has been successfully employed to visualize the endogenous H_2S in lysosomes in living cells. We expect that **AIED** can serve as a useful tool to investigate the roles of lysosomal H_2S in H_2S-associated diseases.

Introduction

As important membrane-bound acidic organelles (pH 4.5–5.5), lysosomes serve as primary sites for the degradation of biological molecules delivered to lysosomes through the biosynthetic and endocytic pathways.[1] Evidence has revealed that endogenous hydrogen sulfide (H_2S), which is naturally produced from L-cysteine *via* catalysis of cystathionine β-synthase (CBS) and/or cystathionine γ-lyase (CSE) in lysosomes, could induce lysosomal membrane destabilization along with the release of lysosomal proteases and cause cell death through the activation of calpain proteases.[2,3] Nevertheless, the function of H_2S in lysosomes is still not well-defined. Therefore, the development of reliable methods for monitoring the lysosomal H_2S levels is very conducive to investigate its role in related diseases in lysosomes.

Fluorescence imaging combined with a fluorescent probe has become an excellent platform for tracking and monitoring biomolecules in living systems as it possesses several advantages including simple operation, high sensitivity, real-time imaging, high spatial resolution, *etc.*[4–13] So far, a number of fluorescent probes for H_2S have been engineered,[14–20] however, only a few of them could monitor lysosomal H_2S.[21–27] Despite the intensive efforts, these small molecule-based probes comprised of hydrophobic planar structures usually undergo an aggregation caused quenching (ACQ) phenomenon in the aqueous or aggregate state, largely reducing their sensing performance.[28] In addition, most of them with a small Stokes shift also cause the self-quenching of fluorescence due to the "self-absorption" effect.[29] On the other hand, the above-mentioned lysosome-targeted H_2S fluorescent probes could mainly accumulate in lysosomes by introducing a morpholine moiety. Some pieces of evidence indicated that an enhancement of lysosome pH and subsequent cell apoptosis can be

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† Electronic supplementary information (ESI) available: Synthesis procedures, ^1H NMR spectra, GPC curve, absorption spectrum, fluorescence spectra, AIE behaviour, detection limit, cell viability, *etc.* See DOI: 10.1039/c7py01696d

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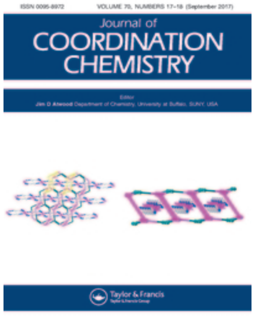

Journal of Coordination Chemistry

ISSN: 0095-8972 (Print) 1029-0389 (Online) Journal homepage: http://www.tandfonline.com/loi/gcoo20

Crystal structure and NMR study of a bisperoxovanadium complex $[NH_4][VO(O_2)_2(ima)]$

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To cite this article: Shaowei Zhang, Wen Xia, Yueyue Yang, Xianyong Yu & Xiaofang Li (2017) Crystal structure and NMR study of a bisperoxovanadium complex $[NH_4][VO(O_2)_2(ima)]$, Journal of Coordination Chemistry, 70:17, 2958-2968, DOI: 10.1080/00958972.2017.1374380

To link to this article: https://doi.org/10.1080/00958972.2017.1374380

JOURNAL OF COORDINATION CHEMISTRY, 2017
VOL. 70, NO. 11, 1882–1892
https://doi.org/10.1080/00958972.2017.1328736

NMR and theoretical study on the linking properties of peroxovanadium(V) complexes with the 3-aminomethyl-pyridine derivatives

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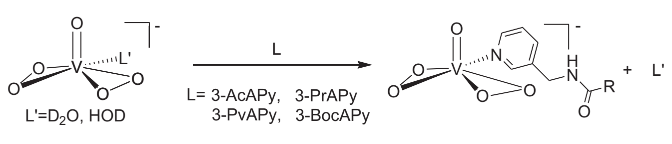
ABSTRACT

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



ARTICLE HISTORY
Received 30 January 2017
Accepted 25 April 2017

KEYWORDS
Diperoxovanadium; 3-aminomethyl-pyridine derivatives; solvation effect; NMR; DFT-calculation

1. Introduction

Vanadium complexes, particularly vanadates and recently reported heteroligand peroxido-vanadium(V) complexes (abbr. pVs), have attracted much attention because vanadium plays key roles in biological processes and many of them can act as biomimetic agents such as the inhibitors of cancer tumor growth, insulinomimetics, *etc.* [1–7]. Therefore, the coordination chemistry and biological mechanism of vanadium compounds have been a hot scientific

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Supplemental data for this article can be accessed at https://doi.org/10.1080/00958972.2017.1328736.

Journal of Alloys and Compounds 691 (2017) 1018–1023

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Sonochemical synthesis of a Mn_3O_4/MnOOH nanocomposite for electrochemical energy storage

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ARTICLE INFO

Article history:
Received 18 July 2016
Received in revised form
27 August 2016
Accepted 29 August 2016
Available online 30 August 2016

Keywords:
Supercapacitor
Manganese oxides
Binary nanocomposite
Sonochemical synthesis

ABSTRACT

A Mn_3O_4/MnOOH nanocomposite was synthesized through a sonochemical process and used for supercapacitor applications. The obtained samples were characterized using a transmission electron microscope (TEM), a high-resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD) and selected-area electron diffraction (SAED). The electrochemical performance of the Mn_3O_4/MnOOH nanocomposite was investigated as supercapacitor electrode material through cyclic voltammetry (CV), galvanostatic charge/discharge (GC/D) and electrochemical impedance spectroscopy (EIS). Results indicated that ultrasonic time strongly influenced the MnOOH contents in the nanocomposite. The Mn_3O_4/MnOOH nanocomposite electrode of 0.22 MnOOH content provided a high specific capacitance of 307.8 F g^{-1} as well as excellent cycling stability (2% decay after 2000 cycles). Furthermore, the symmetric supercapacitor based on Mn_3O_4/MnOOH nanocomposite has a reasonable energy density of 10.6 W h kg^{-1} and a high power density of 7.4 kW kg^{-1}. The excellent capacitive performance of the Mn_3O_4/MnOOH nanocomposite is due to synergistic effect between the Mn_3O_4 and the MnOOH.

1. Introduction

In recent decades, supercapacitors, also known as electrochemical capacitors (ECs), have attracted extensive attention due to their higher power density, longer cycle life than batteries, and higher energy density than conventional dielectric capacitors [1,2]. Depending on the charge storage mechanism, supercapacitors are generally divided into two types [3]. The first type is based on the formation of electrical double layers (EDLs) at the interface between surface of a conductive electrode and an electrolyte. The second type is based on a Faraday-type reaction occurring on the electrode material surface, which is called pseudocapacitance because it exhibits a capacitive behavior rather than a distinctly peaked redox behavior normally associated with intercalation. The transition metal oxides with variable valence have been used as electrode materials in pseudocapacitors [4–10]. Among the transition metal oxides, manganese oxides have evoked considerable interest because of their multi-oxidation states for charge transfer, wider charge/discharge potential range, higher specific capacitance, low cost and good environmental compatibility [11–17]. Especially, MnOOH with a stable trivalence under ambient conditions has been expended to apply in supercapacitors in recent years [17–21]. For example, γ-MnOOH coaxial nanocable films deposited on multiwalled carbon nanotube show an electrochemical capacitance of about 145 F g^{-1} at current density of 0.1 A g^{-1}, based on a moderate mass loading of 1.38 mg cm^{-2} [19]. Mn_3O_4 is another stable manganese oxide and has been investigated as favorable electrode material for supercapacitor. A few reports have indicated that Mn_3O_4 can be electrochemically oxidized (conditioned) to birnessite-type MnO_2 after successive potential cycles [22–26]. For example, Komaba S. et al. studied the conditioning process of the ball-milled Mn_3O_4 in detail and obtained a specific capacitance of 190 F g^{-1} in 1 mol L^{-1} Na_2SO_4 aqueous solution after 250 potential cycles [23]. Guo, Liu, et al. reported the synthesis of Mn_3O_4 microspheres and obtained a specific capacitance of 219 F g^{-1} in 1 mol L^{-1} Na_2SO_4 aqueous solution after 400 potential cycles [24]. Though manganese oxides are regarded as promising electrode materials for commercial supercapacitors, they suffer from the low rate capability and poor stability caused by their low electric

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http://dx.doi.org/10.1016/j.jallcom.2016.08.309
0925-8388/

Polymer Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Cite this: *Polym. Chem.*, 2017, **8**, 5795

Ratiometric imaging of lysosomal hypochlorous acid enabled by FRET-based polymer dots†

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Received 1st August 2017,
Accepted 29th August 2017

DOI: 10.1039/c7py01289f

rsc.li/polymers

The development of an effective method for imaging of lysosomal hypochlorous acid (HClO) is of great significance to better understand the roles of HClO-related diseases. Herein, we report on the fabrication of fluorescence resonance energy transfer (FRET)-based fluorescent polymer dots (**FPD**) for the ratiometric imaging of lysosomal HClO in living cells *via* a simple co-precipitation method. This FRET-based construction strategy takes the advantage of flexible design by incorporating target-inert fluorogen (donor) and target-sensitive fluorogen (acceptor) into the nanoparticle to avoid leakage and photobleaching problems. The as-prepared **FPD** exhibits good water dispersibility, fast response (<30 s), high sensitivity (~5.1 nM), outstanding selectivity, excellent photostability and long-term stability (>15 weeks). Moreover, the resultant **FPD** with good membrane permeability could mainly locate in the lysosomes and act as a probe for the ratiometric imaging of lysosomal HClO in living HeLa cells.

Introduction

Lysosome, as a key intracellular organelle that comprises single membrane-bound vesicles, serves as a major degradation compartment for the degradation of molecules through the biosynthetic and endocytic pathways in cells.[1] An abnormal regulation of the lysosome leads to many diseases, such as tumors, inflammation, neurodegeneration and various lysosomal storage disorders.[2–4] Importantly, hypochlorous acid (HClO), which can be generated from hydrogen peroxide *via* the catalysis of myeloperoxidase (MPO) in lysosomes, associates with the redox balance in the lysosome system and maintains the normal lysosomal function.[5,6] It has been documented that a number of chronic diseases are related to the disruption of HClO generation in lysosomes, such as cardiovascular diseases, neuron degeneration, arthritis, and even cancers.[7,8] Therefore, the selective monitoring of lysosomal HClO may represent a potential methodology for effective diagnoses of human diseases in lysosomes.

Recently, a number of fluorescent probes have been developed and they serve as efficient analytical methods for lysosomal HClO detection due to their high sensitivity and non-invasive, real-time and high spatial resolution imaging in living cells.[9–20] Despite extensive efforts, most of the fluorescent sensors are small molecules, which suffer from less satisfactory water solubility, and can only operate in organic or mixed aqueous organic solvents. In addition, as most of them exhibit only one single emission band (turn-on), the detection result may be affected by sensor concentration, photobleaching, fluctuation of instrumental parameters, *etc.*[21–26] On the other hand, these lysosome-targeted fluorescent probes for HClO are mainly based on a morpholine moiety, which could obtain the ability of the orientation of lysosomes.[15–20] Recent evidence has demonstrated that the introduction of the morpholine group could cause an enhancement in lysosome pH and induce cell apoptosis due to the alkalizing effect of the morpholine moiety.[9,27] To solve the above problems, the design of a water-soluble (or dispersible) probe without morpholine moiety for the ratiometric detection of lysosomal HClO is of vital importance.

Recently developed fluorescent polymer dots (**FPD**) containing one or more types of conjugated polymers have attracted great interest in various applications due to some outstanding properties, including good water solubility, improved biocompatibility, excellent photostability and so on.[28–30] In view of their advantages, **FPD** have been utilized in sensors, imaging, and gene/drug delivery.[31–35] For example, Chiu and co-workers developed far-red to near-infrared (NIR) based **FPD** for the

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† Electronic supplementary information (ESI) available: ^{1}H NMR spectra, absorption spectrum, fluorescence spectra, GPC curve, cell viability, *etc.* See DOI: 10.1039/c7py01289f

JOURNAL OF MACROMOLECULAR SCIENCE®, PART B: PHYSICS
2017, VOL. 56, NO. 7, 505–515
https://doi.org/10.1080/00222348.2017.1330132

Preparation and Properties of Novel Maleated Poly (D, L-lactide-co-glycolide) Porous Scaffolds for Tissue Engineering

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ABSTRACT
Three-dimensional biodegradable porous scaffolds play an important role in tissue engineering. A new polymer based on maleated poly (lactic-co-glycolic acid) (MPLGA) was synthesized using direct melt copolymerization from maleic anhydride (MAH), D, L-lactide, and glycolide monomers. MPLGA porous biodegradable scaffolds were prepared by a solution-casting/salt-leaching method. The effects of content and size of the $NaHCO_3$ porogen on the compressive strength of the MPLGA scaffolds were investigated, and the effect of content of the porogen on the porosity of the MPLGA scaffolds was also studied. The results indicated that MAH was grafted onto PLGA successfully and MPLGA scaffolds with interconnective and open pore structure were obtained. Increasing content of $NaHCO_3$ porogen resulted in an increase of porosity and decrease of the compressive strength of the MPLGA scaffolds with the compressive strength of the scaffolds also decreasing with increasing porogen size.

ARTICLE HISTORY
Received 24 December 2015
Accepted 14 April 2017

KEYWORDS
Maleic anhydride; poly (lactic-co-glycolic acid); scaffold

Introduction

Tissue engineering research aims to provide new methods for tissue regeneration by applying engineering principles to developmental cell biology. From the perspective of material science and biomedical engineering, tissue can be considered as a cell composite consisting of cells and their extracellular matrices (ECM). To design a scaffold is a promising research area in tissue engineering materials. In general, scaffolds provide the necessary support as an artificial ECM, allowing cells to proliferate and maintain their differentiated functions, and also serves as a template in guiding the development of new tissue.[1–3] Synthetic polymers with many beneficial properties, such as high flexibility, good shape-forming ability, timely biodegradation rate, non-toxic degradation products, and appropriate mechanical

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JOURNAL OF MACROMOLECULAR SCIENCE®, PART B: PHYSICS
2017, VOL. 56, NO. 5, 315–323
http://dx.doi.org/10.1080/00222348.2017.1302117

Influence of Mass Ratio of Polyols on Properties of Polycaprolactone-Polyethylene Glycol/Methylene Diphenyl Diisocyanate/Diethylene Glycol Hydrogels

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ABSTRACT

Polyurethane (PU) hydrogels with good hydrophilicity and biocompatibility have been applied as biomedical materials. A series of polyurethane prepolymers based on methylene diphenyl diisocyanate (MDI), polycaprolactone (PCL) and polyethylene glycol (PEG), using diethylene glycol (DEG) as the chain-extender, were synthesized; then the polyurethane hydrogels were obtained from the prepolymers using benzoyl peroxide (BPO) as a cross-linker by free radical polymerization. The influences of the ratio of polyols (PCL and PEG) on the contact angle, swelling ratio and morphology of the polyurethane hydrogel were investigated. The loading capacity and release behavior of chloramphenicol from the PCL-PEG/MDI/DEG hydrogels with different compositions were also studied. The contact angle and swelling degree results showed that the PCL-PEG/MDI/DEG hydrogel with PCL/PEG mass ratio of 3:1 had higher hydrophilicity than that with PCL/PEG mass ratios of 1:1 and 1:3. All PCL-PEG/MDI/DEG hydrogels showed three dimensional porous structures; however, the pore size increased with increasing PEG content. The chloramphenicol release kinetics from PCL-PEG/MDI/DEG hydrogels indicated Fickian diffusion, and the drug release rate increased with increasing PEG content in the PU hydrogels.

ARTICLE HISTORY
Received 6 January 2016
Accepted 8 February 2017

KEYWORDS
Drug delivery; methylene diphenyl diisocyanate; polyurethane hydrogels; polycaprolactone; polyethylene glycol; hydrophilicity

Introduction

Hydrogels are defined as colloidal gel polymers in which water is the dispersion medium.[1] Water-swellable and water-insoluble polymeric materials are generating increasing interest for a wide range of biomedical applications.[2, 3] Hydrogels are generally comprised of hydrophilic polymeric networks that are formed by chemical/physical cross-linking. They are

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JOURNAL OF MACROMOLECULAR SCIENCE®, PART B: PHYSICS
2017, VOL. 56, NO. 4, 245–253
http://dx.doi.org/10.1080/00222348.2017.1293364

Preparation and Properties of 2, 4-2-Isocyanic Acid Methyl Ester/Poly(ε-caprolactone)/Diethylene Glycol Hydrogels

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ABSTRACT

The hydrophilic polyurethane (PU) hydrogels have become attractive in the biomedical field for drug delivery. In this work 2, 4-2-isocyanic acid methyl ester (TDI), poly(ε-caprolactone) (PCL), and poly(ethylene glycol) (PEG) were used to prepare a prepolymer and then diethylene glycol (DEG) was used as a chain extender to prepare a novel hydrophilic polyurethane, TDI/PCL-PEG/DEG. The obtained PU hydrogels were characterized by Fourier transform infrared (FT-IR) spectroscopy and scanning electronic microscopy (SEM). By varying the ratio of PCL to PEG in the copolymer, modulations of hydrophilicity and drug release behavior were observed. FT-IR analysis confirmed the successful synthesis of the TDI/PCL-PEG/DEG hydrogels. The introduction of PEG into the PU hydrogels led to a porous structure. The water contact angle and swelling ratio results confirmed that the hydrophilicity increased with increasing amounts of the PEG segments. The introduction of PEG also increased the release rate of chloramphenicol, used as model drug, from the PU hydrogels.

ARTICLE HISTORY
Received 25 October 2015
Accepted 11 January 2017

KEYWORDS
2, 4-2-isocyanic acid methyl ester; hydrophilicity; polyurethane hydrogel; polyethylene glycol; polycaprolactone

Introduction

Hydrogels are basically three-dimensional hydrophilic or amphiphilic polymer networks, formed by chemical or physical crosslinking, that are capable of retaining large amounts of water or biological fluids yet remaining insoluble in physiological conditions.[1,2] Hydrogels have found use in a wide range of biomedical applications, such as suture and catheter coatings, contact lenses, drug delivery vehicles, scaffolds for tissue engineering, and as artificial organs due to its excellent properties, including biocompatibility, high water holding, and network porosity, for biomedical utilization.[3,4]

However, hydrogels in the swollen state exhibit weak mechanical strength and, hence, they are unsuitable for applications under load.[5] On the other hand, their mechanical

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物理化学学报(*Wuli Huaxue Xuebao*)
April *Acta Phys. -Chim. Sin.* **2017,** *33* (4), 729−735

[Article] doi: 10.3866/PKU.WHXB201611291 www.whxb.pku.edu.cn

间位基团激发态取代基常数的扩展及应用

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摘要：合成了七个系列含间位取代基X的二苯乙烯*m*-XArCH=CHArY-*p*(简称*m*-XSBY-*p*)，其中X为NO_2、I、$CHCH_2$、Ph、Et、NMe_2和CCH。在无水乙醇中测定它们的紫外(UV)吸收光谱，得到紫外吸收最大波长λ_{max} (nm)。对λ_{max}的波数v_{max} (cm^{-1})进行定量相关，采用曲线拟合方法，得到上述7个间位基团的激发态取代基常数$\sigma^{ex}_{CC(m)}$。将对位基团和间位基团的σ^{ex}_{CC}与Hammett常数σ进行对比，表明σ^{ex}_{CC}与σ分别表达取代基不同的电子效应。另外，合成了含上述间位基团的二芳基希夫碱(10个)和二苯乙烯(14个)，用所得$\sigma^{ex}_{CC(m)}$预测它们的λ_{max}，并用实验测定它们的λ_{max}，结果表明预测值与实验值相吻合，验证了所得$\sigma^{ex}_{CC(m)}$常数的可靠性。收集了225个化合物(涉及二取代苯及二苯乙烯)的v_{max}，建立了一个统一的定量方程来表达这些化合物v_{max}的变化规律。

关键词：激发态常数；间位基团；紫外吸收光谱；二苯乙烯；二芳基希夫碱
中图分类号：O641

Extension and Application of Excited-State Constants of *meta*-Substituents

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Abstract: Seven series of 3,4′-disubstituted stilbenes were synthesized, with *meta*-substituents X (*m*-XSBY-*p*) including: NO_2, I, $CHCH_2$, Ph, Et, NMe_2, and CCH (*m*-XSBY-*p*). The longest wavelength maximum λ_{max} (nm) in ultraviolet absorption spectra of the compounds were measured. A quantitative correlation analysis was performed in terms of energy, the v_{max} (cm^{-1}) for 3,4′-disubstituted stilbenes. The excited-state substituent constants $\sigma^{ex}_{CC(m)}$ of the seven *meta*-substituents were determined by curve-fitting. The constants σ^{ex}_{CC} of the *meta*- and *para*-substituents were compared with their Hammett constants σ. The results indicated that σ^{ex}_{CC} and σ express the substituent electrostatic effects in the excited- and ground-states, respectively. In addition, 10 samples of aryl Schiff bases and 14 samples of 3,3′-disubstituted stilbenes with *meta*-substituents X were synthesized, and their $\lambda_{max,pred.}$ were predicated based on the obtained constants $\sigma^{ex}_{CC(m)}$. These results showed that the $\lambda_{max,pred.}$ values agreed well with the experimental values, and confirmed the reliability of the obtained $\sigma^{ex}_{CC(m)}$ values. We also collected v_{max} values of 225 samples of disubstituted stilbenes and disubstituted benzenes and established a general quantitative equation to express the change regularity of their v_{max}.

Key Words: Excited-state substituent constant; *meta*-Substituent; Ultraviolet absorption spectrum; Stilbene; Aryl Schiff base

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Received: October 13, 2016; Revised: November 29, 2016; Published online: November 29, 2016.

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The project was supported by the National Natural Science Foundation of China (21272063, 21672058), Scientific Research Fund of Hunan Provincial Education Department, China (14C0466), and Natural Science Foundation of Hunan Province, China (14JJ3112).
国家自然科学基金(21272063, 21672058), 湖南省教育厅科研项目(14C0466)和湖南省自然科学基金(14JJ3112)资助

SPECTROSCOPY LETTERS
2017, VOL. 50, NO. 6, 322–329
https://doi.org/10.1080/00387010.2017.1327446

Influences of urea on the interaction of 32π-Norcorrole with bovine serum albumin

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ABSTRACT
The aim of the present study is to investigate the urea-induced denaturation of bovine serum albumin. The native and denatured bovine serum albumin interactions with 32π-Norcorrole were investigated, respectively. The circular dichroism spectra indicated that the *α*-helix content of bovine serum albumin reduces in the presence of urea and 32π-Norcorrole. The Stern–Volmer quenching constant indicated that both dynamic and static quenching exist in the interaction; moreover, the denaturation of bovine serum albumin leads to the decrease of Stern–Volmer quenching constant. Binding constant illustrated that the native bovine serum albumin has stronger combination capacity than the denatured bovine serum albumin. The fluorescence lifetime studies demonstrated that denaturation lead to the fluorescence decay of bovine serum albumin. The binding sites experiment and molecular docking studies demonstrated that the binding site of 32π-Norcorrole on bovine serum albumin is mainly located in site I.

ARTICLE HISTORY
Received 20 February 2017
Accepted 3 May 2017

KEYWORDS
32π-Norcorrole; Bovine serum albumin; denaturation; interaction; urea

Introduction

It is well known that serum albumin is the most abundant protein in blood, which acts as the carrier and depot for various substances.[1] However, the transporting function and combination capacity can be disturbed when the albumin is in pathogenous states.[2] Urea is a widely exploited chemical denaturant in the field of chemicobiology, which can result in the exposure of the protein chromophores to water.[3] Therefore, studies on serum albumin in the absence and presence of urea can stimulate the serum albumin in healthy and pathogenous states.[4]

Bovine serum albumin is a globular protein and has a compact ellipsoidal structure. The stability of this structure originates mainly from hydrophobic interactions.[5] The existence of 583 amino acids and 17 disulfide bridges in bovine serum albumin has been reported. Bovine serum albumin is markedly polar with a potential for 100 negative and 82 positive charges at neutral pH. Thus, the net negative charge of bovine serum albumin is −18. The charge distribution is not uniform. The overall structure at neutral pH is ellipsoidal with axes 41 × 141 Å. The net charge at pH 7 falls progressively from −10 in domain I, which includes the amino terminal, to zero in domain III, which includes carboxyl terminal. In domain II, between the two domains, the net negative charge is −8.[6]

Porphyrins and their related ramification have attracted considerable attention in recent years due to their unique structural, spectroscopic, and photo-physical properties and the potential application in medicine and chemical engineering fields.[7,8] The 32π-Norcorrole (Fig. 1), as a kind of expanded porphyrin, has been shown intriguing optical and electrochemical properties as well as unique metal coordination behavior.[9] These interesting properties provoke us to investigate the interaction of expanded porphyrin with bovine serum albumin.

Common methods used to investigate the binding of ligands to albumin proteins are UV-Vis spectroscopy,[10,11] fluorescence spectroscopy,[12,13] circular dichroism spectroscopy,[14,15] and equilibrium dialysis.[16] Among these methods, equilibrium dialysis is used widely, but it requires the analysis of free and total ligand concentration and takes a long time. Spectral techniques such as fluorescence and ultraviolet spectrophotometer are widely used to explore the properties of protein.[17] In this paper, a multi-technique approach was applied to understand the combination between urea-induced bovine serum albumin and 32π-Norcorrole.

Materials and methods

Reagents

Bovine serum albumin (≥99%) was obtained from Huamei Bioengineering Co. (Shanghai, China) and was dissolved in a Tris–HCl ($0.05\,\mathrm{mol \cdot L^{-1}}$, $\mathrm{pH} = 7.43$) buffer to form the bovine serum albumin solution with a concentration of $1.00 \times 10^{-5}\,\mathrm{mol \cdot L^{-1}}$. NaCl was purchased from Xilong Chemical Co. (Shantou, China). A Tris–HCl buffer ($0.05\,\mathrm{mol \cdot L^{-1}}$, $\mathrm{pH} = 7.43$) containing $0.10\,\mathrm{mol \cdot L^{-1}}$ NaCl was selected to keep the pH value constant and to maintain the ionic strength of the solution. Urea was obtained from Xilong Chemical Co. (Shantou, China). Warfarin sodium

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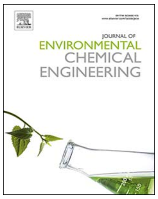
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lstl.

Journal of Environmental Chemical Engineering 5 (2017) 6201–6215

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece



Synthesis of thiol-functionalized mesoporous calcium silicate and its adsorption characteristics for heavy metal ions

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ARTICLE INFO

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

ABSTRACT

Thiol-functionalized mesoporous calcium silicate (MCS-SH) was synthesized using post-grafting with calcium nitrate tetrahydrate and sodium metasilicate nonahydrate as raw materials, cetyl trimethyl ammonium bromide as template, and (3-mercaptopropyl)trimethoxysilane as modifying agent. The structure and composition were characterized using X-ray diffraction, Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller surface analysis, thermogravimetry–differential thermal analysis, scanning electron microscopy, transmission electron microscopy, and energy-dispersive X-ray spectrometry. The adsorption performance and thermodynamic and kinetic characteristics of MCS-SH for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Cr^{3+} were investigated. Results showed that MCS-SH possessed a slit-pore structure with a specific surface area of 129.32 $m^2\,g^{-1}$ and pore size that was mainly distributed in 5–49 nm, which reduced by 28.81 $m^2\,g^{-1}$ and 2 nm compared with those of unmodified mesoporous calcium silicate (MCS), respectively. The amount of —SH grafted to MCS-SH was 0.4594 mmol g^{-1}, according to the determined sulfur content. The maximum adsorption capacities for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Cr^{3+} were 601.51, 509.56, 618.09, and 334.81 mg g^{-1} at 293 K, respectively, which were much higher than those reported in the literature, and follow the order of $Pb^{2+} > Cd^{2+} > Cu^{2+} > Cr^{3+}$. The equilibrium data of the four heavy metal ions adsorbed by MCS-SH fitted the Langmuir model and, especially, the Redlich–Peterson model well. The adsorption processes were all endothermic, entropy increasing, and spontaneous. The adsorption of MCS-SH for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Cr^{3+} was rapid and attained equilibrium within 60 min. The adsorption kinetics can be well fitted by the pseudo-second-order model, and the adsorption activation energy followed the order of Cr^{3+} (29.7526 kJ mol^{-1}) > Pb^{2+} (21.5840 kJ mol^{-1}) > Cu^{2+} (19.6988 kJ mol^{-1}) > Cd^{2+} (18.5377 kJ mol^{-1}). The adsorption mechanisms include physical adsorption, chemical adsorption (especially surface complexing adsorption), and ion exchange, with chemical adsorption being the dominant mechanism. MCS-SH exhibited an excellent performance as adsorption material for Cd^{2+}, Cu^{2+}, Pb^{2+}, and Cr^{3+}.

1. Introduction

With the rapid development of modern industry, a large amount of heavy metal wastewater, especially that containing Pb^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+}, and Hg^{2+}, is produced during the commercial production and has caused serious environmental pollution and threatened human health [1]. Given the toxicity of these metals, the World Health Organization restricts the maximum acceptable concentration of Pb^{2+}, Cd^{2+}, Cr^{3+}, Cu^{2+} and Hg^{2+} in drinking water to be 0.01, 0.003, 0.05, 2.0 and 0.001 mg L^{-1}, respectively [2]. The problem motivated the scientific community to develop new methods to detect and remove toxic contaminants from wastewater in efficient and economically practicable approaches. Although various methods, such as conventional chemical precipitation [3], chelating–flocculation method [1], ion exchange [4], electrochemical method [5,6], flotation [7,8], membrane filtration [9–12], liquid membrane separation [13], and adsorption method [14–17], have been used to manage heavy metal wastewater, these strategies present several disadvantages [9,15]. For example, in conventional chemical precipitation, emission standards are difficult to meet, a large amount of sludge is easily produced, and the heavy metal could be released and thus produce secondary pollution. With chelating–flocculation, the chelating flocculant cannot be

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https://doi.org/10.1016/j.jece.2017.11.046
Received 16 September 2017; Received in revised form 10 November 2017; Accepted 16 November 2017

Rare Metal Materials and Engineering
Volume 46, Issue 1, January 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(1): 0078-0082.

ARTICLE

Electrochemical Performance of $LiMnBO_3$/C Composite Synthesized by Wet Impregnating Method

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Abstract: Hexagonal-$LiMnBO_3$/C composite was prepared by a wet impregnating method using the 3D-network ketchen black (KB) as both a temple and a conductive framework. The crystal structure, morphology and specific surface area were characterized by X-ray diffraction, scanning electron microscopy and nitrogen sorption measurements, respectively. The electrochemical properties of the composite were studied by galvanostatic charge/discharge and cyclic voltammetry measurements. Results show that when tested at C/20 rate for Li ion insertion/extraction properties, $LiMnBO_3$/C composite exhibits good cycle capability with discharge capacity retention of 87.4% at the 30th cycle. As the current rate increases from C/20, C/10 to C/5, good rate capability is obtained for all rates with initial discharge specific capacities of 138.8, 124.5 and 100.5 $mAh \cdot g^{-1}$, respectively.

Key words: $LiMnBO_3$; lithium ion batteries; cathode

Lithium metal borates ($LiMBO_3$, M=Mn, Fe, Co) have been recently reported as promising alternative cathodes for lithium-ion battery due to their high theoretical specific capacity (~220 $mAh \cdot g^{-1}$), thermal stability, electrochemical stability and environmentally benign nature[1-8]. Among the above borates, $LiMnBO_3$ generally exists in two structures, namely the monoclinic structure and the hexagonal structure, and has higher energy density along with high redox voltage (4.1 V/3.7 V) compared to $LiFeBO_3$. However, the lithium metal borates in general suffer from poor electronic conductivity, Li^+ diffusivity and Li-blockage by anti-site defects, poor electronic and ionic conductivity similar to those of the olivine framework[1,9,10]. Recently, these obstacles have been overcome for $LiMBO_3$ by employing conductive carbon coatings, nano-sizing and preventing the surface poisoning of the materials in recent studies[2, 3, 11-13], particularly in the case of $LiFeBO_3$. The series of work presents new possibilities for the development of cathodes made with $LiMBO_3$ that have both high energy density and stability. In comparison to $LiFeBO_3$, $LiMnBO_3$ is an attractive cathode material owing to its higher Li^+ intercalation potential of 3.7 V for monoclinic $LiMnBO_3$ and 4.1 V for hexagonal $LiMnBO_3$ (3.0 V for $LiFeBO_3$), providing higher theoretical energy density than $LiFeBO_3$. Nevertheless, these adverse effects such as poor electronic conductivity and Li^+ diffusivity are more prominent in case of $LiMnBO_3$ with very higher energy barrier in Li-ion channels than in case of $LiFeBO_3$, making it challenging to achieve high capacity for $LiMnBO_3$ using methods developed for $LiFeBO_3$[1,9-11,14]. Thus, only a smaller fraction of the theoretical capacity of $LiMnBO_3$ could be accessed up to date[1,13-16].

In the present investigation, $LiMnBO_3$/C composite was synthesized by a wet impregnating method using 3D-network KB as both a template and a conductive framework. The templating function of KB can be attributed to its unique properties, such as the 3D connectivity of the pore system, high pore volume and narrow pore size distribution, which can control the particle size of $LiMnBO_3$ and the morphology of $LiMnBO_3$/KB composite. The conductive framework function of KB can be attributed to the continuous and connected nano

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Received date: December 6, 2015
Foundation item: National Natural Science Foundation of China (51262008, 51202087); Hunan Provincial Natural Science Foundation of China (12JJ2022); Scientific Research Fund of Hunan Provincial Education Department (14A052)
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JOURNAL OF CHEMICAL RESEARCH 2017 VOL. 41 DECEMBER, 709–711 **RESEARCH PAPER** 709

Synthesis of chromeno[3,4-*c*]pyrazole from *N*-tosylhydrazones and 3-nitro-2-phenyl-2*H*-chromene

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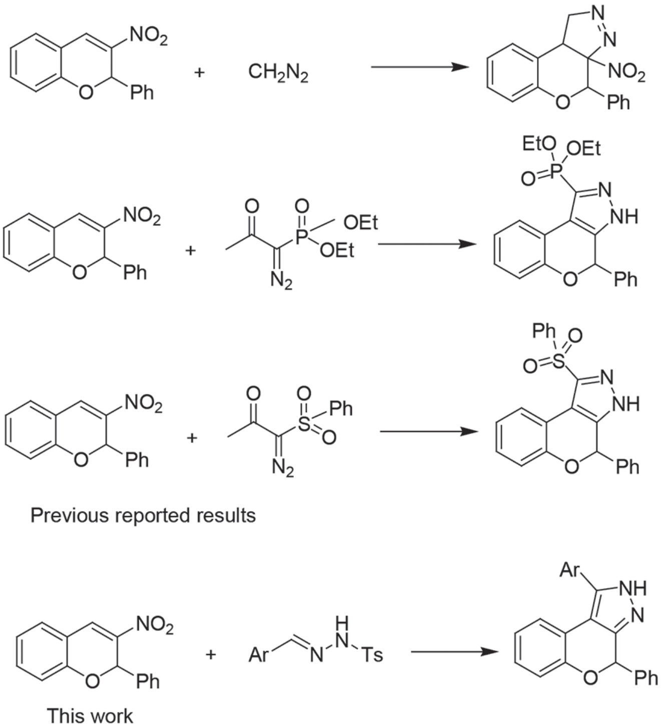
The intermolecular 1,3-dipolar cycloaddition of *N*-tosylhydrazones and 3-nitro-2-phenyl-2*H*-chromene afforded 1-aryl-4-phenyl-2,4-dihydro-chromeno[3,4-*c*]pyrazoles in moderate to good yields. The structures of all the products were characterised by NMR, IR, HRMS and X-ray crystallographic analysis.

Keywords: 3-nitro-chromene, pyrazoles, *N*-tosylhydrazones, chromeno[3,4-*c*]pyrazoles

The chromene moiety is an important structural component in many natural products and biologically active compounds, such as alkaloids,[1] antitumour agents[2] and antibacterial agents.[3] Chromenes are also a key building block in the preparation of 2*H*-benzopyran derivatives, such as flavonols,[4] amines, *etc*.[5,6]

Pyrazoles show important bioactivity, such as anticancer, antimicrobial, phosphodiesterase inhibitory and antiarthritis acitivity,[7] and some pyrazole-containing drugs such as Celebrex and Viagra are commercially available. Owing to this significant bioactivity, the application of pyrazoles as ligands in chemistry has been reported.[8]



Scheme 1 Construction of chromene-fused pyrazole rings.

In view of the abovementioned bioactivity of pyrazoles and chromenes, chromene-fused pyrazoles may exhibit potential biological activity. Chromene-fused pyrazoles are usually prepared by cycloadditions of 3-nitrochromenes with diazo compounds such as diazomethane,[9] diethyl 1-diazo-2-oxopropylphosphonate[10,11] and α-diazo-β-ketosulfone[12] (Scheme 1). The disadvantages of these methods are that diazo compounds are hazardous, unstable and difficult to prepare.

N-Tosylhydrazones are useful reagents in many organic reactions.[13–15] They can generate diazo intermediates *in situ* in the presence of bases. In continuation of our work[16–19] on the synthesis of pyrazole derivatives, here we report the synthesis of chromeno[3,4-*c*]pyrazole derivatives by reaction of 3-nitro-2-phenyl-2*H*-chromene and *N*-tosylhydrazones under basic conditions (Scheme 2).

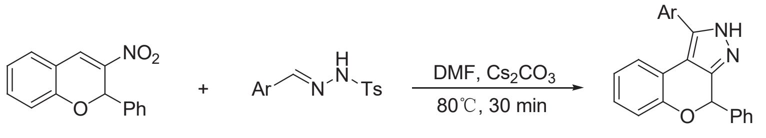
Results and discussion

The 1,3-dipolar cycloaddition reaction of 3-nitro-2-phenyl-2*H*-chromene **1** to the diazo generated *in situ* from *N*-tosylhydrazones and Cs_2CO_3 yielded 1-aryl-4-phenyl-2,4-dihydro-chromeno[3,4-c]pyrazoles.

The structures of all compounds **3a–j** were established by different spectroscopic techniques (NMR, IR) and HRMS. The high-resolution mass spectrum of **3f** gave a molecular ion peak at *m*/*z* 355.1437, which indicates the addition of one molecule of 4-methoxyphenyl diazo to **1**. The IR spectrum of **3f** displayed $\nu_{C=N}$ at 1613.0 cm^{-1}. The ^1H NMR spectrum of **3f** revealed two singlet signals at δ 3.86 ppm ($-OCH_3$) and δ 6.25 ppm (–CH). The presence of signals at δ 6.82–7.47 ppm corresponded to the aromatic protons.

The ^{13}C NMR spectrum of the product **3f** exhibited the presence of a $-OCH_3Ph$ carbon at δ 55.36 ppm. The signal at δ 76.28 ppm was assigned to the carbon of –CH. Furthermore, the structure of the product **3f** was confirmed by X-ray diffraction analysis (Fig. 1).

A plausible reaction pathway for the formation of 1-aryl-4-phenyl-3,4-dihydrochromeno[3,4-*c*]pyrazole **3** is illustrated in Scheme 3. First, the 1,3-dipolar cycloaddition reaction of 3-nitro-2-phenyl-2*H*-chromene **1** and the diazo intermediate,



1 **2a-j** **3a-j**

Ar: a, 4-F-C_6H_4; **b,** 4-Br-C_6H_4; **c**, 4-Cl-C_6H_4; **d**, C_6H_5; **e,** 4-CH_3-C_6H_4; **f**, 4-CH_3O-C_6H_4;
g, 4-CH_3S-C_6H_4; **h**, 4-CO_2Me-C_6H_4; **i**, 4-CN-C_6H_4; **j**, 4-t-Bu-C_6H_4;

Scheme 2 Synthesis of chromeno[3,4-*c*]pyrazole derivatives.

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Synthesis of 2-cyano-3-nitroporphyrin derivatives with silyl cyanide

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2-Cyano-3-nitroporphyrin derivatives were synthesised by the reaction of 2-nitroporphyrin with trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride with moderate yields. The reaction took place regioselectively on the 3-position carbon of the porphyrins, which was confirmed by X-ray analysis.

Keywords: trimethylsilyl cyanide, 2-nitroporphyrin, tetrabutylammonium fluoride

2-Nitroporphyrins[1] have attracted considerable attention in recent years due to their high reactivity as starting materials for the synthesis of other porphyrin derivatives. The nitro group can be converted to amino and diazonium groups and can also undergo nucleophilic substitution directly by other groups containing thiolates,[2] Grignard reagents,[3] alkoxides,[4] 1,3-dicarbonyl compounds[5] and the azide ion.[6] Moreover, the existence of the nitro group activates the peripheral 2,3-double bond of meso-tetraarylporphyrins, the 2-nitro-2,3-double bonds having similar reactivity to normal nitroalkenes for reactions such as cycloaddition[7] and the sulfa-Michael/aldol cascade reaction.[8]

Nitriles are important building blocks in organic synthesis, and they can be transformed into other functional groups such as carboxylic acids,[9] amides[10] and amines.[11] Trimethylsilyl cyanide (TMSCN) is a better source of cyanide than the alkali metal cyanides, being readily available, easy to handle and possessing high activity.[12]

In continuation of our previous work on the synthesis of porphyrinoid derivatives,[13–20] in this paper we report the synthesis of 2-cyano-3-nitroporphyrin derivatives by the reaction of 2-nitroporphyrin with TMSCN in the presence of tetrabutylammonium fluoride (TBAF) in tetrahydrofuran (THF) at room temperature (Scheme 1).

Results and discussion

The reaction of the 2-nitroporphyrins (**1a–h**) and TMSCN in the presence of TBAF in THF at room temperature for 40 min afforded novel 2-cyano-3-nitroporphyrin derivatives (**2a–h**) in moderate yields with high regioselectivity. The structures of all of the compounds **2a–h** were established by various spectroscopic techniques (UV, NMR and HRMS).

The high-resolution mass spectrum of **2c** gave the molecular ion peak at *m/z* 685.2347, which indicates the addition of just one –CN to **1c**. The electronic absorption spectra of both **1c** and **2c** in CH_2Cl_2 are shown in Fig. 1. From the spectra, the Soret band (437 nm), accompanied by a set of three Q bonds (537, 584, 687 nm), can be seen. All of the bands of **2c** are bathochromically shifted with respect to the 2-nitroporphyrin **1c**. These changes may result from additional conjugation of the nitrile group with the 2-nitroporphyrin chromophore.

The ^1H NMR spectrum of **2c** (298 K, $CDCl_3$) is characterised by four doublets at 8.65, 8.83, 8.85 and 8.97 ppm (*J* = 5.0 Hz), which are assigned to six protons of the pyrrole moiety. The signals of two inner NHs appeared at –2.26 ppm as a broad peak. The singlet for H3 (9.06 ppm) on the pyrrole of **1c** has disappeared in **2c**, which confirmed that the cyanation reaction had taken place on the 3-position carbon of the pyrrole of **1c**. Furthermore, the structure of the product was confirmed by X-ray diffraction analysis of **2c** (Fig. 2).

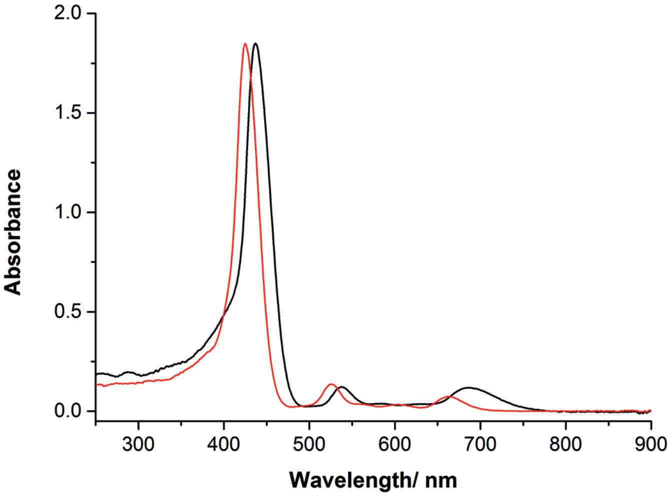
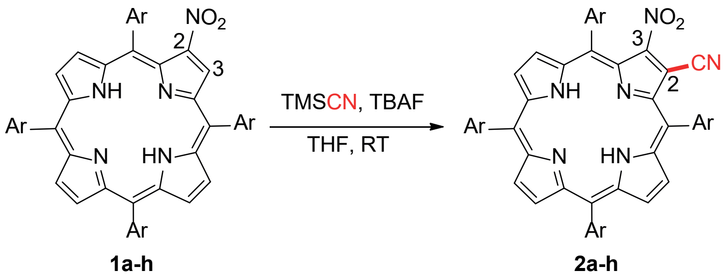


Fig. 1 UV-Vis spectra of **1c** (red line) and **2c** (black line) in CH_2Cl_2.



Ar: **a** 4-CH_3-C_6H_4; **b** 4-CO_2Me-C_6H_4; **c** Ph; **d** 4-Cl-C_6H_4; **e** 4-F-C_6H_4; **f** 4-Br-C_6H_4; **g** 4-CH_3O-C_6H_4; **h** 4-t-Bu-C_6H_4

Scheme 1 Synthesis of 2-cyano-3-nitroporphyrin derivatives.

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Synthesis of novel spiro(indolizine-pyrazole) derivatives *via* 1,3-dipolar cycloaddition of nitrilimine

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The 1,3-dipolar cycloaddition of nitrilimine, generated *in situ* from *N′*-phenylbenzohydrazonoyl chloride and triethylamine, to 7-arylmethylidene-6,7-dihydroindolizin-8(*5H*)-one afforded novel 4′-aryl-2′,5′-diphenyl-2′,4′,5,6-tetrahydro-8*H*-spiro(indolazine-7,3′-pyrazol)-8-ones in moderate yields. The structures of all the products were characterised thoroughly by NMR, infrared spectroscopy and HRMS. The structure and stereochemistry was confirmed by X-ray diffraction analysis.

Keywords: indolizine, spiroheterocycle, 1,3-dipolar cycloaddition, nitrilimine

The indolizine moiety is an important structure found in alkaloids with biological activities, such as (+)-monomorine,[1] indolizidine 209D,[2] polygonatines[3] and kinganone.[4] Some compounds containing the indolizine structure have aroused great interest because of their broad spectrum of biological activities, such as antitumour,[5] antimicrobial,[6] 5-hydroxytryptamine (5-HT3) receptor antagonists,[7] anti-HIV,[8] hypoglycemic[9] and glycogen synthase kinase-3β inhibitors.[10]

The spiroheterocycles are important structures found in many biologically active natural products.[11] Their biological properties make them good targets for drug candidates and clinical pharmaceuticals.[12,13]

1,3-Dipolar cycloaddition reaction of nitrilimine is a classic method to synthesise pyrazole compounds.

In continuation of our work[14–17] on the synthesis of spiroheterocycles, we now report the synthesis of spiroindolizine-pyrazole derivatives by the cycloaddition of nitrilimine and 7-arylmethylidene-6,7-dihydroindolizin-8(5*H*)-ones (Scheme 1).

Results and discussion

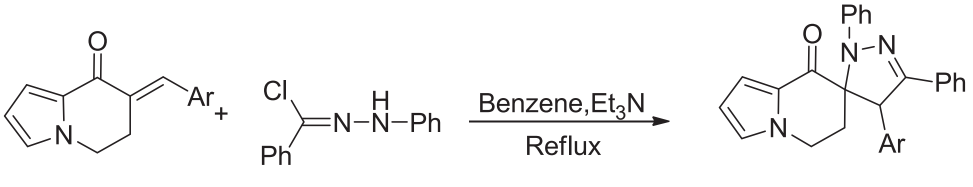
The 1,3-dipolar cycloaddition reaction of 7-arylmethylidene-6,7-dihydroindolizin-8(5*H*)-ones **1** to nitrilimine, generated *in situ* from *N′*-phenylbenzohydrazonoyl chloride and triethylamine, yielded 4′-aryl-2′,5′-diphenyl-2′,4′,5,6-tetrahydro-8*H*-spiro[indolazine-7,3′-pyrazol]-8-ones.

The structures of compounds **2a–h** were established by different spectroscopic techniques (NMR, IR) and HRMS. The high-resolution mass spectrum of **2g** gave a molecular ion peak at *m*/*z* 432.2077, which indicates the addition of one molecule of diphenylnitrilimine to **1g**. The IR spectrum of **2g** displayed $\nu_{C=O}$ at 1648.3 cm^{-1}. The ^{1}H NMR spectrum of **2g** revealed two doublet of doublet of doublets signals at δ 2.16 ppm (J_1 = 14.0 Hz, J_2 = 4.0 Hz, J_3 = 2.0 Hz, H_2C3') and δ 3.00 (J_1 = 14.0 Hz, J_2 = 12.5 Hz, J_3 = 6.0 Hz, H_2C3'), a triplet of doublets signals at δ 3.41 (J_1 = 13.0 Hz, J_2 = 4.0 Hz, H_2C4'), a doublet of doublet of doublets signals at δ 3.78 (J_1 = 13.0 Hz, J_2 = 6.0 Hz, J_3 = 2.0 Hz, H_2C4'), a singlet at δ 2.31 for $-CH_3Ph$, another singlet at δ 5.01 resulting from HC4, two triplets at δ 6.77 (J = 2.0 Hz) and δ 6.88 (J = 7.0 Hz) and one doublet of doublets at δ 6.36 (J_1 = 4.0 Hz, J_2 = 2.5 Hz) assignable to the protons of the pyrrole ring, The presence of signals at δ 7.08–7.55 ppm corresponded to the aromatic protons.

The ^{13}C NMR spectrum of the product **2g** exhibited the presence of $CH_3C_6H_4$ carbon at δ 21.16 and carbonyl carbons at δ 184.17 (C1′). The signals at δ 26.97 and 42.08 were assigned to the carbons of H_2C3' and H_2C4' respectively (based on HMQC). The signal at δ 73.87 represented the spiro carbon of C3. The signal at δ 61.45 indicated the carbon of HC4. In the ^{1}H–^{13}C HMBC map of **2g** (Fig. 1), protons of H_2C3', H_2C4' and HC4 correlated with a spiro carbon (C3) (73.87 ppm) and the carbonyl carbons at δ 184.17 (C1′) correlated with protons of H_2C3' and HC4. Furthermore, the structure of the product was confirmed by X-ray diffraction analysis of **2g** (Fig. 2).

Conclusion

A facile and novel synthesis of spiro compounds was accomplished by the 1,3-dipolar cycloaddition of diphenylnitrilimine and 7-arylmethylidene-6,7-dihydroindolizin-8(5*H*)-ones in moderate yields. The regioselectivity of this reaction was demonstrated by single-crystal X-ray diffraction. Studies of the synthesis of spiroheterocycles are being carried out in our research group.



1a-1h **2a-2h**

Ar: a, C_6H_5; **b,** 4-ClC_6H_4; **c,** 2-ClC_6H_4 **d,** 2,4-$Cl_2C_6H_3$; **e**, 4-FC_6H_4;
f, 4-$CH_3SC_6H_4$; **g**, 4-$CH_3C_6H_4$; **h**, 3,4,5-$(OCH_3)_3C_6H_2$;

Scheme 1 Synthesis of spiroindolizine derivatives.

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Synthesis of 3-cyano-21-nitro-*N*-confused porphyrin derivatives by isoamyl nitrite

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The 3-cyano-21-nitro-*N*-confused porphyrin derivatives were synthesised by the nitration reaction of 3-cyano-*N*-confused-porphyrin with isoamyl nitrite at room temperature in moderate yield. The reaction took placed regioselectively in 21-position carbon of inverted pyrrole of *N*-confused porphyrins.

Keywords: *N*-confused porphyrin, isoamyl nitrite, porphyrin, nitration

2-Aza-21-carbaporphyrins (*N*-confused porphyrins, NCP)[1] are porphyrin isomers containing an inverted pyrrole, have attracted considerable attention in recent years due to their unique structure and potential applications.[2–4] Their reactivity is also attractive, allowing fine-tuning of the properties of the system or profound modification of the structure without destruction of the macrocyclic ring. The inverted pyrrole possesses three sites of varying reactivity (2-N, 3-C, and 21-C), and each of them can be a target of substitution or addition reactions. The reactions possible on the inverted pyrrole ring include halogenation,[5] cyanisation,[6] oxygenation,[7] internal fusions,[8] alkylation[9] and hydroxylation.[10] These reactions drove us to do a further study on the modification of NCP at "inverted" pyrrole.

Porphyrinoid derivatives contained β-nitro group are useful intermediates in synthesis of π-extended porphyrins.[11–13] Generally, β-nitration of porphyrinoid compounds were performed under acid media using HNO_3,[14] $LiNO_3$[15] as $Cu(NO_3)_2$[16] as nitration reagents. These traditional nitration procedures require a large volume of solvent and the work-ups were tedious.

In continuation of our work[17–23] on the synthesis of porphyrinoid derivatives, we now report the synthesis of 3-cyano-21-nitro-*N*-confused porphyrin derivatives by the nitration of 3-cyano-*N*-confused porphyrin with isoamyl nitrite at room temperature (Scheme 1).

Results and discussion

The reaction of the *N*-confused porphyrins (**1a–h**) and excess of isoamyl nitrite in CH_2Cl_2 at room temperature for 4 hours afforded novel 3-cyano-21-nitro-*N*-confused porphyrin derivatives (**2a–h**) in moderate yields. This nitration reaction proceeded with high regioselectivity to afford only one product, which was evident from TLC and ^1H NMR of the crude reaction mixture. The structures of all compounds **2a–h** were established by different spectroscopic techniques (UV, NMR and HRMS).

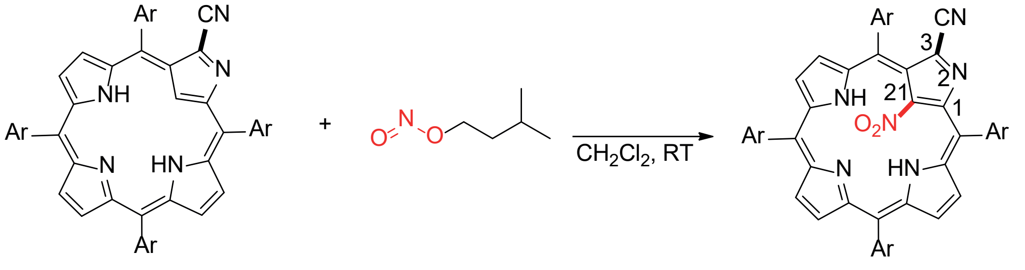
The high resolution mass spectrum of **2b** gave the molecular ion peak at *m/z* 741.2973, which just indicates the addition of one nitro group to **1b**.

The electronic adsorption spectrum of **2b** and **1b** in CH_2Cl_2 are shown in Fig. 1. From the spectrum, we can see the Soret band (492 nm) accompanied by a set of three Q bonds (599, 661, 751 nm). The Soret band of **2b** is bathochromically shifted with respect to the parent 3-cyano-NCP **1b**. These changes maybe result from additional conjugation of the nitro group with the porphyrin chromophore.

The ^1H NMR spectrum of **2b** (298 K, $CDCl_3$) is characterised by six doublets at 8.41, 8.42, 8.61, 8.63, 9.11, 9.17 ppm with $J = 5.0$ Hz which are assigned to six pyrrole protons. The singlet of H21 (–4.23 ppm) on inverted pyrrole of **1b** was disappeared in **2b** which confirmed that nitration reaction had taken place in the 21-position carbon of inverted pyrrole of **1b**. In HMQC the C-21 at 106.6 ppm didn't have correlation with any proton which also confirmed the nitration took place at C-21 on the inverted pyrrole.

Conclusion

In summary, we have developed a method for the synthesis of 3-cyano-21-nitro-NCP derivatives by nitration of 3-cyano-NCP with isoamyl nitrite in dicholoromethane under mild reaction conditions. This simple and efficient method gives products that should be able to be converted into other useful compounds.



1a-h **2a-h**

Ar: **a** Ph; **b** 4-CH_3Ph; **c** 4-OCH_3Ph; **d** 4-SCH_3Ph; **e** 3,4,5-$(OCH_3)_3$Ph; **f** 3,5-$(OCH_3)_2$Ph; **g** 4-ClPh; **h** 4-FPh

Scheme 1 Synthesis of 3-cyano-21-nitro-NCP derivatives.

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RESEARCH PAPER VOL. 41 JULY, 420–422 JOURNAL OF CHEMICAL RESEARCH 2017

Synthesis of 3-cyano-*N*-confused porphyrin derivatives by silyl cyanide

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3-Cyano-*N*-confused porphyrin derivatives were synthesised by the reaction of *N*-confused porphyrin with trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride in moderate yield. The reaction took placed regioselectively in the 3-position carbon of the inverted pyrrole of *N*-confused porphyrins.

Keywords: *N*-confused porphyrin, trimethylsilyl cyanide, porphyrin, tetrabutylammonium fluoride

N-Confused porphyrin (NCP),[1] a porphyrin isomer, has attracted the concern of many chemists due to its unique structure and potential applications.[2] Synthesis of new NCP derivatives have been developed in recent years.[3] NCP has three main reaction sites at N2 (external nitrogen), C3 (external carbon) and C21 (internal carbon). The reactivity of all three sites is due to the "inverted" pyrrole ring. The reaction on the inverted pyrrole ring include nitration,[4] halogenation,[5] cyanisation,[6] oxygenation,[7] internal fusions,[8] alkylation[9] and hydroxylation.[10] These reactions prompted us to do a further study on the modification of NCP at "inverted" pyrrole.

Nitriles are useful intermediates in organic synthesis and they could be transformed into highly valuable compounds such as carboxylic acids,[11] amides[12] and amines.[13]

In continuation of our work[14–17] on the synthesis of *N*-*c*onfused porphyrin derivatives, in this paper, we report the synthesis of 3-cyano-*N*-confused porphyrin derivatives by the reaction of *N*-confused porphyrin with trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride (Scheme 1).

Results and discussion

The reaction of the *N*-confused porphyrins (**1a–i**) and trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride in THF at room temperature for 30 min afforded novel 3-cyano-*N*-confused porphyrin derivatives (**2a–i**) in moderate to high yields. This cyanation reaction proceeded with high regioselectivity to afford only one product, which was evidenced from TLC and ^{1}H NMR of the crude reaction mixture. The structures of all compounds **2a–i** were established by different spectroscopic techniques (UV, NMR and HRMS).

The high resolution mass spectrum of **2a** gave the molecular ion peak at *m/z* 696.3129, which just indicates the addition of one CN to **1a**.

The electronic adsorption spectra of **2a** and **1a** in CH_2Cl_2 are shown in Fig. 1. From the spectra, we can see the Soret band (457 nm) accompanied by a set of three Q bonds (553, 603, 785 nm). All the bands of **2a** are bathochromically shifted with respect to the parent NCP **1a**. These changes may result from additional conjugation of the nitrile group with the porphyrin chromophore.

The ^{1}H NMR spectrum of **2a** (298 K, $CDCl_3$) is characterised by two singlets at 2.67 and 2.71 ppm which are assigned to four methyls of the meso *p*-tolyl substituents, the singlet at –4.23 ppm represents 21-H in inverted pyrrole ring. The signals of inner NHs appear at –1.44 ppm as a broaden peak. The singlet of H3 (7.24 ppm) on inverted pyrrole of **1a** was disappeared in

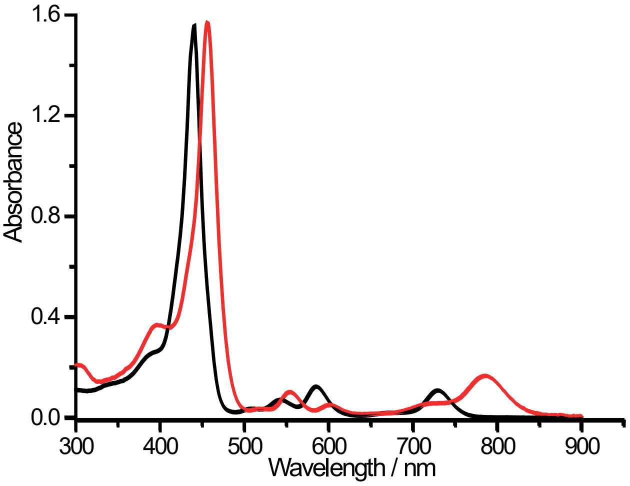
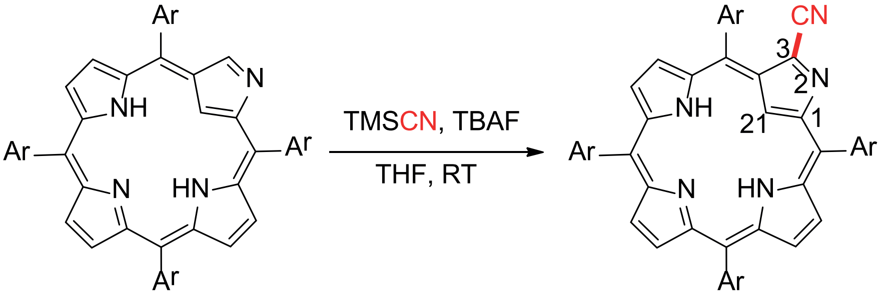


Fig. 1 UV-Vis spectra of **1a** (black line) and **2a** (red line) in CH_2Cl_2.



1a-i **2a-i**

Ar: **a** 4-CH_3Ph; **b** 3-CH_3OPh; **c** 4-CO_2MePh; **d** 3,4,5-$(OCH_3)_3$Ph;
e 4-SCH_3Ph; **f** Ph; **g** 4-ClPh; **h** 4-FPh; **i** 3,5-$(OCH_3)_2$Ph

Scheme 1 Synthesis of 3-cyano-NCP derivatives.

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JOURNAL OF CHEMICAL RESEARCH 2017 VOL. 41 NOVEMBER, 641–644 **RESEARCH PAPER** 641

Synthesis of spiro indazole-tetrahydrothiophenes *via* sulfa-Michael/aldol cascade reactions

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The sulfa-Michael/aldol cascade reaction of 5-arylmethylidene-1-phenyl-6,7-dihydro-1H-indazol-4(5H)-ones and 1,4-dithiane-2,5-diol yielded novel 2'-(4-aryl)-4'-hydroxy-1-phenyl-4',5',6,7-tetrahydro-2'H-spiro[indazole-5,3'-thiophen]-4(1H)-ones in moderate yields. The structures of all the products were characterised thoroughly by NMR, IR and HRMS, together with X-ray crystallographic analysis.

Keywords: 1,4-dithiane-2,5-diol, indazole, tetrahydrothiophene, sulfa-Michael/aldol reaction

Tetrahydrothiophenes are important units of many natural products and pharmaceutical agents with important biological activities, including anti-HIV,[1] antibacterial,[2] A3 adenosine receptors,[3] glucosidase inhibitors[4] and antitumour behaviour.[5]

The sulfa-Michael/aldol cascade reaction of 1,4-dithiane-2,5-diol and olefins, which are activated by electron withdrawing groups, is the most efficient and straightforward process for synthesis of tetrahydrothiophene derivatives.[6] The catalyst used in this kind of reaction has significant effects on the yield and stereochemistry of the product. The catalysts include chiral organocatalysts,[7–9] 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU),[10] pyrrolidine,[11] triethylaluminium (TEA),[12,13] K_2CO_3[14,15] and piperidine.[16]

The indazole moiety is also an important structure found in natural products such as nigellidine-4-O-sulfite,[17] nigellidine,[18] nigellicine[19] and nigeglanine,[20] having diverse biological activities. Indazole is found in many synthetic derivatives having a broad spectrum of biological activities, including antitumour,[21] antiarrhythmic and analgesic activities,[22] and as NO-synthase inhibitors[23] and HIV protease inhibitors.[24]

Spiroheterocycles are interesting structural motifs present in a number of bioactive natural products.[25] The presence of a spirocarbon considerably influences the biological activities, including antimicrobial, antitumour, antibiotic and inhibitors of human NK-1 receptor.[26]

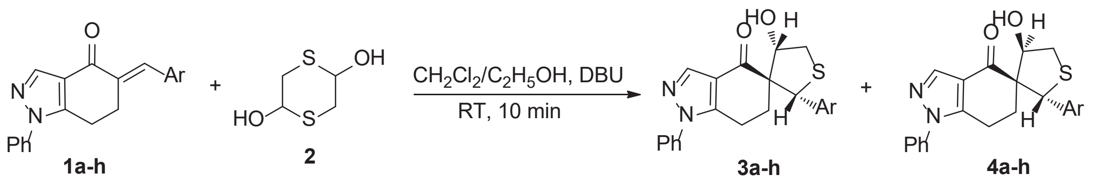
In continuation of our work on the synthesis of spiroheterocycles,[27–30] we now report the synthesis of spiro indazole-tetrahydrothiophene derivatives by means of the sulfa-Michael/aldol cascade reaction of 1,4-dithiane-2,5-diol and 5-arylmethylidene-1-phenyl-6,7-dihydro-1H-indazol-4(5H)-ones (Scheme 1).

Results and discussion

A mixture of 5-arylmethylidene-1-phenyl-6,7-dihydro-1H-indazol-4(5H)-ones **1** (1 mmol), 1,4-dithiane-2,5-diol **2** (1 mmol) and DBU (50 mol%) in dichloromethane/ethanol (5 mL, 4:1 v/v) was stirred at room temperature for 10 min, which afforded 2'-(4-aryl)-4'-hydroxy-1-phenyl-4',5',6,7-tetrahydro-2'H-spiro[indazole-5,3'-thiophen]-4(1H)-one diastereomers **3** and **4** in moderate yields.

The structures of all compounds **3** and **4** were established by different spectroscopic techniques (NMR, IR) and by HRMS. The high-resolution mass spectrum of **3e** gave the molecular ion peak at *m/z* 391.1475, which indicates the addition of just one molecular equivalent of 2-mercaptoacetaldehyde to **1e**. The IR spectrum of **3e** displayed $\nu_{C=O}$ at 1655.1 cm^{-1}. The ^{1}H NMR spectrum of **3e** revealed two multiplets at δ 1.98–2.05 and 2.35–2.42 ppm, which were assigned to H_2C-6, a multiplet at δ 2.05–2.10 ppm and a doublet of triplet signals at δ 3.41 ppm (J_1 = 17.0 Hz, J_2 = 6.0 Hz), assigned to H_2C-7, and a singlet at δ 2.28 ppm, assigned to $-CH_3Ph$. The triplet at δ 2.98 ppm (J = 10.0 Hz) and a doublet of doublets signals at δ 3.18 ppm (J_1 = 10.0 Hz, J_2 = 6.5 Hz) were assigned to H_2C-5'. The singlets at δ 5.16 and 8.00 ppm resulted from HC-2' and H-3, respectively, the doublet of doublets at δ 5.02 (J_1 = 9.0 Hz, J_2 = 6.5 Hz) were assigned to H-4'. The presence of signals at δ 7.02–7.43 ppm corresponded to the aromatic protons.

The ^{13}C NMR spectrum of the product **3e** exhibited the presence of $-CH_3Ph$ carbon at δ 20.96 ppm and a carbonyl carbon at δ 194.51 ppm (C-4). The signals at δ 20.14 and 21.95 ppm are assigned to the carbons of H_2C-6 and H_2C-7, respectively (based on heteronuclear multiple-quantum coherence, HMQC). The signal at δ 60.60 ppm represents the spiro carbon of C-5. The signals at δ 33.80 and 79.65 ppm indicate the carbons of C-5' and C-4'. In the ^{1}H–^{13}C heteronuclear multiple-bond correlation (HMBC) map of **3e** (Fig. 1), the protons of H-2', H-4' and H-6 correlate with a spiro carbon (C-5) (60.60 ppm) and the carbonyl carbons at δ 194.51 ppm (C-4) correlate with the protons of H-4' and H-6. Furthermore, the structure of the product was confirmed by X-ray diffraction analysis of **3e** (Fig. 2).



Ar: a, C_6H_5; **b,** 4-ClC_6H_4; **c**, 4-BrC_6H_4; **d,** 4-FC_6H_4 **e,**4-$CH_3C_6H_4$;
f, 4-$CH_3SC_6H_4$; **g**, 3,5-$(OCH_3)_2C_6H_3$; **h**, 3,4,5-$(OCH_3)_3C_6H_2$;

Scheme 1 Synthesis of dispiro derivatives.

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Anal Bioanal Chem (2017) 409:4001–4008
DOI 10.1007/s00216-017-0343-5

RESEARCH PAPER

Highly sensitive and selective determination of hydrogen sulfide by resonance light scattering technique based on silver nanoparticles

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Received: 21 January 2017 / Revised: 17 March 2017 / Accepted: 28 March 2017 / Published online: 17 April 2017

Abstract We have developed a green approach to prepare DNA-templated silver nanoparticles (Ag-NPs) from the direct reaction between Ag^+ and ascorbic acid in the presence of DNA and sodium hydroxide. The Ag-NPs showed strong resonance light scattering (RLS) intensity property. Then, the interaction between hydrogen sulfide (H_2S) and Ag-NPs was studied by measuring their RLS spectra. The results showed that there is a strong interaction between Ag-NPs and H_2S, which resulted in a decrease in the size of Ag-NPs and a decrease in the RLS intensity of the Ag-NPs solution at the wavelength of 467 nm. The results demonstrated that the RLS technique offers a sensitive and simple tool for investigating the interaction between Ag-NPs and H_2S, which can be applied to detect H_2S with high sensitivity and selectivity without complex readout equipment. The linear range for H_2S determination was found to be the range from 5.0×10^{-9} to 1.0×10^{-7} mol L^{-1}, and the detection limit ($3\sigma/k$) was 2.8×10^{-9} mol L^{-1}. Moreover, the proposed method was applied for the determination of H_2S in natural water samples with satisfactory results.

Keywords H_2S determination · Silver nanoparticles · Resonance light scattering

Introduction

Hydrogen sulfide (H_2S) is a toxic gas with the characteristic odor of rotten eggs, which is usually derived from rotting organic matter, bacterial fermentation, industrial production, petroleum refining, etc. Some studies have found that H_2S can damage the human respiratory system and also affect the oxidation process in cells at certain concentrations, leading to oxygen starvation of cells and tissues [1, 2]. On the other hand, it can prevent myocardial ischemia through exogenously perfuse Na_2S at doses ranging from 10 to 500 μg/kg, and effectively treat the heart failure caused by myocardial ischemia [3, 4]. This is probably because H_2S acts as a potent antioxidant slowing the aging process of cells [5]. Moreover, endogenous H_2S is an important gaseous signal molecule that is involved in the regulation of the central nervous [6–8], respiratory, digestive, and endocrine systems [9]. Other studies have shown that the concentration of H_2S in the human body is related to 21-trisomy syndrome [10] and Alzheimer's disease [11]. Thus, H_2S is an important molecule involved in many biological processes, and various techniques have been developed for determination of H_2S concentrations in different samples. Some of the common H_2S determination methods include electrochemistry [12, 13], inductively coupled plasma atomic emission spectroscopy (ICP-AES) [14], gas chromatography [15], chemiluminescence (CL) methods [16], colorimetry [17], and the methylene blue assay [18]. These methods provide excellent performance, but they are generally complicated, costly, and time-consuming. Hence, it is important to develop a rapid, simple, and inexpensive method for H_2S determination.

Resonance light scattering (RLS) is a relatively new spectral analysis technique, which has received much attention since it was originally proposed by Pasternack et al. in 1993 [19]. The RLS signal is obtained by simultaneous scanning of

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Electronic supplementary material The online version of this article (doi:10.1007/s00216-017-0343-5) contains supplementary material, which is available to authorized users.

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ANALYTICAL SCIENCES MAY 2017, VOL. 33

Fabrication of Water-soluble Fluorescent Polymeric Micelles for Selective Detection of Hg^{2+} in Blood Serum

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In this study, amphiphilic diblock copolymers were designed and synthesized *via* the incorporation of reversible addition-fragmentation chain transfer radical polymerization (RAFT) and a subsequent grafting technique. Subsequently, Hg^{2+}-sensitive water-soluble fluorescent polymeric micelles (FNs) were prepared by a reprecipitation strategy. The spectroscopic characteristics demonstrate that the fluorescein isothiocyanate (FITC) was successfully linked into the polymer. Due to the promoted reaction of desulfurization cyclization by Hg^{2+}, the fluorescence of fluorescein in FNs was obviously quenched. The as-prepared FNs showed admirable Hg^{2+}-sensitivity (detection limit: 54 nM), excellent water-solubility and high selectivity. In addition, FNs were successfully used to determine Hg^{2+} in blood serum. We expected that the as-prepared FNs could perform potential applications in imaging, sensing, and bioanalytic chemistry.

Keywords Fluorescence polymeric micelles, Hg^{2+}, blood serum, RAFT

(Received September 29, 2016; Accepted November 29, 2016; Published May 10, 2017)

Introduction

Obtaining simple and convenient nanosensors, which were cost-effective and applicable to imaging and sensing, became a sought-after goal.[1-5] Mercury ion (Hg^{2+}) posed a tremendous menace owing to its bioaccumulation, such as permanent damage and slow accumulation in the central nervous and endocrine systems.[6] Moreover, it can easily give rise to a wide variety of diseases, including prenatal brain damage, serious cognitive problems, motion disorders and Minamata disease.[7,8] In addition, once introduced into the marine environment, some bacteria transform inorganic Hg^{2+} into methylmercury.[9,10] As we know, this is implicated as a cause of mercury pollution related to serious irreversible neurological damage due to its highly neurotoxic property.[9-11] The Hg^{2+} also caused the deterioration of water quality due to its notorious water and environmental pollution property.[12,13] Hence, highly sensitive and selective detection of Hg^{2+} was of significance for organisms and environment.

A number of methods have been used to detect Hg^{2+}, such as atomic absorption/emission spectroscopy,[14] gas chromatography,[15] cold vapor atomic fluorescence spectrometry,[16] voltammetry,[17] *etc.* However, these conventional methods are not commendably applied in living biosystems due to several common faults, including being time-consuming, meading complicated sample preparation and a sophisticated process.[18,19] In contrast, fluorescence spectroscopy reveals a promising way owing to its ease of operation, being non-invasive, and having highly sensitive and selective properties.[20-23]

To date, many fluorescent sensors for Hg^{2+} have been reported.[24-32] However, many of these sensors are small molecules, which can only work in organic or mixed solvents, may restrict their applications in the environmental or bio-related fields due to their low water solubility and high toxicity.[33,34] To overcome these limitations, polymeric micelles-based sensors have recently attracted considerable interest owing to their excellent properties, including improved water solubility and longer *in vivo* circulation times, effective distribution of fluorescent dyes, *etc.*[35,36] Also, several polymeric particles-based fluorescence nanosensors have been developed for Hg^{2+} detection.[36-38] So far, an excellent fluorescent sensor for Hg^{2+} in a totally aqueous solution is still rare. Therefore, designing water-soluble (dispersible) fluorescent nanosensors for detecting Hg^{2+} is of great significance.

Herein, we firstly prepared amphiphilic diblock copolymers (PEO-b-P(St-co-VBA-co-VBF) *via* reversible addition-fragmentation chain transfer radical polymerization (RAFT) and a subsequent grafting technique (Scheme 1). Then, the amphiphilic diblock copolymers could be easily turned to form polymeric micelles in aqueous solution by a reprecipitation strategy, as illustrated in Scheme 2. With the addition of Hg^{2+}, the fluorescence of the fluorescein units could be effectively quenched through desulfurization cyclization of the thiourea moiety, resulting in the selectively fluorescent sensing of Hg^{2+} in a totally aqueous media and slectivitly detecting Hg^{2+} in blood serum (Scheme 2).

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Received: 9 August 2016 | Revised: 14 September 2016 | Accepted: 20 September 2016
DOI: 10.1002/bio.3237

WILEY LUMINESCENCE
The Journal of Biological and Chemical Luminescence

RESEARCH ARTICLE

Silver nanoclusters stabilized with denatured fish sperm DNA and the application on trace mercury ions detection

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Funding information
National Natural Science Foundation of China, Graduate Innovation Foundation of Hunan University of Science and Technology. 21445008 to SC. 21275047 to YL.

Abstract

In this study, fluorescent silver nanoclusters (Ag NCs) were synthesized using denatured fish sperm DNA as the template. In contrast to other methods, this method did not use artificial DNA as the template. After their reaction with denatured fish sperm DNA, Ag^+ ions were reduced by $NaBH_4$ to form Ag NCs. The Ag NCs showed a strong fluorescence emission at 650 nm when excited at 585 nm. The fluorescence intensity increased fourfold at pH 3.78, controlled with Britton–Robinson buffer solution. The fluorescence of the Ag NCs was quenched in the presence of trace mercury ions (Hg^{2+}) in a weakly acidic medium and nitrogen atmosphere. The extent of the fluorescence quenching of Ag NCs strongly depends on the Hg^{2+} ion concentration over a linear range from 2.0 nmol L^{-1} to 3.0 μmol L^{-1}. The detection limit (3σ/k) for Hg^{2+} was 0.7 nmol L^{-1}. Thus, a sensitive and rapid method was developed for the detection of Hg^{2+} ions.

KEYWORDS

Ag nanocluster, fluorescence quenching, Hg^{2+} detection

1 | INTRODUCTION

Metal nanoclusters (NCs) are special metal nanoparticles, usually composed of several metal atoms.[1] Metal NCs, such as Au and Ag NCs, exhibit unique optical, electrical and chemical properties that differ from those of the corresponding metal nanoparticles; therefore, metal NCs have attracted much attention in recent years.[2] Because of their smaller size and lack of toxicity, in particular, Ag NCs have promising prospects in the field of biological labeling,[3,4] optical sensing, metal ion detection[5–7] and so on.[8–10] However, it is difficult to synthesize Ag NCs in aqueous solution because they easily aggregate to form larger nanoparticles in order to decrease their surface energy.[1] Therefore, templates or capping agents are usually added to avoid the aggregation of Ag NCs during their synthesis. Currently, the templates used in the synthesis of Ag NCs include dendrimer,[11,12] polymers,[13–15] some small molecules,[16] oligonucleotides[17–21] and protein.[22–24] Recently, the use of oligonucleotide as a template in the synthesis of Ag NCs has attracted increasing attention because Ag NCs that used oligonucleotide as the template had a higher quantum yield, were size-tunable and showed good biocompatibility. For example, Dickson and co-workers successfully synthesized Ag NCs by first using a 12-base oligonucleotide (5′-AGGTCGCCGCCC-3′) as the template; the Ag NCs showed stronger interactions with cytosine bases than other bases.[17] Based on this phenomenon, the 12-cytosine oligonucleotide has been used as a template for the synthesis of Ag NCs.[18,25] Many chemists, such as Petty and Dickson, have studied the synthesis and mechanism of DNA-templated Ag NCs (DNA–Ag NCs). The results indicate that the size and emission wavelength of Ag NCs can be controlled by adjusting the base sequence of DNA.[19,20,26] Gwinn and her team found that the fluorescence of Ag NCs is related to the sequence and secondary structure of DNA at the same time.[27] Wang and his team designed specific DNA sequences with an inserted cytosine loop as a template for the synthesis of Ag NCs; the results showed that the properties of Ag NCs are highly sequence dependent.[28] Native DNA was not used as the template for Ag NCs synthesis before Kononov used native calf thymus DNA.[29] However, the chemical yield of the fluorescent species was relatively weak. Thus, it is important to synthesize Ag NCs with strong fluorescence emission using native DNA as the template.

We developed a strategy for the synthesis Ag NCs using denatured fish sperm DNA as the template, the resulting Ag NCs showed strong fluorescence emission at 650 nm when excited at

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Abbreviations used: Ag NC, Silver nanocluster; BR, Britton–Robinson buffer; dsDNA, Double-stranded DNA; HAc, Acetic acid; HRTEM, High-resolution transmission electron microscopy; ssDNA, Single-stranded DNA; TEM, Transmission electron microscopy; UV, Ultraviolet; Vis, Visible.

Tetrahedron 73 (2017) 3099–3105

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Cesium-catalyzed highly regioselective synthesis of (Z)-vinylic selenosulfides via thioselenation of alkynes with unsymmetrical diorganoyl dichalcogenides

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ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form
1 April 2017
Accepted 6 April 2017
Available online 8 April 2017

Keywords:
Thioselenation
(Z)-vinylic selenosulfide
Unsymmetrical diorganoyl dichalcogenide
Cesium hydroxide monohydrate
Terminal alkyne

ABSTRACT

A novel one-pot approach for the synthesis of (*Z*)-vinylic selenosulfides is demonstrated through the thioselenation of a wide range of alkynes with unsymmetrical diorganoyl dichalcogenides (RSSePh) catalyzed by cesium hydroxide monohydrate, avoiding the use of the transition metal catalyst and the previous preparation of chalcogen alkynes. Other outstanding features include mild reaction conditions, high regio- and stereo-selectivity, excellent yields and wide functional group tolerance.

1. Introduction

Owing to their useful biological activities and regio-, chemo-stereo-selectivity, organochalcogen compounds have become attractively synthetic goal in organic chemistry,[1] especially for the preparation of tri- and tetra-substituted alkenes, which are main framework for lots of natural products such as Nileprost analogues[2] and Ratjadone,[3] as well as drugs such as Tamoxifen[4] and Roaccutane[5] (Scheme 1). Among these organochalcogen compounds, vinylic selenides, vinylic sulfides and vinylic selenosulfide are the most versatile intermediates.[6] In spite of the great success achieved so far in this area,[7] some important challenges still remain. Harsh reaction conditions,[8] limited functional group compatibility,[9] and low regio- and srereo-selectivity[10] for the generation of vinnylic selenosulfides and the requisite use of expensive precious metal catalysts[11] or effluvial reagents[12] are some drawbacks of the stated methods.

Comparing to vinylic selenides and vinylic sulfides, vinylic selenosulfides containing both C–S and C–Se on the same double bond present especial activities, which make it can be more useful candidate materials for drug development.[6i,13] Many procedures for the synthesis of vinylic selenosulfides have been reported.[14] Thioselenation of alkynes is one of the most efficient methods for preparation of vinylic selenosulfides.[15] The thioselenation of terminal alkynes using diaryl disulfides and diaryl diselenides as chalcogenide reagents under photoirradiation[16a] or hν[14e] were reported (Scheme 2, a and b). However, products were obtained as a mixture of (E)- and (Z)-isomers, which were difficult to be purified due to their similar polarity, and only diaromatic dichalcogenide derivatives were described in this thioselenation. Later, Zeni's group reported an efficient route to (Z)-vinylic selenosulfides via thioselenation of propargylic alcohols with unsymmetrical diorganoyl dichalcogenides (RSSePh) in the presence of 3.0 equivalent of *n*-butyllithium (Scheme 2, c).[17] This method is only suitable for propargylic alcohols, and the reaction must be performed under strict anhydrous conditions. In our previous work, we reported an one-pot thioselenation of alkynes with a binary system of diaryl disulfides and diaryl diselenides for highly regio-selective synthesis of (Z)-vinylic selenosulfides (Scheme 2, d).[6i] Even though the

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http://dx.doi.org/10.1016/j.tet.2017.04.009

Received: 16 August 2016 | Revised: 31 October 2016 | Accepted: 5 November 2016

DOI: 10.1002/poc.3672

WILEY Journal of Physical Organic Chemistry

RESEARCH ARTICLE

Abnormal effect of hydroxyl on the longest wavelength maximum in ultraviolet absorption spectra for bis-aryl Schiff bases

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Funding information
Scientific Research Fund of Hunan Provincial Education Department, Grant/Award Number: 14C0466 National Natural Science Foundation of China, Grant/Award Number: 21272063

Abstract

Two sets of bis-aryl Schiff bases that contain 4(or 4′)-OH and 2(or 2′)-OH were synthesized. The first set consists of 4-HOArCH=NArY and XArCH=NArOH-4′, and the second set consists of 2-HOArCH=NArY and XArCH=NArOH-2′. Their ultraviolet absorption spectra were measured and investigated. A very interesting phenomenon was observed by analyzing their wave number ν_{max} (cm^{-1}) of longest wavelength maximum λ_{max} (nm) of ultraviolet. Compared with the change regularity of the ν_{max} of XArCH=NArY (where the X and Y excluded OH), the 4′-position hydroxyl (4′-OH) and 2′-position hydroxyl (2′-OH) have abnormal performance. The details are the following: the 4′-OH contributes an additional red shift to the ν_{max} of XArCH=NArOH-4′ (λ_{max} increase), whereas the 2′-OH contributes an additional blue shift to the ν_{max} of XArCH=NArOH-2′ (λ_{max} decrease). In addition, there are ortho steric effects of all 2-OH and 2′-OH on the ν_{max} for 2-HOArCH=NArY and XArCH=NArOH-2′, and the ortho steric effect contributes a red shift to their ν_{max}. These experimental facts can provide an important theoretical reference for us using aryl Schiff base compounds as optical materials and performing the molecular design.

KEYWORDS

hydroxyl, ortho steric effect, Schiff base, substituent effect, ultraviolet absorption spectra

1 | INTRODUCTION

Photoelectric material is a kind of functional materials,[1–7] and its energy of light absorption is an important property for its application. Aryl Schiff bases that contain classical π-conjugated system have potential optoelectronic properties and were applied well in many fields of optical functional materials.[8–11] The substituents at the aromatic rings of an aryl Schiff base molecule have important influence on the molecular photoelectric properties. Therefore, the clear understanding on the relationship between their molecular structure and optical property is the basis for the molecular design and application of optoelectronic materials of aryl Schiff bases.

Recently, Hasan Tanak[12,13] investigated the energetic and structural properties of the Schiff base compounds, 2-methyl-6-[2-(trifluoromethy) phenylimino-methyl] phenol and (E)-2-[(2-chlorophenyl) iminomethyl]-4-trifluoromethoxyphenol. He used density functional theory to calculate their optimized geometry and optical properties. The calculated results are in agreement with the experimental facts. Cao et al[14,15] investigated systematically the relationship between the substituent effect and the longest wavelength maximum λ_{max} (nm) of ultraviolet (UV) absorption for some aryl Schiff bases, and obtained good results, where the used parameters included excited-state substituent parameter σ_{CC}^{ex} [14,15] and ground-state substituent polarity parameter (ie, Hammett constant σ).[16] The compounds involved are the following: 4,4′-disubstituted N-(benzylidene)-anilines p-XArCH=NArY-p,[17] symmetrical Schiff bases derived from 1,4-phenylenediamines p-XArCH=NArN=CHArX-p,[18] extended benzylidene anilines p-XArCH=NArCH=CHArY-p,[19] N-(4-substituted bezylidene) cyclohexylamines p-XArCH=NC$_6$H$_{11}$,[20] N-(phenyl-ethylene)-anilines XArC

Received: 17 January 2017 | Revised: 7 March 2017 | Accepted: 16 March 2017

DOI: 10.1002/poc.3705

RESEARCH ARTICLE

WILEY Journal of Physical Organic Chemistry

Influence of the methyl group at C=C bridging bond of stilbene on the longest wavelength maximum in ultraviolet absorption spectra

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Funding information
National Nature Science Foundation of China, Grant/Award Number: 21672058, 21272063

Abstract

The compounds stilbenes XArCH=CHArY(XSBY) and 1,2-diphenylpropylenes XArC(Me)=CHArY(XSMBY) have bridging groups CH=CH and $C(CH_3)$=CH, respectively, in which the $C(CH_3)$=CH has a side-group CH_3 at the carbon-carbon double bond. A series of XSMBY were synthesized, and their longest wavelength maximum λ_{max} (nm) in ultraviolet absorption spectra were measured in this work. We investigated the change regularity of the ν_{max} (cm^{-1}, $\nu_{max} = 1/\lambda_{max}$) of XSMBY and compared it with that of XSBY. The results indicate that (1) there is no good linear relationship between the ν_{max} of XSMBY and that of XSBY. (2) Because of the influence of the side-group CH_3, in case of the same couple of groups X and Y, the λ_{max} of XSMBY is shorter than that of XSBY, that is, it has a blue shift. (3) The cross-interaction between the side-group CH_3 and Y has an important effect on the ν_{max} of XSMBY, while the cross-interaction between the side-group CH_3 and X has a little effect on the ν_{max} and can be ignored. (4) The specific cross-interaction between X and Y has important effect on the ν_{max} of XSMBY, whereas it has no important effect on the ν_{max} of XSBY.

KEYWORDS

diphenyl propylene, side-group, stilbene, substituent effect, wavelength of ultraviolet absorption

1 | INTRODUCTION

Stilbene molecule has a classic π-conjugated system in which 2 benzene rings are connected by a carbon-carbon double bond. It has good chemical properties and is widely used in medicines, foods, functional materials, dyes, and other industries.[1–9] Especially because of its good 2-photon absorption effect,[10] molecular adjustability, excellent fatigue resistance, photoelectric discoloration, and fluorescence adjustability,[11] it is prospected wide applications in many fields of optical functional materials. Therefore, stilbene derivatives received significant attention and were a hot point of the optical study in the past decades.[12,13]

Stilbene and its derivatives were taken as model molecules for the study of luminophores,[14,15] in which a chemical modification of the parent molecule was performed. Then the relationship between the molecular structures and optical properties of the compounds was theoretically and experimentally explored, to find out the change regularity of their optical property for instructing the synthesis of various functional materials.[16–18]

To quantify the influence of substituents at aromatic ring on the chemical property of aromatic compounds, in 1937, Hammett[19] proposed σ-constant to express the contribution of substituent electronic effect to the ground-state molecule. Hammett constant σ was widely used but was less successful in quantifying the UV absorption spectra of organic compounds. In 2008, Cao et al.[20] proposed excited-state substituent constant σ_{cc}^{ex} to express the contribution of substituent electronic effect to the excited-state molecule, and then they used the σ_{cc}^{ex} to quantify the UV absorption spectra of many kinds of compounds.[21–25] They observed that the

Bioorganic & Medicinal Chemistry Letters 27 (2017) 530–532

Contents lists available at ScienceDirect

Bioorganic & Medicinal Chemistry Letters

journal homepage: www.elsevier.com/locate/bmcl

Synthesis and biological evaluation of novel hydroxybenzaldehyde-based kojic acid analogues as inhibitors of mushroom tyrosinase

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ARTICLE INFO

Article history:
Received 9 August 2016
Revised 17 November 2016
Accepted 8 December 2016
Available online 9 December 2016

Keywords:
Kojic acid
Tyrosinase inhibitors
Benzaldehyde
1,2,4-Triazole

ABSTRACT

Two series of novel kojic acid analogues (**4a–j**) and (**5a–d**) were designed and synthesized, and their mushroom tyrosinase inhibitory activities was evaluated. The result indicated that all the synthesized derivatives exhibited excellent tyrosinase inhibitory properties having IC_{50} values in the range of 1.35 ± 2.15–17.50 ± 2.75 μM, whereas standard inhibitor kojic acid have IC_{50} values 20.00 ± 1.08 μM. Specifically, 5-phenyl-3-[5-hydroxy-4-pyrone-2-yl-methylmercap-to]-4-(2,4-dihydroxyl-benzylamino)-1,2,4-triazole (**4f**) exhibited the most potent tyrosinase inhibitory activity with IC_{50} value of 1.35 ± 2.15 μM. The kinetic studies of the compound (**4f**) demonstrated that the inhibitory effects of the compound on the tyrosinase were belonging to competitive inhibitors. Meanwhile, the structure-activity relationship was discussed.

Introduction

Tyrosinase (EC 1.14.18.1) is copper-containing metalloenzyme that are widespread among microorganisms, plants, and animals. They catalyze the *ortho*-hydroxylation of monophenols, which leads to the corresponding o-diphenols, as well as the oxidation of catechols, which leads to the corresponding o-quinones,[1] under many conditions, these then react further to result in the formation of various pigments.[2] Although the melanin production in human skin is a major defense mechanism against UV light, excessive accumulations of epidermal pigmentation can cause various hyperpigmentation disorders. Therefore, the regulation of melanin synthesis via the inhibition of tyrosinase is an important research topic.[3] In clinical usage, tyrosinase inhibitors are used for treatments of dermatological disorders related to melanin hyperaccumulation and are essential in cosmetics for depigmentation,[4] such as age spots and freckle, caused by the accumulation of an excessive level of epidermal pigmentation.[5] Inhibition of tyrosinase is equally important commercially. In most fruits and vegetables, the enzyme is responsible for undesired browning that takes place during senescence or damage during post-harvest handling, leading to faster degradation and shorter shelf life.[6] Taking into account the key role of tyrosinase in melanin production, many tyrosinase inhibitors have been found application in cosmetics and pharmaceutical products.[7,8] A large number of tyrosinase inhibitors have been reported but only a few are used because of their limitations with regards to cytotoxicity, selectivity and stability. Thus, it is great need of developing new tyrosinase inhibitors without causing adverse reactions.

So far, a number of kojic acid and benzaldehyde analogues have been reported as mushroom tyrosinase inhibitors,[9,10] such as Rho et al. reported that Kojyl thioether 2-((4-Hydroxyphenylthio)methyl)-5-hydroxy-4*H*-pyran-4-one inhibited mushroom tyrosinase with an IC_{50} of 0.54 μM which is better kojic acid ($\text{IC}_{50} = 48.52$ μM),[11] Li et al. reported that chlorobenzaldehyde thiosemicarbazones had inhibitory activity on tyrosinase.[12] Previously, we have also reported the synthesis of 1,2,4-triazoles-containing kojic acid derivatives by reactions of 5-hydroxy-2-chloromethyl-4H-pyran-4-one with 5-substituted-3-mercapto-4-amino-1,2,4-triazole,[13] and most of them showed significant tyrosinase inhibitory activity. As a part of our continuous project aimed at searching for new effective mushroom tyrosinase inhibitors, we hybridized the kojic acid with Hydroxybenzaldehyde by a linker 1,2,4-triazole to form 5-substituted-3-[5-hydroxy-4-pyrone-2-yl-methylmercapto]-4-aryl-methylamino-1,2,4-triazole **(4)** and 5-substituted-3-[5-hydroxy-4-pyrone-2-yl-methylmercapto]-4-arylmethyleneamino-1,2,4-triazole **(5)**.

The synthetic procedure employed to obtain the target compounds **4a–j** and **5a–d** was depicted in Scheme 1. The intermediate

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http://dx.doi.org/10.1016/j.bmcl.2016.12.027
0960-894X/

Chemical Physics Letters 667 (2017) 254–259

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Research paper

A novel D2-A-D1-A-D2-type donor–acceptor conjugated small molecule based on a benzo[1,2-*b*:4,5-*b*′]dithiophene core for solution processed organic photovoltaic cells

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ARTICLE INFO

Article history:
Received 26 July 2016
In final form 28 October 2016
Available online 31 October 2016

Keywords:
Organic solar cells
Bulk heterojunction
Donor-acceptor
Quinoxaline
Photovoltaic performances

ABSTRACT

A novel D2-A-D1-A-D2-type donor–acceptor conjugated small molecule (DTPA-Q-BDT-Q-DTPA) with a benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) core and two D2-A arms has been synthesized and employed as electron donor for organic solar cells. Solution-processed organic photovoltaic (OPV) devices were fabricated with a configuration of ITO/PEDOT:PSS/DTPA-Q-BDT-Q-DTPA:[6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$)/LiF/Al. A power conversion efficiency (PCE) of 1.22% with an open-circuit voltage (V_{OC}) of 0.64 V, a short-circuit current (J_{SC}) of 6.10 mA cm^{-2}, and a fill factor (*FF*) of 31.0% was achieved. The PCE is 2.9 times higher than that in the other devices using D2-A-type small molecule TPA-Q-TPA as donor.

1. Introduction

Solution processable organic solar cells (OSCs) have drawn great attention in recent years, due to their advantages of easy fabrication, low cost, light weight, and flexibility like polymer solar cells (PSCs), as well as their high purity and definite molecular weight, which may give the photovoltaic properties of the organic molecules good reproducibility [1–8]. Among the developed OSCs based on small molecular donor materials, most of them are built by some electron donor (D) and electron acceptor (A) units because of the broad absorption spectra which resulting from intermolecular charge transfer (ICT) transitions between the D and A units [9,10]. To date, solar power conversion efficiencies (PCE) of 10.10% have been demonstrated, representing a promising important advance in the development of solution processable OSCs [11]. However, with regard to efficiency, OSCs can still not compete with silicon-based solar cells. Therefore, it remains a great challenge to the research community to prepare new high performance solution-processable small organic molecules for organic photovoltaic (OPV) applications. Among the small molecule materials tested for OSCs, new D-A organic small molecules are urgently needed which require new design concepts and novel building blocks to maximize the solar cell parameters [12–22].

To date, the molecular architectures of most D-A organic small molecules for OSCs can be classified into two main categories: acceptor-donor-acceptor (A-D-A) and donor-acceptor-donor (D-A-D) systems. A-D-A systems, in which D units are end-capped with various A units are currently among the most successful molecular architectures because of the lower highest occupied molecular orbital (HOMO) energy levels and better light-harvesting properties. For instance, Zhan et al. reported a A-D-A organic small molecules of BDT-2DPP containing a benzo[1,2-*b*:4,5-*b*′]-dithiophene (BDT) core and two diketopyrrolopyrrole (DPP) arms, which demonstrated a PCE of 5.79% in OSCs [13]. In 2015, Chen et al. reported a A-D-A organic small molecules of DRCN5T and achieved a PCE of 10.10% which is the highest PCE ever reported [11]. Recently, our group reported an A-Ar-A system, in which the central aryl fused ring was end-capped with two DPP units and a PCE of 5.88% was obtained, the result demonstrates that the planar structure of the aryl fused ring can improve the photovoltaic performance of OSCs [16].

Inspired by the work mentioned above, we reported a novel D2-A-D1-A-D2-type (DTPA-Q-BDT-Q-DTPA) conjugated small molecule with a BDT core and two D2-A arms. BDT was used as the central core for symmetrical planar structure and higher mobility. Moreover, BDT is a well-known D unit in the D-A copolymers

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http://dx.doi.org/10.1016/j.cplett.2016.10.076
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Journal of Molecular Structure 1151 (2018) 230–235

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

A highly sensitive and selective fluorescent sensor for detection of sulfide anion based on the steric hindrance effect

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ARTICLE INFO

Article history:
Received 10 May 2017
Received in revised form
9 August 2017
Accepted 15 August 2017
Available online 18 August 2017

Keywords:
Sulfide anion
Mercapto amino-acid
Fluorescent sensor
Steric hindrance effect

ABSTRACT

Sulfide anions are not only generated as a byproduct from industrial processes but also as a crucial kind of element in biological systems. Therefore, fluorescent probes for detecting sulfide anion with sensitive and selective characters are highly popular. In this study, we report a highly sensitive and selective fluorescent sensor **M1** for detection of sulfide anion based on the steric hindrance effect, where the recognition unit, dinitrobenzenesulfonate ester group is linked to aromatic *ortho*-position in the porphyrin, and correspondingly the fluorescence of fluorescein is efficiently quenched. Compared with the sensors with recognition unit linked to the other aromatic positions, the fluorescent sensor **M1** has a lower fluorescence background. Furthermore, the corresponding fluorescence responses (*F/F0*) of **M1** for mercapto amino-acid GSH, Hcy and Cys, were all far lower than the relative fluorescence ratio *F/F0* values for S^{2-}. It means that **M1** is sensitive and selective to detection of S^{2-}, and has an anti-disturbance ability to the biologically-relevant thiols, GSH, Hcy and Cys, and has the prospect of application in the exact detection of sulfide anions in living organisms. This approach offers some useful insights for realizing sensitive and selective fluorescent turn-on sensing in the detection assays for other analytes.

1. Introduction

Sulfide anion (S^{2-}) played a crucial role in the area of environmental, chemical and biological systems [1–3]. However, long period exposure to a high level of sulfide can cause diseases like Alzheimer's disease, Down's syndrome, diabetes, and liver cirrhosis [4–7], and even short-term exposure brings about nausea and dizziness. Therefore, it has considerable attention over the past few years to develop simple, highly sensitive and selective methods for the detection of S^{2-}.

Compared with ion chromatographys [8], electrochemical techniques [9] and conventional titration methods [10], etc. fluorescence methods [11–14] are much simpler with detection by fluorescence spectroscopy, which are more sensitive and possessed advantages such as rapid detection, low cost and in situ analysis. Thousands of fluorescent sensors for S^{2-} had been studied [15–31]· however, it is still the most significant challenge to design and synthesize the sensitive and selective fluorescent sensor for the detection of S^{2-}, because the biologically-relevant thiols, such as cysteine (Cys), homocysteine (Hcy) and glutathione (GSH), usually have responses to the fluorescent sensors of S^{2-} detection, and maybe affect the measurement result of S^{2-}. To our surprise, there is little attention to investigate further the anti-disturbance ability of the fluorescent sensors towards detecting S^{2-} to high concentration of mercapto amino-acids. With the different nucleophilic ability between S^{2-} and three mercapto amino-acids (Cys, Hcy, GSH), Wu et al. reported a water-soluble, low-cytotoxic and sensitive fluorescent sensor for detecting S^{2-} [28], whose research gave us an inspiration. Compared to the biologically-relevant thiols, sulfide anion is a nucleophile with the much smaller volume. We thus anticipated that, enhancing the steric effect of recognition unit

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https://doi.org/10.1016/j.molstruc.2017.08.049
0022-2860/© 2017 Published by Elsevier B.V.

第33卷第12期
2017年12月

无 机 化 学 学 报
CHINESE JOURNAL OF INORGANIC CHEMISTRY

Vol.33 No.12
2201-2207

1,3,5,7-四甲基氟硼二吡咯甲川的合成、晶体结构及密度泛函理论研究

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摘要:以2,4-二甲基吡咯、原甲酸三乙酯以及对甲苯磺酸为原料,无溶剂下合成了1,3,5,7-四甲基对甲苯磺酸二吡咯甲川(T1);以T1、三氟化硼乙醚以及三乙胺为原料,无溶剂下合成了1,3,5,7-四甲基氟硼二吡咯甲川(F1)。利用^{1}H NMR和X射线单晶衍射对其进行了表征。结果表明:T1属于单斜晶系,$P2_1/c$空间群,晶胞参数为a=0.777 3(3) nm,b=1.518 5(5) nm,c=1.612 2(5) nm,β=91.923(12)°,V=1.901 9(11) nm^3,Z=4;F1属于单斜晶系,$P2_1/n$空间群,晶胞参数为a=0.775 02(1) nm,b=1.444 20(3) nm,c=1.174 35(2) nm,β=107.779 5(9)°,V=1.251 65(4) nm^3,Z=4。在4种不同溶剂中,测定了T1的紫外可见光谱、F1的紫外可见光谱和稳态荧光光谱。将密度泛函计算与前线轨道理论相结合,研究了T1和F1可能的衍生方式。

关键词:1,3,5,7-四甲基氟硼二吡咯甲川;核磁共振;晶体结构;荧光光谱;密度泛函理论
中图分类号:O613.8^{+}1 **文献标识码**:A **文章编号**:1001-4861(2017)12-2201-07
DOI:10.11862/CJIC.2017.271

Synthesis, Crystal Structure and Density Functional Theoretical Study of 1,3,5,7-Tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene

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Abstract: 1,3,5,7-tetramethyl-3a,4a-diaza-s-indacene p-toluenesulfonate (T1) was synthesized by solvent-free method using 2,4-dimethylpyrrole,triethyl orthoformate and p-toluenesulfonic acid. 1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (F1) was synthesized by solvent-free method using T1, boron trifluoride diethyl ether and triethylamine. The structures of compounds have been characterized by ^{1}H NMR and single-crystal X-ray diffraction. The results show that T1 belongs to monoclinic system, space group $P2_1/c$ with a=0.777 3(3) nm, b=1.518 5(5)nm, c=1.612 2(5) nm, β=91.923(12)°, V=1.901 9(11) nm^3, Z=4 and that F1 belongs to monoclinic system, space group $P2_1/n$ with a=0.775 02(1) nm, b=1.444 20(3) nm, c=1.174 35(2) nm, β=107.779 5(9)°, V=1.251 65(4) nm^3, Z=4. In four different solvent, the UV-Vis spectrum of T1, the UV-Vis and steady-state fluorescence spectra of F1 were determined. The possible derived way of T1 and F1 were investigated by the density functional calculation and the front orbital theory. CCDC: 1578792, T1; 1578790, F1.

Keywords: 1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3a,4a-diaza-s-indacene; NMR; crystal structure; fluorescence spectra; density functional theory

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收稿日期:2017-05-15。**收修改稿日期**:2017-09-11。
国家自然科学基金(No.21172066)、**湖南省高校科技创新团队项目**(湘教通[2012]318)**和湖南省教育厅重点科研项目**(No.17A065)**资助**。

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Synthesis and Fungicidal Activity of 1-(Carbamoylmethyl)-2-aryl-3,1-benzoxazines

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Received: 8 June 2017; Accepted: 27 June 2017; Published: 3 July 2017

Abstract: A series of new 1-(carbamoylmethyl)-2-aryl-3,1-benzoxazines were prepared in moderate to good yields by $BF_3 \cdot OEt_2$-catalyzed reactions of aromatic aldehydes with 2-(*N*-substituted carbamoylmethylamino)benzyl alcohols. The structures of the target compounds were confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, and elemental analyses. The fungicidal activities of the target compounds against plant fungi were preliminarily evaluated, and some of them exhibited good activity.

Keywords: disubstituted-3,1-benzoxazine; heterocycles; synthesis; $BF_3 \cdot OEt_2$; fungicidal activity

1. Introduction

3,1-Benzoxazine and 3,1-benzoxazinone derivatives have received growing attention due to their broad biological activities. 3,1-Benzoxazine derivatives show anticonvulsant [1], herbicidal [2], fungicidal [3,4], and anticancer activity [5], and some are potent progesterone receptor (PR) agonists [6] or DNA-binding antitumor agents [7]. 3,1-Benzoxazinones exhibit antihypertensive [8] and antiproliferative activities [9], or are potent PR agonists/antagonists [10,11], potent human leukocyte elastase inhibitors [12], serine protease inhibitors [13–15], long chain fatty acid elongase 6 inhibitors [16], NK_1/NK_3 receptor antagonists [17], α-chymotrypsin inhibitors [18], mineralocorticoid receptors antagonists [19], and are even used as anti-HIV-1 reverse transcriptase inhibitors [20,21]. Therefore, the synthesis of 3,1-benzoxazines and 3,1-benzoxazinone has attracted considerable interest. The condensation of 2-aminobenzyl alcohol or its derivatives with aldehydes using acetic acid or *p*-toluenesulfonic acid (TsOH) as catalyst is the widely-used way to synthesize 3,1-benzoxazines [6,22,23]. Palladium-catalyzed cyclization of 2-alkynylanilides also provides a route to substituted 3,1-benzoxazines [24]. Recently, hypervalent iodine-mediated oxygenation of tertiary amines afforded a new way [25]. As for 3,1-benzoxazinones, the frequently used protocol is the reaction of 2-aminobenzyl alcohol or its derivatives with phosgene [8,26]. More recently, silver-catalyzed incorporation of carbon dioxide into 2-alkynylanilides afforded a new route [27]. In spite of the progress in their preparation, the development of more efficient ways and the synthesis of novel 3,1-benzoxazine derivatives are still highly desirable for drug discovery, as well as medicinal and pesticide chemistry. To our knowledge, 3,1-benzoxazines have received less attention compared with 3,1-benzoxazinones. Particularly, there are only few reports about the activities of benzoxazines against plant fungi [3,4]. Thus, we present herein the synthesis of novel 1-(carbamoylmethyl)-2-aryl-3,1-benzoxazines, as a continuation of our ongoing project aimed at searching for novel fungicidal active compounds, by condensation reactions of 2-(*N*-substituted carbamoylmethylamino)benzyl alcohols with aldehydes in the presence of $BF_3 \cdot OEt_2$, and also report their fungicidal activities against plant fungi.

Molecules **2017**, *22*, 1103; doi:10.3390/molecules22071103 www.mdpi.com/journal/molecules

Journal of
Biobased Materials and Bioenergy
Vol. 11, 491–498, 2017

A Novel Thermal- and pH-Sensitive Polyurethane Hydrogel for Adsorption of Pb^{2+} from Aqueous Solutions

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Novel, thermal- and pH-sensitive polyurethane (PU) hydrogels were successfully synthesized in this study via three-step polymerization, and their application as adsorbents for Pb^{2+} removal was also demonstrated. Scanning electron microscope (SEM), Fourier transform infrared (FTIR), differential scanning calorimetry (DSC) and X-ray powder diffraction (XRD) were used to observe the morphology and organic groups from the PU hydrogels, respectively. SEM results showed that the PU hydrogels possessed a honeycomb-like structure, while FTIR analysis indicated that the PEG and −COOH groups were successfully incorporated into the PU hydrogels. The DSC analysis revealed that onset and phase transition temperature for the PU hydrogel appeared at 33.4 °C and 54.7 °C, respectively. Moreover, the XRD analysis found that the crystallinity for the PU hydrogels was introduced by PEG. The swelling tests were simultaneously applied to investigate thermal- and pH-sensitive properties of the PU hydrogels. Concretely, the equilibrium swelling ratio (ESR) obviously decreased from 14.6 to 9.4 at 30 °C to 45 °C temperature range, exhibiting high thermal-sensitive property. Meanwhile, when pH was increased from 4.0 to 7.0, the ESR for the PU hydrogels significantly increased from 11.5 to 15.5, exhibiting pH-sensitivity property. Moreover, the adsorption experiments demonstrated that the adsorption capacity (q_e) and removal rate (R) of Pb^{2+} decreased from 30 °C to 45 °C at temperature range while increasing from 3.5 to 4.5. It can therefore be concluded that the PU hydrogels were successfully prepared and their adsorption property for Pb^{2+} removal was influenced by environmental temperature and pH value.

Keywords: Polyurethane Hydrogel, Thermal-Sensitive, pH-Sensitive, Pb^{2+} Adsorption.

1. INTRODUCTION

Hydrogel is a polymer with three-dimensional (3D) network composed of hydrophilic and hydrophobic chains. Hydrogels have been extensively applied in many field such as drug-delivery,[1,2] food industry,[3] tissue engineering,[4] molecular imprinting materials,[5] etc. Due to their diverse functional groups and sophisticated structure, hydrogels have shown obvious advantages in the field of adsorption and removal of various pollutants (e.g., heavy metals,[6] dyes[7]) from aqueous solutions.

Metal materials have been widely applied in many fields,[8–13] which leads to environmental pollution, especial the heavy metal ions.[14–16] As known, Pb^{2+} is one of the most common and toxic heavy metals that can accumulate in organisms through food chains or water intake and then cause damage to nerves, liver, kidney, and other organs of human body.[17] Many methods have been designed for the removal of Pb^{2+}, such as ion exchange treatment,[18] chemical precipitation,[19] adsorption[20] and membrane separation.[21] Among these methods, adsorption is regarded as the most economical and efficient one. For example, hydrogels have been used as adsorbents to remove Pb^{2+} from aqueous solutions, and anticipated adsorption efficiency could be achieved.

Thermal-sensitive and pH-sensitive hydrogels have been widely used in recent years to remove Pb^{2+} from aqueous solutions, because they can reversibly change their structure and properties on receiving external stimuli, such as temperature, pH value and ionic strength.[22,23] Ju et al.[24] reported that poly(N-isopropylamide) (PNIPAM) and benzo-18-crown-6-acrylamide (BCAm) were

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1556-6560/2017/11/491/008
doi:10.1166/jbmb.2017.1692

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 177 (2017) 63–68

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

One-pot fabrication of FRET-based fluorescent probe for detecting copper ion and sulfide anion in 100% aqueous media

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ARTICLE INFO

Article history:
Received 26 August 2016
Received in revised form 8 January 2017
Accepted 16 January 2017
Available online 17 January 2017

Keywords:
Copper ion
Sulfide anion
FITC
Fluorescence quenching
FRET

ABSTRACT

The design of effective tools for detecting copper ion (Cu^{2+}) and sulfide anion (S^{2-}) is of great importance due to the abnormal level of Cu^{2+} and S^{2-} has been associated with an increase in risk of many diseases. Herein, we report on the fabrication of fluorescence resonance energy transfer (FRET) based fluorescent probe PF (PEI-FITC) for detecting Cu^{2+} and S^{2-} in 100% aqueous media via a facile one-pot method by covalent linking fluorescein isothiocyanate (FITC) with branched-polyethylenimine (b-PEI). PF could selectively coordinate with Cu^{2+} among 10 metal ions to form PF-Cu^{2+} complex, resulting in fluorescence quenching through FRET mechanism. Furthermore, the in situ generated PF-Cu^{2+} complex can be used to selectively detect S^{2-} based on the displacement approach, resulting in an off-on type sensing. There is no obvious interference from other anions, such as Cl^-, NO_3^-, ClO_4^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, Br^-, HPO_4^{2-}, F^- and $S_2O_3^{2-}$. In addition, PF was successfully used to determine Cu^{2+} and S^{2-} in human serum and tap water samples. Therefore, the FRET-based probe PF may provide a new method for selective detection of multifarious analysts in biological and environmental applications, and even hold promise for application in more complicated systems.

1. Introduction

Recently, the development of selective and efficient fluorescent probes for anion detection has attracted continuous attention due to their promising application in biological, industrial and environmental monitoring [1–9]. Sulfide anion (S^{2-}), as one type of biologically and environmentally important anions, is extensively utilized in industrial processes including sulfur and sulfuric acid production, dyes and cosmetic manufacturing, etc. [10–12]. It is also a toxic traditional pollutant that can be generated from industrial processes and biological metabolism [13–15]. Moreover, its protonated form, HS^- and H_2S become even more toxic than S^{2-} self [16,17], and abnormal levels of S^{2-} are involved in a variety of diseases, such as hypertension, liver cirrhosis, diabetes and Alzheimer's disease [18–24]. Thus, to better understand the biological functions of S^{2-}, development of highly selective and sensitive fluorescent probes for detecting S^{2-} is urgently required.

So far, a large number of fluorescent probes for detecting S^{2-} have been conducted mainly based on three strategies, such as (a) reduction of azides to amines [25–27], (b) nucleophilic addition [28–31], (c) copper sulfide precipitation [32–34] and (d) a coordinative-based approach [35–39]. For fluorescent probes based on reduction (a), addition (b) and coordinative-based (d) strategies, the reactions are relatively slow and irreversible. In contrast, fluorescent probes based on CuS precipitation strategy have been highly concerned due to their extremely fast recognition process. In addition, there are two outstanding properties: one is the fast kinetics of precipitation of CuS; another one is the corresponding quite low-solubility constant ($k_{sp} = 6.3 \times 10^{-36}$) [40]. In view of these advantages, a variety of fluorescent probes for S^{2-} detection using CuS precipitation strategy have been reported [41–43]. However, most of them can only work in organic co-solvents media, which would significantly limit their practical applications in physiological condition and environmental systems. Despite of several examples can detect S^{2-} in 100% aqueous media, they generally requires complicated synthesis pathway and exhibits poor photostability [44–48]. Therefore, it is desirable to develop robust fluorescent probes for detecting S^{2-} that are simple, fast-responding and water soluble.

With these factors in mind, herein, we report a facile one-pot method for designing a novel fluorescence probe PF for reversible sensing of Cu^{2+} and S^{2-} in 100% aqueous media via fluorescence resonance energy transfer (FRET) mechanism. In this probe, branched-polyethylenimine (b-PEI) can not only improve the solubility of PF in water, but also facilitate enhanced binding affinity for Cu^{2+}. As shown in Scheme 1, the probe PF could firmly bind Cu^{2+} to form stable complex PF-Cu^{2+}, leading to an obvious fluorescence quenching due to the FRET effect. Upon addition of S^{2-}, its fluorescence recovers quickly

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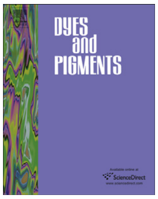
http://dx.doi.org/10.1016/j.saa.2017.01.031

Dyes and Pigments 141 (2017) 21–28

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



Structure-performance correlation of indacenodithiophene-based narrow band-gap polymers with pendant diketopyrrolopyrrole units

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ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form
19 January 2017
Accepted 24 January 2017
Available online 6 February 2017

Keywords:
Donor-acceptor
Conjugated copolymer
Diketopyrrolopyrrole
Side chain
Polymer solar cells

ABSTRACT

Two novel indacenodithiophene (IDT) based narrow band-gap polymers (PIDT-BDTDPP and PIDT-TDPP) with pendant diketopyrrolopyrrole (DPP) units onto different main chains were designed and synthesized. The structures and properties of these main chain donor-side chain acceptor D-A copolymers were fully characterized. The PIDT-TDPP with pendant DPP units onto thiophene (T) units exhibited better light-harvesting properties and charge transport properties. While the PIDT-BDTDPP with pendant DPP units onto benzo[1,2-*b*:4,5-*b*′]dithiophene (BDT) units displayed lower the highest occupied molecular orbital energy levels (HOMO). By blending these polymers as light-harvesting electron donors with (6,6)-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) electron acceptors in bulk heterojunction solar cells, it was found that the PIDT-TDPP-based PSCs shown better photovoltaic performance and a power conversion efficiency (PCE) of 3.62%, an open-circuit voltage (V_{OC}) of 0.79 V, a short-circuit current (J_{SC}) of 9.27 mA cm^{-2} and a fill factor (*FF*) of 49.7% were achieved. The PCE level is 1.88 times higher than that in the PIDT-BDTDPP-based PSCs.

1. Introduction

The advance in donor-acceptor (D-A) conjugated polymers with alternating electron-rich (donor) and electron-deficient (acceptor) units along the polymer main chain has been the major driving force for the improvement of the power conversion efficiency (PCE) of polymer solar cells (PSCs) up to 10% in single junction PSCs [1–3]. However, most of the present polymers are in main-chain D-A frame, which may suffer from lower hole mobility due to the influence of acceptor units in the main chain [4–9]. Side-chain D-A conjugated polymers is a new molecular design strategy, in which D moieties were employed to construct the main chain and A units were pended onto the D units in the side chain [10–15]. Compared with main chain D-A copolymers, side-chain D-A copolymers are expected to have some interesting features for optoelectronic applications, such as higher hole mobility of the polymer main chains and having the advantage of allowing charge separation through sequential transfer of electrons from the main chains to the acceptor side chains and then to fullerene acceptor in the active layer of PSCs. As a result of these merits, PSCs based on these previously reported side-chain D-A polymers exhibited a maximal PCE of 8.04% [16].

However, in most side-chain D-A polymers, the acceptor units are pended onto the thiophenyl units to build the side chain. It is well known that the random polymerization of asymmetric 3-substituted thiophene may result in three different coupling structures along the polymer main-chains and the resulted side-chain D-A polymers have a twisted conformation, which leads to poor packing and low crystallinity [17,18]. Therefore, there is still a strong need for developing new side-chain D-A polymers with

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http://dx.doi.org/10.1016/j.dyepig.2017.01.076
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Dyes and Pigments 139 (2017) 201–207

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

D-A copolymers based on lactam acceptor unit and thiophene derivatives for efficient polymer solar cells

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ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form
5 December 2016
Accepted 8 December 2016
Available online 9 December 2016

Keywords:
Polymer solar cells
D-A copolymers
Lactam acceptor unit
Thiophene
Power conversion efficiency

ABSTRACT

Two donor-acceptor (D-A) polymers PTTBDTP and PBTBDTP were developed by copolymerizing lactam acceptor [7,7′-bidithieno[3,2-*b*:2′,3′-*d*]pyridine]-5,5′(4*H*,4′*H*)-dione (BDTP) with thieno[3,2-*b*]thiophene (TT) or 2,2′-bithiophene (BT) in good yields. PTTBDTP and PBTBDTP exhibited excellent thermal stability and low HOMO energy levels of −5.52 eV ~ −5.54 eV. Compared with PTTBDTP, PBTBDTP possessed broader absorption spectra, better crystallinity, and higher hole mobility. Therefore inverted polymer solar cells based on PBTBDTP:$PC_{71}BM$ achieved a higher PCE of 6.86%, with an open-circuit voltage (V_{oc}) of 0.87 V, a short-circuit current (J_{sc}) of 10.97 mA/cm^2 and a fill factor (FF) of 71.85%. Meanwhile, PTTBDTP:$PC_{71}BM$ solar cells gave a PCE of 5.84%. These results have demonstrated that lactam BDTP is a good building block for PSC applications.

1. Introduction

At present, the highest power conversion efficiencies (PCEs) of single-junction polymer solar cells (PSCs) are over 11% [1–5], which are close to the threshold of commercial production. The active layers of PSCs contain two important components: polymer donor materials and acceptor materials. There are three main types of donor materials: poly(p-phenylenevinylene)s (PPVs), polythiophenes (such as poly(3-hexylthiophene), or namely P3HT), and D-A copolymers [6]. Among them, D-A copolymers with alternating electron donating (D) and electron-accepting (A) units in the backbones are the best polymer donor materials due to their superior light-harvesting capability, suitable energy levels, and good mobilities [6–8]. Fullerene derivatives, such as phenyl-C61-butyric acid methyl ester ($PC_{61}BM$), phenyl-C71-butyric acid methyl ester ($PC_{71}BM$) and others [9,10], were the most commonly used acceptor materials. In order to overcome the weak absorption and limited energy level variability of fullerenes derivatives, non-fullerene acceptor materials have been developed and their photovoltaic performance have caught up with fullerene counterparts [2,3,11–16].

We are focused on developing highly efficient D-A polymer donor materials. Since 2013, we have reported a series of lactam units TPTI, BDTP, TD1, TD2, TITI and TTP [17–22]. D-A copolymers based on these acceptor units have achieved decent PCEs. Among them, copolymer PThBDTP using [7,7′-bidithieno[3,2-*b*:2′,3′-*d*]pyridine]-5,5′(4*H*,4′*H*)-dione (BDTP) as the acceptor unit and thiophene as the donor unit showed excellent thermal stability, deep HOMO energy level, good hole mobility and face-on orientation both in pure and blend films. Inverted solar cells based on PThBDTP:$PC_{71}BM$ gave a PCE of 9.13% with a V_{oc} of 0.96 V [19]. Furthermore, tandem solar cells using PThBDTP:$PC_{71}BM$ as the front-cell and narrow bandgap DPPEZnP-TEH:$PC_{61}BM$ as the back-cell have achieved high PCEs over 11% [23], which among the best tandem devices. These results indicated that BDTP is one of the best acceptor unit and need to be studied further.

Thieno[3,2-*b*]thiophene (TT) or 2,2′-bithiophene (BT) are excellent donor units and D-A copolymers based on TT or BT possess extended effective conjugation length, enhanced interchain interaction, good crystallinity, high mobilities, and good photovoltaic performance [24–28]. In order to further investigate the photovoltaic performance of BDTP, we have synthesized two D-A copolymers PTTBDTP and PBTBDTP by using thieno[3,2-*b*]thiophene or 2,2′-bithiophene as donor units (Fig. 1). The thermal, optical and electrochemical properties, crystallinity, and hole

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http://dx.doi.org/10.1016/j.dyepig.2016.12.014
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Received: 10 May 2017 | Revised: 30 June 2017 | Accepted: 14 July 2017
DOI: 10.1002/qua.25443

FULL PAPER

WILEY International Journal of QUANTUM CHEMISTRY

Theoretical study on the interactions of halogen-bonds and pnicogen-bonds in phosphine derivatives with Br_2, BrCl, and BrF

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Funding information
This work was supported by the National Natural Science Foundation of China (21401055, 21402048, 91545122); the Fundamental Research Fund for the Central Universities (JB 2015 RCY 03); the Scientific Research Fund of Hunan Provincial Education Department (14C0462).

The MP2 ab initio quantum chemistry methods were utilized to study the halogen-bond and pnicogen-bond system formed between PH_2X (X = Br, CH_3, OH, CN, NO_2, CF_3) and BrY (Y = Br, Cl, F). Calculated results show that all substituent can form halogen-bond complexes while part substituent can form pnicogen-bond complexes. Traditional, chlorine-shared and ion-pair halogen-bonds complexes have been found with the different substituent X and Y. The halogen-bonds are stronger than the related pnicogen-bonds. For halogen-bonds, strongly electronegative substituents which are connected to the Lewis acid can strengthen the bonds and significantly influenced the structures and properties of the compounds. In contrast, the substituents which connected to the Lewis bases can produce opposite effects. The interaction energies of halogen-bonds are 2.56 to 32.06 kcal·mol^{-1}; The strongest halogen-bond was found in the complex of $PH_2OH\cdots BrF$. The interaction energies of pnicogen-bonds are in the range 1.20 to 2.28 kcal·mol^{-1}; the strongest pnicogen-bond was found in $PH_2Br\cdots Br_2$ complex. The charge transfer of lp(P) —σ*(Br—Y), lp(F) —σ*(Br—P), and lp(Br) —σ*(X—P) play important roles in the formation of the halogen-bonds and pnicogen-bonds, which lead to polarization of the monomers. The polarization caused by the halogen-bond is more obvious than that by the pnicogen-bond, resulting in that some halogen-bonds having little covalent character. The symmetry adapted perturbation theory (SAPT) energy decomposition analysis showes that the halogen-bond and pnicogen-bond interactions are predominantly electrostatic and dispersion, respectively.

KEYWORDS
ab initio calculation, halogen-bond, interaction energy, pnicogen-bond, symmetry adapted perturbation theory

1 | INTRODUCTION

Noncovalent interactions often play an important role in the stabilization of macromolecular, such as proteins and nucleic acids. Typically, noncovalent interactions include van der Waals forces, electrostatic interactions, hydrophobic interactions, and hydrogen bonds, in which the hydrogen bonding has been extensively investigated partially due to its high importance in systems involving water molecules. There are still some other types of noncovalent bonding, such as halogen bonding and lithium bonding.[1] 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. In our previous

Received: 17 June 2016 | Revised: 29 August 2016 | Accepted: 5 September 2016

DOI: 10.1002/poc.3658

WILEY Journal of Physical Organic Chemistry

RESEARCH ARTICLE

Recognition of nucleophilic substitution reaction mechanisms of carboxylic esters based on support vector machine

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Abstract

The nucleophilic substitution reactions of carboxylic esters (R^1COOR^2) follow 2 possible mechanisms, namely, stepwise mechanism and concerted mechanism. The reaction mechanism is affected by the structures of the nonleaving group (NLG, ie, R^1), the leaving group (LG, ie, OR^2) of carboxylic esters, and the nucleophiles (Nu). The traditional approach for the determination of reaction mechanism by dynamic experiments is not only laborious and time consuming but also only applicable for the situation with single structural factor variation. Benefiting from the ample existing kinetic data, this article aimed to construct a molecular structure-based classification model by support vector machine (SVM). The polarizability effect index of the NLG (PEI(NLG)), the pK_a of the conjugate acid of the LG (pK_a(LG)), and the pK_a of the conjugate acid of the Nu (pK_a(Nu)) were used to characterize the structural information of the 3 influencing factors, respectively. On the basis of these structural descriptors, the SVM classification model was established for the reaction mechanisms of 225 nucleophilic substitution reactions in the training set. The total prediction accuracy of 99.11% was achieved by 5-fold cross validation. Then the reaction mechanisms of 56 reactions in test set A were predicted by this SVM model, and the prediction accuracy was up to 98.21%. Furthermore, test set B consisting of 24 reactions were used as another external data set for prediction, where the reaction mechanisms were controversially reported by different studies. The prediction results of test set B by the SVM model built in this article were amazingly consistent with the conclusions drawn by Um et al.

KEYWORDS

carboxylic esters, nucleophilic substitution reaction, reaction mechanism, structural descriptors, support vector machine (SVM)

1 | INTRODUCTION

The nucleophilic substitution reaction of esters, as one class of the important organic reactions, plays an important role in a variety of fields such as chemistry, life science, and environmental science. Many processes involve such reaction, for example, the acyl-transfer reaction in organic synthesis,[1] the hydrolysis of esters catalyzed by enzymes in biochemical reactions,[2] the degradation of organophosphorus insecticides and nerve poisons,[3] and the preparation of optically pure drug by lipase-catalyzed ammonolysis.[4] The understanding of the influence of molecular structure on the reaction rate and mechanism has great significance to organic synthesis, design of functional molecules, environmental treatment, and various regulating processes at cell level in chemical biology. Therefore, the kinetics and mechanisms of the nucleophilic substitution reactions of esters have received much attention and have been intensively investigated since the 1930s. For instance, Jencks group[2,5,6] have been long devoted to studying on the nucleophilic substitution reaction mechanisms of phosphate esters in life systems. Castro et al[7–11] have been engaged in the investigation of the

Journal of
Biobased Materials and Bioenergy
Vol. 11, 267–273, 2017

Novel Thermal- and pH-Sensitive Polyurethane Hydrogels for Removal of Acid Brilliant Scarlet GR from Aqueous Solutions

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A series of novel thermal- and pH-sensitive polyurethane (PU) hydrogels were successfully prepared via three-step polymerization for removal of acid brilliant scarlet GR from aqueous solutions. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscope (SEM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were employed to investigate organic groups, morphology, phase transition temperature and crystallinity of the polyurethane hydrogels, respectively. The FTIR analysis showed that the thermal-sensitive component (PEG) and pH-sensitive groups ($-N(CH_3)-$) were successfully incorporated into the PU hydrogels. The SEM observation revealed that all PU hydrogels possessed irregular porous structures. DSC and XRD studies indicated that the crystallinity for all the PU hydrogels were negatively correlated with increased inventory of *N*-methyldiethanolamine (MDEA), and phase transition temperature appeared at 60.2 °C, 59.4 °C, 57.6 °C and 54.8 °C, respectively. The swelling tests indicated that the PU hydrogels possessed thermal- and pH-sensitive properties. The adsorption experiments demonstrated that the adsorption capacity (q_e) of acid brilliant scarlet GR decreased with increased temperature or initial pH value. Findings from this work suggest that the thermal- and pH-sensitive hydrogels were successfully synthesized and adsorption of acid brilliant scarlet GR was strongly affected by the temperature and initial pH value.

Keywords: Polyurethane Hydrogels, Multi-Sensitive, Swelling Behaviors, Acid Brilliant Scarlet GR.

1. INTRODUCTION

A lot of new materials with excellent properties are emerging constantly with the development of material science, which make great progress in these research fields, such as chemical analysis,[1–3] biosensor,[4,5] new energy,[6,7] biomedical materials,[8,9] material separation[10] and so on. Intelligent hydrogels as a polymer material has been attracted considerable attention in recent years because it has the advantages of responding rapidly to external stimuli such as temperature or pH. Intelligent hydrogels have been extensively applied in the field of drug delivery, molecular imprinting, chemical separation, etc.[11–13] Thermal-sensitivity and pH-sensitivity properties in these hydrogels are frequently studied and widely used.[14] This is largely because temperature and pH value are most important factors in physiological, ecological, and other systems.[15,16]

It is nowadays well-known that the presence of synthetic dyes in wastewater can cause many problems such as allergic reaction, skin irritation, water pollution, etc.[17] Besides, the synthetic dyes are resistant to biological degradation under sunlight because of complex aromatic molecular structure.[18] Generally, coagulation and flocculation, electrochemical oxidation, photocatalytic degradation and adsorption are conventional methods for removal of dyes.[19] Among these methods, adsorption is regarded as the most effective and economical method owing to its simple operation as well as wide application.[20,21]

Intelligent hydrogels have been used in recent years as an adsorbent with obvious advantage in the field of dyes removal from aqueous solutions.[22] Sakthivel et al.[23] prepared pH-sensitive hydrogel using itaconic acid (IA), ethylene glycol (EG) and acrylic acid (AA) as raw

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1556-6560/2017/11/267/007 doi:10.1166/jbmb.2017.1672

Functional Materials Letters
Vol. 10, No. 5 (2017) 1750055 (4 pages)
© World Scientific Publishing Company
DOI: 10.1142/S1793604717500552

A novel $ZrHIO_6 \cdot 4H_2O$ catalyst for degradation of organic dyes at room temperature

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Received 21 February 2017; Accepted 18 July 2017; Published 14 August 2017

It is interesting to obtain catalysts to degrade organic dye pollutants at room temperature for simultaneous purposes of environment-treating and energy-saving. In this work, a novel $ZrHIO_6 \cdot 4H_2O$ catalyst was synthesized by reacting $ZrO(NO_3)_2$ with H_5IO_6 in aqueous nitric acid. The catalyst was found effective in degradation of rhodamine B (RhB) or methylene blue (MB) dyes at room temperature without light illumination. We used the ultraviolet–visible (UV–Vis) absorption spectra of dye solution as well as X-ray photoelectron spectroscopy (XPS) of $ZrHIO_6 \cdot 4H_2O$ to confirm that the dye degradation was due to its catalytic role. Importantly, the $ZrHIO_6 \cdot 4H_2O$ catalyst can be recycled five times without obvious activity loss and it achieved higher mineralization efficiency than the previously reported analogue in the degradation experiments.

Keywords: $ZrHIO_6 \cdot 4H_2O$; catalyst; dye; degradation; room temperature.

Dye wastewater from industries of dyeing, paper, printing and petrochemical generally contains a great deal of hazardous organic dye pollutants that caused severe environment problems.[1,2] Dyes are highly resistible to biodegradation because of their retained color and structural integrity when under exposure to sunlight, soil, and bacteria.[1,2] Photocatalytic technology has been frequently researched due to its application in degrading organic dye pollutants with sustainable solar energy.[3–12] The key issue of utilizing solar energy through photocatalysis is to develop visible-light-responsive photocatalysts to fully use visible light (much abundant in solar radiation) during photocatalytic process.[9–12] However, it still remains as a challenge to obtain visible-light-responsive photocatalysts with high performance in dye pollutants degradation.[9–12]

As a technologically feasible oxidation process for wastewater treatment, catalytic wet air oxidation (CWAO) might be a promising solution to the issue.[1,2] Through the CWAO process, organic dye pollutants can be degraded without light illumination at room temperature.[1,2] It is generally accepted that using a favorable catalyst is very important to a CWAO process because this would reduce harshness of the reaction conditions like reaction temperature, reaction pressure, etc., thus minimizing energy-consumption and operation-cost of the process.[1,2] However, in most cases, the operating temperature of CWAO is beyond 100°C.[1,2] If the operating temperature of the CWAO degradation of dye pollutants could be lowered to room temperature, energy consumed in the process would be fully saved.

So far, several catalysts like $Ce(IO_3)_4$,[13] Fe_2O_3–CeO_2–TiO_2/γ–Al_2O_3,[14] Ce-doped MoO_3,[15] $CeGeO_4$,[16] and Ce-doped MoO_3,[17] etc. have been used to degrade organic dyes by the CWAO method at room temperature. However, it is still highly desirable to develop new catalysts with higher performance in the CWAO degradation process. This would bring about more insights into the CWAO mechanism and in turn further enhances the efficiency of dye degradation process.

In 2005, Hector found that reacting $ZrO(NO_3)_2$ with H_5IO_6 in acid aqueous solution can yield a precipitate of $ZrHIO_6 \cdot 4H_2O$.[18] Up to now, the physicochemical and functional properties of $ZrHIO_6 \cdot 4H_2O$ have not been reported. In this paper, we successfully prepared the $ZrHIO_6 \cdot 4H_2O$

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有机化学 DOI: 10.6023/cjoc201704053 研究简报
Chinese Journal of Organic Chemistry NOTE

氯磷酸二苯酯介入的芳香醛与砜缩合制备非对称芳香炔烃

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摘要　氯磷酸二苯酯促进芳香醛与砜缩合反应在室温下有效进行, 能高收率形成对应的非对称芳香炔烃. 考察了醛及砜芳环上取代基对反应的影响, 结果表明不论是吸电子基还是给电子基对反应都无明显影响, 制备了一系列官能团化的非对称二苯基炔烃、噻吩及吡啶类炔烃、香豆素类炔烃及二苯基膦酰基保护的二炔烃和三炔烃, 并从分子结构上阐明了本缩合反应可在室温下有效进行的原理.

关键词　缩合反应; 非对称芳香炔烃; 香豆素炔烃; 二苯基膦酰基炔烃

Synthesis of Unsymmetrical Aromatic Acetylenes by Diphenyl Chlorophosphate-Promoted Condensation Reaction of Aromatic Aldehydes and Sulfones

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Abstract　Diphenyl chlorophosphate-promoted condensation reaction of aromatic aldehydes and sulfones, proceeding at room temperature, could been applied to synthesize unsymmetrical aromatic acetylenes. It was found that functional groups on aromatic ring of aldehydes and sulfones had little effect on the reaction. A series of unsymmetrical diphenyl, thienyl, pyridyl, coumarin and diphenylphosphoryl aromatic acetylenes were prepared by the reaction. Based on the molecular structure, the reason why this reaction could proceed at room temperature is explained The reaction showed some outstanding features including simple operation, wide functional group tolerance, high yields and mild reaction conditions.

Keywords　condensation reaction; unsymmetrical aromatic acetylene; coumarin acetylene; diphenylphosphoryl aromatic acetylene

含有碳碳叁键官能团的炔烃由于其独特刚性直线结构在药物及光电材料等领域有广泛应用: 刚性直线型亲脂性炔烃类衍生物具有一定的生物活性, 可用于抗菌抗癌等[1]; π共轭芳香炔烃刚性骨架具有丰富的π电子常

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Received April 30, 2017; revised July 24, 2017; published online August 16, 2017.
Project supported by the General Project of Hunan Education Department (No. 17C0629), the Doctoral Foundation of Hunan University of Science and Technology (No. E51693), the Open Foundation of Key Laboratory of Theoretical Organic Chemistry and Functional Molecule of Ministry of Education, Hunan University of Science and Technology (No. E21630), the National Natural Science Foundation of China (No. 21402048).
湖南省教育厅一般项目(No. 17C0629)、湖南科技大学博士启动基金(No. E51693)、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开放基金(No. E21630)和国家自然科学基金(No. 21402048)资助项目.

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TMPyP Inhibits Amyloid-β Aggregation and Alleviates Amyloid-Induced Cytotoxicity

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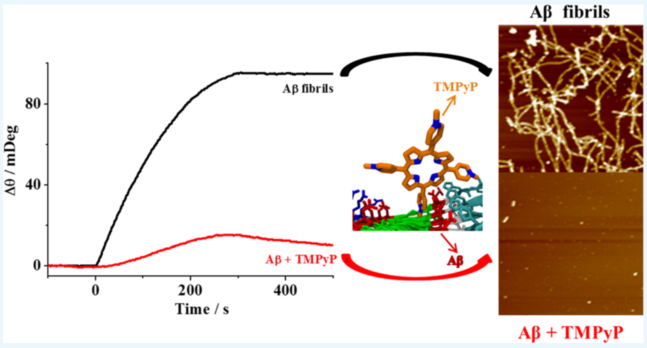
ABSTRACT: The aggregation or misfolding of amyloid-β (Aβ) is a major pathological hallmark of Alzheimer's disease (AD). The regulation of Aβ aggregation is thought to be an effective strategy for AD treatment. The capability of a water-soluble porphyrin, 5,10,15,20-tetrakis(*N*-methyl-4-pyridyl)-porphyrin (TMPyP), to inhibit Aβ aggregation and to lower Aβ-induced toxicity was demonstrated. As evidenced by surface plasmon resonance and circular dichroism, TMPyP can not only disrupt Aβ aggregation but also disassemble the preformed Aβ aggregates. The atomic force microscopy imaging proves that TMPyP inhibits the formation of both oligomers and fibrils. Molecular dynamic simulations provide an insight into the interaction between TMPyP and Aβ at the molecular level. The half-maximal inhibitory concentrations of TMPyP acting on the oligomers and fibrils were determined to be 0.6 and 0.43 μM, respectively. As a member of porphyrin family, TMPyP is of rather low cytotoxicity, and the cytotoxicity of the Aβ aggregates was also relieved upon coincubation with TMPyP. The excellent performance of TMPyP thus makes it a potential drug candidate for AD therapy.



INTRODUCTION

Alzheimer's disease (AD) is one of the common neurodegenerative disorders characterized by the accumulation of amyloid-β (Aβ) in brain.[1,2] Aβ is composed of 39−42 amino acids and produced by the cleavage of the amyloid precursor protein (APP) by β- and γ-secretases.[3] The aggregation of Aβ leads to the formation of fibrillar deposits known as senile plaques. The amyloid aggregates, which are self-assembled from misfolded Aβ, have been presumed to affect the structure and function of neuronal cells and to stimulate cell apoptosis, leading to synaptic dysfunction and neurodegeneration.[4,5]

The suppression of Aβ production or inhibition of Aβ aggregation is considered as potential strategies for preventing and treating AD.[1] The production of Aβ can be suppressed by decreasing the expression of APP[6] or inhibiting the activity of β- and γ-secretases.[7,8] On the other hand, once generated, Aβ is readily aggregated, and the development of effective inhibitors against Aβ aggregation or drug candidates that dissociate toxic Aβ aggregates plays an important role in AD treatment.[9,10] Short peptides (β-sheet breaker peptides)[11,12] and small organic molecules[8,13−16] have been explored for their inhibitory abilities. For example, short peptides of Aβ(17−21) (LVFFA)[11,12] and Aβ(39−42) (VVIA)[17] have been shown to reduce Aβ aggregation and to alleviate Aβ-induced neurotoxicity. Small molecules, such as anthocyanins,[18] resveratrol,[15] carotenoid,[16] and tabersonine,[8] have proven to inhibit amyloid fibrillation via specific aromatic and hydrophobic interactions. However, peptide-based inhibitors are difficult to cross the blood−brain barrier (BBB) and most small-molecule-based modulators are not suitable for AD therapy due to their high cytotoxicity.[9] Developing less cytotoxic and BBB-permeable therapeutic candidates for AD is still a challenge.

Porphyrins possess physiological activity and widely exist in organisms.[19] Howlett et al. found that the heme-related porphyrins could inhibit Aβ aggregation, leading to reduced cytotoxicity.[20] The half-maximal inhibitory concentration (IC_{50}) of 0.2 μM was attained for the inhibition of Aβ aggregation by ferric dehydroporphyrin IX.[21] The perturbation of Aβ aggregation was ascribed to the π−π interactions between the porphyrin ring of heme and the Phe[19] residue of Aβ.[22] The regulation of Aβ aggregation by photosensitizing *meso*-tetra(4-sulfonatophenyl)phorphyrin (TPPS) was also reported and TPPS could suppress the neural cell death and synaptic toxicity.[23] However, some of the porphyrins are insoluble and

Received: June 27, 2017
Accepted: July 20, 2017
Published: August 3, 2017

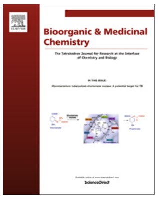
DOI: 10.1021/acsomega.7b00877
ACS Omega 2017, 2, 4188−4195

Bioorganic & Medicinal Chemistry 25 (2017) 1939–1948

Contents lists available at ScienceDirect

Bioorganic & Medicinal Chemistry

journal homepage: www.elsevier.com/locate/bmc



Design, synthesis and preliminary biological evaluation of indole-3-carboxylic acid-based skeleton of Bcl-2/Mcl-1 dual inhibitors

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ARTICLE INFO

Article history:
Received 24 November 2016
Revised 7 February 2017
Accepted 8 February 2017
Available online 11 February 2017

Keywords:
Bcl-2/Mcl-1
Indole-3-carboxylic acid-based derivatives
Anti-tumor
Inhibitors

ABSTRACT

The B-cell lymphoma-2 (Bcl-2) family proteins are attractive targets for cancer therapy. In our previous work, the structure-activity relationship of WL-276 was studied. According to the results, rhodanine derivatives show potent binding affinity for Bcl-2 and Mcl-1 protein and show weaker activity against Bcl-X_L protein. Based on the previous results, a new class of indole-3-carboxylic acid-based derivatives were designed and synthesized as Bcl-2/Mcl-1 dual inhibitors. Among them, compound **17** has a K_i value of 0.26 μM for Bcl-2 protein and is better than WL-276. Furthermore, it inhibits the myeloid cell leukemia sequence 1 (Mcl-1) protein with a K_i value of 72 nM. Especially, compound **31** can selectively acting on Bcl-2 and Mcl-1 protein but not Bcl-X_L protein, which has great significance for developing dual inhibitors targeting Bcl-2 and Mcl-1 protein, as well as specific antitumor abilities in cells.

1. Introduction

Apoptosis is considered as a major type of programmed cell death (PCD),[1] which can maintain the homeostasis in normal organisms. In addition, it is related to embryogenesis and development of the immune system.[2] The existent phenomenon suggests that elevating anti-apoptotic Bcl-2 proteins expression levels can be observed in many cancer lines and primary tumor biopsy samples, which may be a critical reason for tumor cells to evade apoptosis and subsequently acquire drug resistance for chemotherapy.[3]

The Bcl-2 proteins family contains at least 17 members. They all have the BH homology domains which mean B-cell lymphoma-2 homology domains. Structural studies have established that they can regulate intrinsic apoptosis and form the interaction sites of the Bcl-2 family.[4] According to the difference of the structure and function, it is divided into three groups: (1) anti-apoptosis (pro-survival or anti-apoptotic) family includes Bcl-2, Bcl-X_L, Bcl-w, Mcl-1 and A1 which having three or four BH domains (BH1-3 or BH1-4); (2) more BH domain pro-apoptotic family, including Bax and Bak, contains three BH domains; (3) only BH3 domain pro-apoptotic family contains only the BH3 domain of Bcl-2 homology, such as Noxa, Bid, Bik, Bim, Bmf, Hrk, Bad, PUMA and Beclin-1.[5] Only BH3 domain proteins are apoptotic effector molecules.[6] The fate of cells is related to the relative ratio of the three groups mentioned above. As an important regulator in apoptosis, Bcl-2 proteins can suppress the apoptosis to affect the chemotherapy. Therefore, down-regulating anti-apoptotic Bcl-2 proteins can be effective for the treatment of cancers. Along this line, numbers of Bcl-2 family inhibitors have been reported in the past few years, which can be classed into BH3 peptides (Liu et al. designed a BH3-only peptide sequence TATDV3-(PU-MA) BH3),[7] the Bcl-2 antisense oligonucleotides(Genasense)[8] and some non-peptide small molecular inhibitors.[9]

Compared to the BH3 peptides, the non-peptide anti-apoptotic Bcl-2 inhibitors are more potential in the tumor treatment. In recent years, researchers have reported various small molecular anti-apoptotic proteins inhibitors through the advanced technologies, such as virtual screening and structure-based design. Based on their structures, they are grouped into five classes, BH3Is derivatives (BH3I-1),[10] polyphenol derivatives (Gossypol),[11] chromene derivatives (HA14-1),[12] acylsulfonamide derivatives (ABT-263)[13] and others (GX15-070).[14] Recent researches revealed that Bcl-X_L protein can lead to the reduction of platelet.[15] Therefore, there is more and more interest in the development of novel selective Bcl-2 inhibitors. Fortunately, ABT-199 as an effective Bcl-2 inhibitor has been listed recently. However, it shows no binding affinity for Mcl-1 protein, so it has no effect on carcinoma cells which exhibit overexpressed Mcl-1. Besides, the relationship between Mcl-1 and Bcl-2 was studied[16] and the results showed

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http://dx.doi.org/10.1016/j.bmc.2017.02.014
0968-0896/

Coordination Chemistry Reviews 352 (2017) 108–150

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

The coordination chemistry of N-heterocyclic carboxylic acid: A comparison of the coordination polymers constructed by 4,5-imidazoledicarboxylic acid and 1*H*-1,2,3-triazole-4,5-dicarboxylic acid

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ARTICLE INFO

Article history:
Received 5 July 2017
Accepted 28 August 2017
Available online 21 September 2017

Keywords:
Coordination polymers
Crystal structures
4,5-Imidazoledicarboxylic acid
1*H*-1,2,3-Triazole-4,5-dicarboxylic acid
Properties

ABSTRACT

In recent decades, coordination polymers (CPs) constructed by metal ions/clusters as nodes and organic linkers through coordination interactions, have expanded rapidly in both academic and industrial realms. Understanding the coordination chemistry of the organic linkers can greatly help the rational design and synthesis of targeted CPs because a minor change in the organic linker can greatly induce a structural variation of the final coordination structures. 4,5-imidazoledicarboxylic acid (H_3imda) and 1*H*-1,2,3-triazole-4,5-dicarboxylic acid (H_3tda) are two analogue N-heterocyclic carboxylic ligands except for the difference of 2-site N or C, which have the advantages from both imidazole/triazole and carboxylic groups and have been widely used as multifunctional linkers to construct numerous CPs with various architectures and interesting properties such as gas storage and separation, luminescence, catalysis, and magnetism in the past two decades. When the 2-site N donor of H_3tda is not coordinated with metal center, they can present similar architectures; however, when the 2-site N donor is deprotonated and binds to metal centers, they generally exhibit distinct differences in the structures and accessorial properties. In this context, these two ligands provide a valuable model for understanding the key role of donor position to the influence of structures of CPs. This review provides an overview on the coordination chemistry of H_3imda and H_3tda, which are organized as follows: (i) the coordination modes of H_3imda and H_3tda influenced by the various acidity-dependent systems; (ii) the coordination chemistry of homometallic CPs (HOCPs) with H_3imda and H_3tda; (iii) the coordination chemistry of heterometallic CPs (HECPs) with H_3imda and H_3tda. Representative examples are shown in each section that highlights the relationships between the two ligands and targeted structures. Besides, the readers will also be directed to the relevant articles and reviews on N-heterocyclic derivatives, which will guide further investigations into a particular aspect of coordination chemistry with N-heterocyclic derivatives.

Abbreviations: CPs, coordination polymers; MOFs, metal–organic frameworks; ZIFs, zeolitic-imidazole frameworks; POMs, polyoxometalates; H_3tda, 1*H*-1,2,3-triazole-4,5-dicarboxylate; H_3imda, 4,5-imidazoledicarboxylate; Htz, 1*H*-1,2,4-triazole; Hbtz, benzotriazole; 2,2′-bipy, 2,2′-bipyridine; phen, 1,10-phenanthroline; 1,2-dach, 1,2-diaminocyclohexane; 2,2′-bim, 2,2′-biimidazole; Himpy, 2-(1-*H*-imidazol-2-yl)pyridine; 4,4′-bipy, 4,4′-bipyridine; azopy, 4,4′-azobispridine; prz, piperazine; Hina, isonicotinic acid; Hnio, nicotinate *N*-oxide; Hima, imidazol-1-yl-acetate; 1,2-dap, 1,2-propanediamine; eta, ethanolamine; DMF, *N*,*N*-dimethylformamide; DMA, *N*,*N*-dimethylacetamide; H_4mdip, methylenediisophthalic acid; Htma, tetramethylammonium hydroxide; salpn, (salicylideneaminato)-1,3-diaminopropane; H_2but, but-2-ynedioic acid; dtsalpn, (3,5-di-*t*-butylsalicylideneaminato)-1,3-diaminopropane; tmdp, 4,4′-trimethylenedipiperidine; H_2ox, oxalic acid; H_2pyrrld, 2-pyrrolidone-5-carboxylic acid; 2,2′-bipyo, 2,2′-bipyridine-*N*,*N*′-dioxide; 4,4′-bipyo, 4,4′-bipyridine-*N*,*N*′-dioxide; bpe, 1,2-bi(pyridin-4-yl)ethene; Et_3N, triethylamine; en, ethylenediamine; pytpy, 4′-(3-pyridyl)-2,2′:6′,2″-terpyridine; pyz, pyrazine; 1,4-H_2bdc, terephthalate; btc, 1,3,5-benzenetricarboxylate; D-H_2cam, D-camphoric acid; py, pyridine; Him, imidazole; 2,5-bptz, 2,5-bis(pyrid-4-yl)-1,3,4-thiadiazole; H_2imc, 4-imidazolecarboxylate; H_2ip, isophthalate; bbi, 1,1′-(1,4-butanediyl)bis(imidazole); Hpp, 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine; gun, guanidine; bix, 1,4-bis(imidazol-1-ylmethyl)-benzene; bib, 1,4-bis(1-imidazolyl)benzene; dpb, 1,4-di(pyridin-4-yl)benzene; dpbp, 4,4′-di(pyridin-4-yl)-1,1′-biphenyl; H_2aip, 5-aminoisophthalic acid; Hipt, 5-(4-(1*H*-imidazol-1-yl)phenyl)-1*H*-tetrazolate; cyclam, 1,4,8,11-tetraazacyclotetradecane; bpp, 1,3-di(4-pyridyl)propane; Hacac, acetylacetone; Hepes, 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid.

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http://dx.doi.org/10.1016/j.ccr.2017.08.022
0010-8545/

Functional Materials Letters
Vol. 10, No. 2 (2017) 1750008 (4 pages)

DOI: 10.1142/S1793604717500084

$Co_4I_3O_{24}H_{15}{\cdot}3H_2O$: A new amorphous semiconductor with intrinsical photocatalytic performance in organic dye degradation driven by visible light

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Received 2 October 2016; Accepted 12 November 2016; Published 22 December 2016

Amorphous semiconductor photocatalysts are highly desirable because they are facile and low-cost to prepare in comparison with the crystalline ones. The amorphous semiconductor with photocatalytic activity has been rarely reported. In this work, a new amorphous semiconductor photocatalyst, $Co_4I_3O_{24}H_{15} \cdot 3H_2O$, was successfully developed. Its microstructure is composed of irregular particles with size of 2–20 μm. In photocatalytic degradation of rhodamine B (RhB), or methylene blue (MB) dyes driven by visible light, the $Co_4I_3O_{24}H_{15} \cdot 3H_2O$ sample exhibited pronounced activity. Its activity is higher than Degussa P25 (commercial TiO_2) in RhB degradation. It was testified that the degradation of RhB is due to the intrinsical photocatalytic role of $Co_4I_3O_{24}H_{15} \cdot 3H_2O$. The reusability of the $Co_4I_3O_{24}H_{15} \cdot 3H_2O$ photocatalyst was also investigated.

Keywords: Amorphous semiconductor; photocatalysis; degradation; visible light.

Semiconductor photocatalysis is a promising way to utilize solar energy in decomposition of organic contaminants.[1–14] In this way, the current environment pollution and energy crisis are addressed simultaneously. Utilization of abundant visible light of solar radiation through photocatalysis is believed to be the key issue to utilize solar energy during the process.[1–14] Thus, the development of visible-light-responsive photocatalysts is significant for fully utilizing solar energy in photocatalysis.[1–14]

At first, crystalline semiconductors were preferred as photocatalysts because it was ever commonly accepted that amorphous semiconductors are inactive in photocatalysis due to their abundant defects and hence fast recombination of excited carrier.[15] Recent investigations have demonstrated that amorphous semiconductors like MoS_2,[15] TiO_2[16] and $BiVO_4$[17] also can be active in photocatalysis. Although these amorphous semiconductors have been successfully used in photocatalysis, they mostly functioned as the dopants to enhance photocatalytic activity of the whole composite photocatalysts. The amorphous semiconductors with intrinsical photocatalytic performance have been rarely reported. A few amorphous semiconductors like $NaTaO_3$,[18] silver silicates[19] were found to have intrinsical photocatalytic performance. However, the current data on amorphous photocatalysts is scarce, and there is still much room to enhance the photocatalytic performance of amorphous semiconductors.

On the other hand, amorphous materials possess no crystalline phase that was usually obtained at high temperature through calcination or hydrothermal crystallization.[15–19] Therefore, the preparation of amorphous photocatalysts generally avoids the operation at high temperature, and thus might be facile and energy-saving. This makes it possible that the preparation can be easily scaled up at low cost, which is favorable for practical application of the photocatalysis technology. Therefore, exploring new amorphous photocatalysts would not only provide deeper insight into the amorphous semiconductor photocatalysis, but also be of great importance for future development and practical application of photocatalysis.[15–19]

As reported previously, reacting trivalent cobalt salts with $NaIO_4$ in aqueous acid solution inevitably generated dark-green $Co_4I_3O_{24}H_{15} \cdot 3H_2O$ precipitate.[20] In 1967, preparation

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Materials Letters 207 (2017) 169–171

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Preparation of an efficient NiAuPd/graphene nanocatalyst via one-pot reaction

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ARTICLE INFO

Article history:
Received 9 June 2017
Accepted 14 July 2017
Available online 15 July 2017

Keywords:
Hydrogen generation
Hydrogen energy
Graphene

ABSTRACT

The NiAuPd/G nanocatalyst was prepared by one-pot hydrothermal synthesis. The compositional analysis, structural characterization, morphology and performance of the resulting synthetic catalyst were done by Energy Dispersive X-ray Spectroscopy (EDX), X-ray diffraction (XRD) and Transmission electron microscope (TEM). In addition, catalytic activities of the NiAuPd/G catalyst was investigated. It is found that the NiAuPd/graphene exhibits a perfect crystal structure. The NiAuPd/graphene exhibits a high catalytic activity for the dehydrogenation of formic acid at room temperature and without additives.

1. Introduction

Nowadays, searching for the effective hydrogen (H_2) storage/-generation materials remains one of the most difficult challenges toward a fuel-cell-based H_2 economy as a long-term solution for secure energy in the future [1–4]. Recently, homogeneous directional selection dehydrogenation catalysts made some progress. Many researchers have tried to achieve this by adding secondary metals to some precious metals. The improvements in hydrogen selectivity were particularly significant for Pd–Au [6,7] and Pd–Ag [5,8] catalysts. However, these catalysts require higher reaction temperatures in order to have better catalytic activity. Most importantly, these catalysts often contain gold (Au), platinum (Pt), palladium (Pd), silver (Ag) and other precious metals, it is difficult to put into practical production and applications.

The first-row transition metals (FRTM) have been widely investigated as the catalytic materials in many important reactions, such as nickel (Ni) nanoparticles (NPs) because of their potential activities and relatively low costs [9]. Studies have shown that nano-FRTM have a poor stability in FA and can be easily etched [10]. Moreover, the incorporation of FRTM into the noble metals with the alloy structure may not only lead to the enhancement of the catalytic performance, but also could reduce the consumption of the noble metals [11].

Due to its large specific surface area, graphene has been widely used as the supporting material for metal particles in catalysis [12]. Since graphene has excellent thermal conductivity and structural stability, while the modified graphene can enhance the interaction between the support and the metal, so graphene-based catalyst tend to exhibit a better catalytic performance.

Herein, we report the facile synthesis of the NiAuPd nanoalloy based on a non-noble metal and supported on graphene (NiAuPd/G). A NiAuPd alloy-based catalyst with a graphene-based matrix as the supporting material was prepared by one-step hydrothermal synthesis. The catalytic system described here has the following advantages: (i) no requirement for additives, (ii) superior catalytic activity compared with conventional inorganic supports, (iii) Prepared by the reduction of graphene oxide and nano-alloy NiAuPd at the same time, (v) the formation of Ni–Au–Pd nanocatalyst significantly enhanced the catalytic activity.

2. Experimental

2.1. Physical measurements

X-ray diffraction (XRD) measurements were conducted at room temperature using a specular reflection mode (Bruker D-8, Cu Kα radiation, $\lambda = 0.154056$ nm). Transmission electron microscope

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http://dx.doi.org/10.1016/j.matlet.2017.07.067
0167-577X/

Preparation of Doubly Responsive Polymer Functionalized Silica Hybrid Nanoparticles via a One-Pot Thiol-Isocyanate Click Reaction at Room Temperature

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Well-defined poly(*N*-isopropylacrylamide) and poly(2-(diethylamino) ethyl methacrylate) were synthesized first by a reversible addition-fragmentation chain transfer process. These polymers were then reduced to generate an end thiol group to react with isocyanate groups on the surface of silica nanoparticles, which were pretreated with toluene-2,4-diisocyanate, by a one-pot "click" reaction to prepare temperature and pH responsive polymer functionalized hybrid silica nanoparticles. The polymer functionalized silica hybrid nanoparticles were characterized by a range of techniques such as Fourier transform infrared spectroscopy and dynamic light scattering. The doubly responsive polymer functionalized silica hybrid nanoparticles show both temperature and pH responsive behavior and their solution properties were dependent on the ratio of the two polymers on the surface of silica. Covalent functionalization of the silica nanoparticle with well-defined temperature and pH responsive polymers was accomplished via a one-pot thiol-isocyanate click reaction. This reaction was found to be extremely efficient in producing doubly responsive polymer functionalized silica hybrid nanoparticle, even at relatively low reaction temperature and short reaction time. Thermogravimetric analysis indicated that the same ratio of poly(*N*-isopropylacrylamide) and poly(2-(diethylamino)ethyl methacrylate) functionalized silica hybrid nanoparticle consisted of 42.46 wt% polymer. POLYM. COMPOS., 00:000–000, 2015. © 2015 Society of Plastics Engineers

INTRODUCTION

The recent development of hybrid particles made of various inorganic nanoparticle cores and polymeric shells results in properties that cannot be obtained by the core particles or polymers alone [1]. These hybrid particles have been investigated for various applications including sensor, membrane, implantable device, biomedical applications, and chromatography matrices [2–4]. There are several methods that can be used to immobilize a polymer onto a inorganic nanoparticle surface to prepare such hybrid particles. A grafting to, a grafting from, and layer by layer method are often used to immobilize a well defined polymer on the surface of inorganic nanoparticle [5]. Furthermore, the use of highly efficient coupling chemistries, such as "click chemistry," enables polymer chemists to functionalize inorganic nanoparticle with polymer [6]. For instance, a copper (I)-catalyzed azide-alkyne cycloaddition click chemistry method was used to attach well-defined thermoresponsive PNIPAM onto the exterior surface of SiO_2 nanoparticles, and the hydrodynamic diameter of the core-shell nanostructure decreased from 130 to 67 nm gradually with the temperature increasing from 24 to 40°C [7]. However, this type of click chemistry usually needs a metal catalyst. Therefore, metal-free click chemistry approaches such as the

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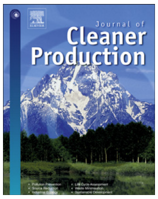
Contract grant sponsor: Hunan Provincial Natural Science Foundation; contract grant number: 13JJA004; contract grant sponsor: Scientific Research Fund of Hunan Provincial Education Department; contract grant number: 15K041; contract grant sponsor: Foundation of State Key Laboratory of Powder Metallurgy; contract grant sponsor: Fund of National Natural Science Foundation, People's Republic of China; contract grant number: 51443002.
DOI 10.1002/pc.23713

Journal of Cleaner Production 161 (2017) 239–244

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro



Conversion of HBr to Br_2 in the flue gas from the combustion of waste printed circuit boards in post-combustion area

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ARTICLE INFO

Article history:
Received 12 January 2017
Received in revised form
9 May 2017
Accepted 21 May 2017
Available online 22 May 2017

Keywords:
Inorganic bromine
Conversion
Post-combustion area
Waste printed circuit boards
Flue gas

ABSTRACT

It is crucial to prevent the secondary pollution when recycling wastes. During the recycling of waste printed circuit boards by the pyrometallurgical process, bromine in the raw materials is normally released in the form of HBr/Br_2 into the flue gas. In the present work, for the first time the conversion of HBr to Br_2 during the cooling of flue gas in the post combustion area (PCA) was studied to provide evidences for the control of PBDD/Fs and the recycling of Br.

The 1200 °C flue gas was cooled down at various cooling rates in a lab-scale system. The influence of PCA operating conditions, i.e., cooling temperature (Tc), residence time in the cooling zone (RTcz) and Oxygen partial pressure (P_{O2}), on the conversion ratio was studied systematically. And the study was based on the newly developed method to determine HBr and Br_2 contents in the flue gas at various temperatures.

For each RTcz, i.e., 0.3, 0.5 and 0.7s, the ratio first increases with decreasing Tc to a maximum value at Tc_{max} and then decreases as Tc further drops. Tc_{max} depends on RTcz. For Tc = 200 °C and RTcz = 0.3s, approximately 31.1% HBr is converted to Br_2. This is 51% lower than the highest. Moreover, at lower Tc and longer RTcz, the ratio can be less than that at higher Tc and shorter RTcz, vice versa. Accordingly, when cooling the system to a certain temperature, the shorter the RTcz is, the lower the conversion ratio will be. P_{O2} slightly influences the ratio. These are vital to the determination of Br sources for PBDD/Fs formation in PCA, which is valuable for the future pollution control. Besides, extension of the cooling time in the lower temperature range (from 200 °C at RTcz = 0.3s to 50 °C) within 300s greatly improves the ratio up to 91%. This provides the basis for the Br recovery rather than removal by chemical agents.

1. Introduction

It is crucial to prevent the secondary pollution when recycling waste.

Waste printed circuit boards (WPCBs) contain approximately 30% metallic materials, approximately 40% organic resin materials, and around 30% glass materials (United Nations Environment Programme, 2009; Choubey et al., 2015). The typical composition of various metals in PCBs is as follows: copper ~16%, Al~4.7%, solder ~4%, iron ~3%, nickel ~2%, silver ~0.05%, gold ~0.03%, palladium ~0.01%, etc. (Zhou and Qiu, 2010; Tuncuk et al., 2012). And the metallic concentrations in WPCBs can be several times higher than their respective ores. Besides, because of its great flame-retardant properties and low cost, the brominated flame retardants are widely used in printed circuit board (PCBs). Normally, the Br content is between 3 and 8 wt%, and typically it is around 6% (Ortuño et al., 2013; Xiao et al., 2014).

Currently, many technologies have been proposed for materials (excluding bromine) recovery from WPCBs. Among them, pyrometallurgical processing featuring high temperature combustion is the most promising: although subject to current technical level,

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http://dx.doi.org/10.1016/j.jclepro.2017.05.117

有机化学 DOI: 10.6023/cjoc201702050 综述与进展
Chinese Journal of Organic Chemistry REVIEW

简单易得试剂与磷-氢化合物交叉偶联合成有机磷化合物

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摘要　综述了近年来利用磷-氢化合物与简单易得试剂交叉偶联合成有机磷化合物的研究进展. 主要包括利用末端炔烃与磷-氢化合物通过 C—H/P—H 交叉偶联合成炔基膦化合物, 利用简单易得的含氧、含硫或含氮有机化合物与磷-氢化合物交叉偶联构建 sp^2/sp^3-C—P 键或 P—Z 键, 并对部分反应的机理进行扼要总结.

关键词　磷-氢化合物; 交叉偶联; 有机磷化合物

Recent Advances in the Synthesis of Organophosphorus Compounds via Cross Coupling between Readily Available Materials and P—H Compounds

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Abstract　This mini-review focuses on the recent advances in the synthesis of organophosphorus compounds via cross coupling of P—H compounds with readily available starting materials, mainly including the reactions of terminal alkynes and heteroatom compounds (oxygen, sulfur or nitrogen-contained compounds) with P—H compounds forming sp-C—P, sp^2-C—P, sp^3-C—P, and P—Z bonds. Related reaction mechanisms are also discussed.

Keywords　P-H compounds; cross coupling; organophosphorus compounds

有机磷化合物在有机合成、医药、农药、材料以及生命科学中都有着广泛的应用[1]. 传统的制备有机磷化合物的方法主要是通过磷卤试剂的亲核取代反应[2], 由于该方法中使用的反应底物大都对空气敏感, 使得反应条件比较苛刻, 底物局限性较大, 且反应产生当量有机卤代副产物, 不符合绿色化学发展要求. 与磷卤试剂相比, 磷-氢化合物更为绿色稳定. 利用磷-氢化合物与其他偶联试剂反应直接构建有机磷化合物, 其反应的原子经济性较高, 更为绿色环保. 近年来, 通过过渡金属催化磷-氢化合物交叉偶联构建有机磷化合物是有机磷化学中的研究热点之一[3]. 该方法主要有以下几点优势: (1)避免对水氧敏感的磷卤试剂的使用, 反应更简单绿色; (2)反应条件温和, 底物适用范围更广; (3)原子经济性和步骤经济性高, 符合绿色化学发展需求.

简单易得试剂来源广泛, 通常具有廉价、稳定、易储存等特点, 因此利用该类化合物作为反应底物进行交叉偶联反应具有较高的研究价值, 且符合绿色化学发展要求. 但部分底物存在惰性强, 难以活化, 选择性较差

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Received February 28, 2017; revised April 8, 2017; published online May 2, 2017.
Project supported by the National Natural Science Foundation of China (Nos. 21373080, 21573065, 21273066), and the Natural Science Foundation of Hunan Province (No. 2016JJ1007)
国家自然科学基金(Nos. 21373080, 21573065, 21273066)和湖南省杰出青年基金(No. 2016JJ1007)资助项目.

Nanoscience and
Nanotechnology Letters
Vol. 9, 873–879, 2017

In-Situ Synthesized Ag@AgCl-Collagen Fiber Nano-Hybrid Materials and Their Photocatalytic Activities

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To expand the utilization of collagen fiber, Ag@AgCl-collagen fiber nano-hybrid materials with photocatalytic activities were successfully prepared in this study via an *in situ* organic–inorganic process. The surface morphology, hybrid mechanism and the chemical composition and structure of these materials are discussed, and the evaluation of photocatalytic activity is included at the end of this paper. The SEM observation showed that the AgCl particles were evenly distributed in the collagen fiber, and the size of the AgCl particles was approximately 300–500 nm. The comparison of these SEM photographs implied the hybrid mechanism of the *in situ* organic–inorganic process. XRD patterns and FTIR analysis certified the existence of AgCl and collagen fiber, respectively. The photocatalytic activity evaluation was carried out by degrading methyl orange (MO) under ultraviolet (UV) light and daylight, respectively. The experimental results indicated that Ag@AgCl-collagen fiber nano-hybrid materials can respond to both UV and daylight, and their photocatalytic activity was notable. The effect of pH on the degradation of MO under daylight was also investigated; the results showed that the photocatalytic activity was restricted as pH value increased. Lastly, the antibacterial performance was investigated by measuring the widths of the bacteriostatic belts, which indicated the antibacterial activity of the material.

Keywords: Functional Composites, Recycling, Surface Treatments, Photocatalytic Activity, Antibacterial Activity.

1. INTRODUCTION

Nanomaterials have been widely applied in biomedicine,[1–3] new energy,[4, 5] biosensor,[6, 7] and environmental treatment[8] with the development of nanotechnology. Nano-fibers have received considerable attentions due to its advantages such as high efficiency and feasibilities in wastewater treatment, and have been rapidly developed in recent years. At present, photocatalytic degradation has been identified as a powerful method for wastewater treatment.[9] Effluents discharged by the textile industry contain large amounts of azo dyes, which are non-biodegradable, toxic and potentially carcinogenic, causing serious environmental pollution.[10] Methyl orange (MO) dye wastewaters that are produced from the textile, photograph and printing industries are highly stable in near UV and visible light.[11] The conventional methyl orange (MO) dye wastewater treatments are non-destructive, and they will generate secondary toxic wastes or concentrate the pollutant-containing phase.[12] In contrast, photocatalytic degradation in treating MO wastewater is complete and environmentally friendly.[13] The metal-oxide photocatalysts such as TiO_2,[14, 15] ZnO,[16] CuO[17] and SnO_2,[18] etc., are the most extensively used photosensitizers, and their decomposition mechanisms of organic substance in wastewaters have been studied thoroughly,[19] however, there is few report on AgCl and it's photocatalytic activity. In fact, AgCl belongs to the "second generation" photocatalysts,[20] which responds to both ultraviolet (UV) and visible light. The sunlight consists of 50% visible light and only approximately 4% UV light.[21] So, the light utilization of AgCl is more efficient than the others, which can only work under UV light during the photocatalytic process.

In addition to the textile industry, the leather industry is another major polluter.[22] Making full use of the raw hides and reusing the trimming wastes are the most economical ways of reducing pollutants. Trimming wastes from the leather industry contain a great quantity of collagen, which is the major structural component of skin, tendon, bone and connective tissue.[23] Many tons

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1941-4900/2017/9/873/007 doi:10.1166/nnl.2017.2406

Journal of Physics and Chemistry of Solids 100 (2017) 33–39

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

A novel $Ce(IO_3)_4$ catalyst: Facile preparation and high activity in degradation of organic dyes without light irradiation at room temperature

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ARTICLE INFO

Article history:
Received 7 June 2016
Received in revised form
3 September 2016
Accepted 13 September 2016
Available online 13 September 2016

Keywords:
Inorganic compounds
Chemical synthesis
Amorphous materials
Photoelectron spectroscopy

ABSTRACT

Developing efficient catalysts capable of degrading organic dye free of light irradiation is highly interesting from the energy-saving point of view. In this work, we prepared a new $Ce(IO_3)_4$ catalyst by a facile precipitation method. The obtained $Ce(IO_3)_4$ sample showed remarkably superior performance to the reported $CeGeO_4$ analog in degradation of rhodamine B (RhB), methyl orange (MO) or methylene blue (MB) dyes in the dark at room temperature. The ultraviolet-visible (UV–vis) absorption spectra of dye solution during degradation, the XPS results of $Ce(IO_3)_4$ and the control experiments confirmed that the dye degradation is a catalytic process. The reusability of it was also investigated in the degradation experiments.

1. Introduction

The large scale of textile industry, which released much organic dyes that are not degradable naturally, constitutes a major source of water pollution. Photocatalysis technology has been increasingly important because of its application in degradation of organic dye pollutants with sustainable solar energy [1–8]. The core issue of utilizing solar energy through photocatalysis is to develop visible-light-responsive photocatalysts to fully use visible light, which is the most abundant in solar radiation, during photocatalytic process [5,9]. However, it is still difficult to obtain visible-light-responsive photocatalysts with high performance for dye pollutants degradation [5,9]. Process of catalytic wet air oxidation (CWAO) might be a promising solution for this issue. Through the CWAO process, organic dye pollutants can be degraded with no need of light illumination at room temperature [10–14]. A favorable catalyst is crucial to a CWAO process because it is able to decrease the severity of oxidation conditions like reaction temperature, reaction pressure, etc [10–14]. Thus, developing favorable catalysts remains desirable for the study and application of CWAO. Several catalysts like $Zn_{1.5}PMo_{12}O_{40}$ [10], $La_4Ni_3O_{10}$ [11], CuO-MoO_3-P_2O_5 [12], Fe_2O_3-CeO_2-TiO_2/γ-Al_2O_3 [13] and Ce-doped MoO_3 [14] have been hitherto prepared to degrade organic dyes by the CWAO method at room temperature. Very recently, we prepared a $CeGeO_4$ catalyst and found that it can be used to degrade RhB or MB dyes under these energy-saving conditions [15]. However, there is still much room to enhance the catalytic efficiency of the CWAO degradation of organic dyes at room temperature. Developing new catalysts for CWAO degradation of organic dyes would not only improve the degradation efficiency, but also provide deeper insight in the CWAO process.

In this work, we successfully prepared a $Ce(IO_3)_4$ compound by a simple precipitation method [16], and interestingly found that Ce $(IO_3)_4$ is an efficient catalyst to degrade organic dyes even in the dark at room temperature. Under these degradation conditions, the $Ce(IO_3)_4$ catalyst is very attractive because it achieved much higher performance than the reported $CegeO_4$ one [15].

2. Experimental

2.1. Preparation

$Ce(SO_4)_2$, $NaIO_3$, RhB, MO, MB, NaN_3, p-benzoquinone and tert-butanol was purchased from Sigma-Aldrich Company. The $Ce(IO_3)_4$ sample was prepared by a simple precipitation method [16]. Typically, 1 mmol of $Ce(SO_4)_2$ and 4 mmol of $NaIO_3$ were dissolved in

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http://dx.doi.org/10.1016/j.jpcs.2016.09.007

第 33 卷第 7 期
2017 年 7 月

高分子材料科学与工程
POLYMER MATERIALS SCIENCE AND ENGINEERING

Vol. 33, No. 7
Jul. 2017

温度和 pH 双重敏感型聚氨酯水凝胶的制备及性能

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摘要: 以聚乙二醇(PEG)、4，4'-二苯基甲烷二异氰酸酯(MDI)、三羟甲基丙烷(TMP)为主要原料，分别采用 1，4-丁二醇(BDO)、N-甲基二乙醇胺(MDEA)、2，2-二羟甲基丙酸(DMPA)为扩链剂，制备了 3 种聚氨酯水凝胶 Hydrogel (a)、Hydrogel (b)、Hydrogel (c)。通过红外光谱、差示扫描量热分析、X 射线衍射和溶胀实验对水凝胶的结构和性能进行了分析。研究结果表明，温度敏感链段(PEG)和 pH 敏感基团(—N(CH$_3$)—、—COOH)均成功地引入到了水凝胶分子链中；3 种水凝胶的相转变温度分别为 55 ℃、60 ℃和 64 ℃，且合成后水凝胶中 PEG 的结晶结构仍然存在；当水溶液温度从 45 ℃上升到 60 ℃时，3 种水凝胶的平衡溶胀度均显著减小，显示出温度敏感性；当 pH 从4.0上升到7.0时，Hydrogel (c) 的平衡溶胀度从11.5增大到15.5，当 pH 从8.5上升到11.5时，Hydrogel (b) 的平衡溶胀度从12.9减小到10.0，均显示出 pH 敏感性；在不同温度(25 ℃和 65 ℃)和 pH (2.5和11.5)的水溶液中反复溶胀，水凝胶 Hydrogel (b) 和 Hydrogel (c) 均表现出良好的可逆性和稳定性。

关键词: 聚氨酯；水凝胶；温度敏感性；pH 敏感性

中图分类号: TQ323.8　　**文献标识码:** A　　**文章编号:** 1000-7555(2017)07-0011-06

进入 21 世纪，具有双重或多重敏感特性的聚氨酯水凝胶在物质分离、分子印迹、医用材料等领域显示出了广阔的应用前景，引起了众多学者的广泛关注与研究[1~3]。双重或多重敏感型聚氨酯水凝胶是一种分子链由聚氨酯组成，能够对外界环境中的双重或多重刺激产生智能响应的高分子聚合物。在双重或多重敏感型聚氨酯水凝胶的研究中，又以温度和 pH 双重敏感型聚氨酯水凝胶的研究最为广泛[4]。这主要是因为温度和 pH 是生理、生态和化学系统中最重要的两个因素[5]。

通常，温度和 pH 双重敏感型聚氨酯水凝胶是通过表面接枝技术在温度敏感型聚氨酯水凝胶上接枝具有 pH 敏感特性的官能团来制备[6]。但是表面接枝技术存在接枝率低、浪费功能单体和 pH 敏感特性不稳定等一系列问题[7,8]。而使用分子共聚技术制备的温度和 pH 双重敏感型聚氨酯水凝胶不仅能控制引入基团的含量和 pH 敏感特性，而且还可以调控 pH 敏感阈值。可见，采用分子共聚技术制备温度和 pH 双重敏感型聚氨酯水凝胶具有潜在的发展优势。

本文采用三步分子共聚技术，选用聚乙二醇(PEG)、4，4'-二苯基甲烷二异氰酸酯(MDI)、三羟甲基丙烷(TMP)为主要原料，分别利用 1，4-丁二醇(BDO)、N-甲基二乙醇胺(MDEA)、2，2-二羟甲基丙酸(DMPA)为扩链剂，制备了 3 种不同的聚氨酯水凝胶。本文不仅对水凝胶的化学结构、相态结构、结晶形态等进行了分析，还对水凝胶的温度敏感特性、pH 敏感特性、溶胀-退胀性能进行了系统研究，有望为聚氨酯水凝胶的开发与应用提供借鉴作用。

1　实验部分

1.1　原料

聚乙二醇(PEG)：$M_w = 6000$，分析纯，日本株式会社；4，4'-二苯基甲烷二异氰酸酯(MDI)：化学纯，烟台万华聚氨酯股份有限公司；1，4-丁二醇(BDO)、N-甲基二乙醇胺(MDEA)：分析纯，上海展云化工有限公司；2，2-二羟甲基丙酸(DMPA)：分析纯，天津威一化工科技有限公司；三羟甲基丙烷(TMP)：分析纯，上海埃彼化学试剂有限公司。其中 PEG、BDO、MDEA、DM-

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doi: 10.16865/j.cnki.1000-7555.2017.07.003

收稿日期: 2016-07-20

基金项目: 国家自然科学基金资助项目(51443002，21402048)；湖南省自然科学基金资助项目(14JJ5013)；湖南省教育厅青年项目(14B064)；湖湘青年英才项目(2015RS4044)

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第 32 卷 第 1 期　　湖南科技大学学报(自然科学版)　　Vol.32 No.1
2017 年　3 月　　Journal of Hunan University of Science & Technology(Natural Science Edition)　　Mar. 2017

doi: 10.13582/j.cnki.1672-9102.2017.01.015

2-(2,5-二羟基苯基) -4(3H) -喹唑啉酮质子转移及七元瓜环限制作用的理论研究

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摘　要: 在 B3LYP/6-311++G(d) 和 ONIOM(B3LYP/6-311++g(d) : PM3) 水平上，研究了 2-(2,5-二羟基苯基) -4(3H) -喹唑啉酮(DHPQ) 及其在七元瓜环(CB7) 限制下的双质子转移过程，确定了 DHPQ 分子各互变异构体的结构、能量以及基态质子转移反应的过渡态. 通过对结构变化和能量差异的分析，探讨了 DHPQ 中的双质子转移机理，考察了质子转移的纳米笼效应以及该笼效应对质子转移热力学性质的影响，同时研究纳米腔与 DHPQ 的几何匹配关系以及水溶剂对包合物质子转移的影响. 计算结果表明: DHPQ 是采取分步转移机理，纳米腔的限制对质子转移过程产生一个很大的能垒，抑制分子内质子转移过程，水溶剂的引入促进 Path 2，抑制 Path 1.

关键词: 双质子转移; 七元瓜环; 喹唑啉酮; ONIOM; 分步转移

中图分类号: O621.1; O621.3　　**文献标志码:** A　　**文章编号:** 1672-9102(2017) 01-0090-07

Theory study on intramolecular proton transfer for 2-(2,5-dihydroxyphenyl) -4(3H) -quinazolinone and restriction effect of cucurbit [7] uril

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Abstract: The ground-state intramolecular double proton transfer process of 2-(2,5-dihydroxyphenyl) -4 (3H) -quinazolinone (DHPQ) and DHPQ@ CB7 was studied systematically at the B3LYP/6-311++G(d) and ONIOM(B3LYP/6-311 ++G(d) : PM3) levels. The structures and energies of all isomers for DHPQ and the transition states in the double proton transfer paths were determined. Through analysising the changes of structures and the differences of energy, the double proton transfer mechanism was explared existed in DHPQ, nanometer cage effect was considered on the thermodynamic properties in the process, at the same time, geometric matching relation between the nanocavity and DHPQ was studied as well as the effect of H_2O medium on DHPQ proton transfer process. The results showed that double proton transfer process in DHPQ carried out step by step, the limit of nano cavity produced a large energy barrier, inhibiting the intramolecular proton transfer process, and the introduction of water solvent promoted the path 2 but inhibited path 1.

Keywords: duble proton transfer; cucurbit [7] uril; quinazolinone; ONIOM; stepwise mechanism

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收稿日期: 2015-12-14

基金项目: 国家自然科学基金资助项目(21172066,20971041) ; 湖南省高校科技创新团队资助项目(湘教通 [2012] 318)

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Material Sciences 材料科学, 2017, 7(7), 655-665

https://doi.org/10.12677/ms.2017.77087

Synthesis of Thiol-Functionalized Mesoporous Calcium Silicate and Its Adsorption Charateristics for Pb^{2+}

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Received: Oct. 7th, 2017; accepted: Oct. 18th, 2017; published: Oct. 27th, 2017

Abstract

Thiol-functionalized mesoporous calcium silicate (MCS-SH) was synthesized by post-grafting method using calcium nitrate tetrahydrate and sodium metasilicate nonahydrate as raw materials, cetyl trimethyl ammonium bromide as template, and (3-mercaptopropyl) trimethoxysilane as modifying agent, and its structures were characterized. The adsorption performance of MCS-SH for Pb^{2+} was investigated, and the adsorptive thermodynamics were explored. The results show that MCS-SH has still maintained mesoporous slit-pore structure in the modification process, with a specific surface area of 129.32 $m^2 \cdot g^{-1}$ and pore size mainly distributed in 5-49 nm. The amount of substance of –SH grafted to MCS-SH is calculated to be 0.4594 $mmol \cdot g^{-1}$ according to the sulfur content determined. The equilibrium adsorption data of MCS-SH for Pb^{2+} fitted to Langmuir model, and fitted better to Redlich-Peterson model. The adsorption of MCS-SH towards Pb^{2+} is an endothermic reaction and spontaneous process driven by an increase in entropy, and there exists both physical and chemical adsorption. The maximum adsorption capacity for Pb^{2+} deduced from the Langmuir model was 618.09 $mg \cdot g^{-1}$, which is much higher than those of adsorbents in the literature. MCS-SH exhibited an excellent adsorption performance for Pb^{2+} in the pH range of 5.0-7.5.

Keywords

Thiol-Functionalized Mesoporous Calcium Silicate, Lead Ion, Adsorption Performance, Thermodynamics for Adsorption

巯基化介孔硅酸钙的合成及其对Pb^{2+}的吸附特性

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文章引用: 刘立华, 李童, 刘金燕, 胡博强, 周智华, 唐安平. 巯基化介孔硅酸钙的合成及其对 Pb^{2+}的吸附特性[J]. 材料科学, 2017, 7(7): 655-665. DOI: 10.12677/ms.2017.77087

第 32 卷 第 3 期　湖南科技大学学报（自然科学版）　Vol.32 No.3
2017 年　9 月　Journal of Hunan University of Science & Technology（Natural Science Edition）　Sep. 2017

doi：10.13582/j.cnki.1672-9102.2017.03.017

介孔硅酸钙的合成及其对 Pb（Ⅱ）的吸附性能

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摘　要：以硝酸钙和硅酸钠为原料、十二烷基磺酸钠为模板剂，通过共沉淀法制备了介孔硅酸钙；采用 X-射线粉末衍射（XRD）、扫描电镜（SEM）、红外光谱（FT-IR）和孔容与比表面积分析仪（BET）等对其结构和形貌进行了表征；考察了其对含 Pb^{2+} 模拟重金属废水的吸附及解吸再生性能.结果表明，合成的硅酸钙具有介孔结构，为狭缝孔，孔径介于 4-50 nm，比表面积为 250.12 $m^2 \cdot g^{-1}$；在 298 K 下，介孔硅酸钙对 Pb^{2+} 的饱和吸附量为 613.42 $mg \cdot g^{-1}$，远比比表面积为 847.47 $mg \cdot g^{-1}$ 的活性炭大；吸附反应为吸热反应，吸附等温线符合 Langmuir 吸附模型；经 5 次洗脱再生后，介孔硅酸钙对 Pb^{2+} 的饱和吸附量和去除率仅分别降低 37.64 $mg \cdot g^{-1}$ 和 5.88%，表明其具有较好的吸附/再生性能.

关键词：介孔硅酸钙；共沉淀法；Pb^{2+}；吸附

中图分类号：TQ450　　**文献标志码：**A　　**文章编号：**1672-9102（2017）03-0096-07

Synthesis of mesoporous calcium silicate and its adsorption properties for Pb（Ⅱ）

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Abstract： Mesoporous calcium silicate was prepared from calcium nitrate and sodium silicate using sodium dodecyl sulfonate as a template by means of co-precipitation. The calcium silicate synthesized was characterized by the X-ray diffraction（XRD），scanning electron microscopy（SEM），infrared spectrum（FT-IR）and Brunauer-emmett-teller（BET）. The adsorption performance of mesoporous calcium silicate synthesized for Pb^{2+}，and its desorption regeneration performance was also studied. The results show that，the mesoporous calcium silicate synthesized has mesoporous slit-pore structure，with a specific surface area of 250.12 $m^2 \cdot g^{-1}$，and 4-50 nm pore size；the adsorption capacities of mesoporous calcium silicate for Pb^{2+} is 613.42 $mg \cdot g^{-1}$ at 298 K，which is far greater than that by activated carbon with a specific surface area of 847.47 $m^2 \cdot g^{-1}$. The adsorption between heavy metal ions and mesoporous calcium silicate synthesized is an endothermic reaction and in line with the theory of Langmuir isothermal adsorption. The adsorption capacity and removal rate for Pb^{2+} have only decreased 37.64 $mg \cdot g^{-1}$ and 5.88% after 5 times elution-regeneration，respectively，indicating that the mesoporous calcium silicate synthesized is of excellent adsorption and regeneration performance.

Keywords： Mesoporous calcium silicate；co-precipitation；Pb^{2+}；adsorption

重金属元素毒性大、难降解，进入水体之后可以直接通过饮用水或生活用水作用于人体，也能为水生

收稿日期：2016-02-21

基金项目：国家自然科学基金资助项目（51378201）；湖南省教育厅科学研究重点项目（16A069）

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第 32 卷 第 4 期　湖南科技大学学报(自然科学版)　Vol.32 No.4
2017 年 12 月　Journal of Hunan University of Science & Technology(Natural Science Edition)　Dec. 2017

doi:10.13582/j.cnki.1672-9102.2017.04.014

生化处理有机物去除率与动力学参数间关系

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摘　要: 污水处理已趋于多样化,生化处理是较为常规的处理有机物的方法,但是从动力学理论上探索其本质动力学参数关系却是屈指可数.本文通过模拟污水生化处理系统,推导出有机物去除率同有机物降解速率常数、活性污泥浓度及水力停留时间关系的数学模型.结合湘潭某污水处理厂工艺试验数据,把有机物实际去除率与理论去除率作比较.结果表明:通过此模型能够指导生产.

关键词: 污水生化处理;有机物去除率;动力学参数;数学模型

中图分类号: X703.1　**文献标志码:** A　**文章编号:** 1672-9102(2017)04-0090-05

Research on the relationship between the removal rate of organic and kinetic parameters in wastewater biochemical treatment

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Abstract: Nowdays,the treatment of the sewage tends to become more and more diversified, biochemical treatment is a more conventional method of treating organic matter.However,it is only a handful to explore its intrinsic kinetic parameters from the theory of dynamics.By simulating the sewage biochemical treatment system, the mathematical expressions were obtained, which contained the ralitionship among the removal rate and degradation rate of organic matter, the concentration of activated sludge and the hydraulic stay time. The actual removal rate of organic matter was compared with the theoretical removal rate by using the process data of a sewage treatment plant located in Xiangtan.The results show that this model is very instructive for production.

Keywords: wastewater biochemical treatment; organic removal rate; kinetic parameters; mathematical model

活性污泥法数学模型不仅可以描述和模拟污泥系统的动态变化过程,还能够优化污水处理工艺,确定最佳运行模式和工况条件[1-4].污水的生化处理模型应用较广泛的有 Eckenfelder 模型[5]、McKinney 模型[6]、Lawrence-Ma Carty 模型[7]以及动态模型 ASM1-ASM3[8-12].这些模型的使用有其限定条件,即模型和现实是有距离的.近年来有关于把动力学模型与污水处理厂实际运行结合起来的报道,但是,关于有机物去除率与生化反应动力学参数间构效关系,仍未见其工业化应用方面的研究报道[13-15].本研究结合现

收稿日期:2016-04-11

基金项目:理论有机化学与功能分子教育部重点实验室开放基金资助项目(LKF1404)

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医药及中间体

TMSCl 催化合成 1–苄基–2–芳基–3，1–苯并噁嗪类化合物

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摘 要：在三甲基氯硅烷（TMSCl）的催化作用下，2–(苄氨基）苯甲醇与硝基苯甲醛反应合成了 1–苄基–2–芳基–3，1–苯并噁嗪类化合物。研究了催化剂种类及用量、反应温度、反应物的物质量之比等因素对反应的影响，获得了较优反应条件。优化条件下反应收率>50%。实验结果表明 TMSCl 比 $BF_3·OEt_2$ 和 $SnCl_4$ 对反应的催化活性要好。

关键词：3，1–苯并噁嗪；催化剂；TMSCl
中图分类号：O626　　**文献标志码**：A　　**文章编号**：1009–9212(2017)04–0029–03
DOI：10.19342/j.cnki.issn.1009–9212.2017.04.006

Synthesis of 1–Bnezyl–2–aryl–3,1–benzoxazines Catalyzed by TMSCl

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Abstract：1–Benzyl–2–aryl–3,1–benzoxazines were prepared by the reaction of 2–(benzylamino)benzyl alcohol with nitrobenzaldehydes in the presence of TMSCl. The effects of catalysts including the amount, temperature, the mole ratio of the reagents on the yields were systematically investigated. The optimized reaction conditions were provided. The results indicated that the catalytic activity of TMSCl was higher than $BF_3·OEt_2$ and $SnCl_4$.

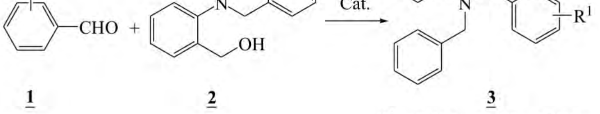
Key words：3,1–benzoxazine; catalyst; TMSCl

1 前 言

3，1–苯并恶嗪类化合物具有广泛的生物活性，如抗高血压[1]，抑制弹性蛋白酶[2–3]，抑制 C1r 丝氨酸蛋白酶[4]、抗菌[5]、抑制 α–胰凝乳蛋白酶[6–7]和抗恶性细胞增生[8]等。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在乙酸或对甲苯磺酸（TsOH）的催化作用下反应来制备[9–10]。最近，Saá 等[11]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–苯并噁嗪类化合物的新方法。然而，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。因此，笔者设计了 1–苄基–2–芳基–3，1–苯并噁嗪类新化合物，并利用三甲基氯硅烷（TMSCl)催化 2–(苄基氨基）苯甲醇与醛的反应来合成目标化合物。

2 实验部分

2.1 1–苄基–2–芳基–3，1–苯并噁嗪的合成路线



R^1 = 2-NO_2, 3-NO_2, 4-NO_2

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收稿日期：2017–08–10

第32卷 第4期　　湖南科技大学学报(自然科学版)　　Vol.32 No.4
2017年　12月　　Journal of Hunan University of Science & Technology(Natural Science Edition)　　Dec. 2017

doi:10.13582/j.cnki.1672-9102.2017.04.013

N-(2-羟基苯亚甲基)苯胺衍生物分子内质子转移取代基效应的密度泛函理论研究

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摘　要: 在B3LYP/6-31+G(d,p)水平上研究了N-(2-羟基苯亚甲基)苯胺衍生物分子内质子转移的取代基效应.结果表明:吸电子基引入后会让分子更加趋于平面构型,而供电子基取代后让分子发生了一定程度的扭转;吸电子取代基引入后减小了分子平面的电子密度,拉近了N_1-H_2距离,增强了分子内氢键的强度,降低了醇式到酮式的结构互变能垒.供电子取代基引入后增加了分子平面的电子密度,加大了N_1-H_2间距,减弱了分子内氢键的强度,使得质子转移能垒升高.对分子的前沿轨道研究表明醇式较酮式结构来说更易形成激发态,并且能隙随着吸电子能力和供电子能力增强变小,说明其生物活性变强.

关键词: N-(2-羟基苯亚甲基)苯胺;密度泛函理论;取代基效应;分子内质子转移
中图分类号: O641　　**文献标志码:** A　　**文章编号:** 1672-9102(2017)04-0084-06

Study on the Substituent Effect of Intramolecular Proton Transfer of *N*-(2-Hydroxybenzylidene) Aniline Derivatives by Density Functional Theory

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Abstract: The substituent effect of intramolecular proton transfer of *N*-(2-hydroxybenzylidene) aniline derivatives were studied at the B3LYP/6-31+G(d,p) level. The results show that the introduction of the electron withdrawing group make the molecules more tending to the planar configuration, and the electron donor replace the molecules to a certain degree of torsion. After the introduction of the electron-withdrawing substituents, the electron density of the molecular plane is reduced The N_1-H_2distance enhances the intramolecular hydrogen bondstrength and reduces the structure of the alcohol to ketone. The electron recombination of the electron donor increases the electron density of the molecular plane, increases the N_1-H_2 spacing, reduces the intensity of the intramolecular hydrogen bonds, and increases the proton transfer energy barrier. The study of the molecular prospective orbit shows that the alcohol is more likely to form an excited state than the ketone structure, and the energy gap decreases with the increase of the electron-withdrawing ability and the electron-supplying ability, which indicates that the biological activity becomes stronger.

Keywords: *N*-(2-hydroxybenzylidene) aniline; density functional theory; substituent effect; intramolecular proton transfer

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收稿日期: 2017-03-24
基金项目: 国家自然科学基金资助项目(21172066;2971041);湖南省教育厅重点科研资助项目(17A065)

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基于拓扑指数对含氧有机化合物闪点的定量构效关系研究

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摘 要 闪点是衡量化合物易燃程度的物理量，也是可燃性液体的一个重要安全性指标。本文对含氧有机化合物（包括醇、酚、醚、醛、酮、羧酸、酯等）的闪点与分子结构之间的关系进行分析，提取并计算了顶点度-距离指数（VDI）、奇偶指数（OEI）、边度-距离指数（EDI）、分子体积参数（MVI）和氢键指示变量（HB）等分子结构参数，并结合分子隐氢图顶点数（N）的2/3次方（$N^{2/3}$），对训练集中81个含氧有机化合物的闪点进行定量结构-性质相关分析。结果表明，由$N^{2/3}$、VDI、EDI、OEI、MVI和HB等6个参数对闪点建立的多元线性回归模型的相关系数（R）为0.9909，标准偏差（s）为6.39K，平均相对误差（ARD）为1.60%。用该模型对测试集中20个含氧有机化合物的闪点进行了预测，ARD为1.84%。

关键词 含氧有机化合物 闪点 定量构效关系 分子结构参数 多元线性回归
DOI:10.14159/j.cnki.0441-3776.2017.04.012

Study on Quantitative Structure-Property Relationship of the Flash Points of Oxygen-Containing Organic Compounds based on Topological Descriptors

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Abstract The flash point is a physical quantity indicating the flammable degree of a compound, and also an important safety index of combustible liquid. This paper analyzed the relationship between flash points and molecular structures of oxygen-containing organic compounds, including alcohols, phenols, ethers, aldehydes, ketones, carboxylic acids and esters. A set of molecular structural descriptors, i. e., the vertex degree-distance index (VDI), odd-even index (OEI), edge degree-distance index (EDI), molecular volume index (MVI), and hydrogen bond indicator (HB) were extracted and calculated. Based on these descriptors and the two-thirds power of the number of vertexes ($N^{2/3}$), quantitative structure-property relationship analysis was carried out for the flash points of 81 oxygen-containing organic compounds in the training set. The multiple linear regression model based on $N^{2/3}$, VDI, EDI, OEI, MVI and HB was established with the correlation coefficient $R = 0.9909$, the standard deviation $s = 6.39$K, and the average relative deviation ARD = 1.60%. The flash points of 20 oxygen-containing organic compounds in the test set were predicted by this model, and the ARD was 1.84%.

Keywords Oxygen-containing compounds, Flash point, Quantitative structure-property relationship, Molecular structural descriptors, Multiple linear regression

在一定温度和压强下，化合物都具有一定的蒸气压。当可燃性液体的蒸气与空气混合，在接触外界点火的情况下，发生闪燃的最低温度称之为闪点（Flash point，FP）[1~3]。闪点是衡量化合物易燃程度的一个重要参数，也是易燃性液体在贮存、运输和使用过程中一个重要的安全性指标。

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国家自然科学基金项目（21402047，21272063）、湖南省自然科学基金项目（14JJ3112）和湖南省高校科技创新团队支持计划项目资助
2016-06-27收稿，2016-11-19接受

第 47 卷第 4 期
2017 年 8 月

精细化工中间体
FINE CHEMICAL INTERMEDIATES

Vol. 47 No. 4
Aug 2017

农药及中间体

基于 1,3-偶极环加成的新型螺[吲唑-异噁唑]衍生物合成及表征

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摘 要：以 1-苯基-6,7-二氢-1*H*-吲唑-4（5*H*）-酮和取代芳香醛为原料，在碱性条件下缩合得到 5-芳亚甲基-1-苯基-6,7-二氢-1*H*-吲唑-4（5*H*）-酮，再与腈氧化物进行 1,3-偶极环加成得到系列 4′-(4-芳基)-3′-(2,6-二氯苯基）-1-苯基-6,7-二氢-4′*H*-螺[吲唑-5,5′-异噁唑]-4(1*H*)-酮新化合物，采用 NMR、IR、MS 以及元素分析表征其结构。

关键词：螺杂环；1,3-偶极环加成；腈氧化物；异噁唑

中图分类号：O626.2 **文献标志码**：A **文章编号**：1009-9212(2017)04-0018-07

DOI:10.19342/j.cnki.issn.1009-9212.2017.04.004

Synthesis and Characterization of Novel Spiro[Indazole-Isoxazol] Derivatives *via* 1,3-Dipolar Cycloaddition

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Abstract: The condensation of 1-phenyl-6,7-dihydro-1*H*-indazol-4 (5*H*)-one and substituted aromatic aldehyde yielded 5-arylmethylene-1-phenyl-6,7-dihydro-1*H*-indazol-4 (5*H*)-one under alkaline condition. The 1,3-dipolar cycloaddition of nitrile oxide to these materials acquired above afforded a series of novel 4′-(4-aryl)-3′-(2,6-dichlorophenyl)-1-phenyl-6,7-dihy-dro-4′*H*-spiro[indazole-5,5′-isoxa-zol]-4(1*H*)-ones. The structures of all the products were characterized by NMR, IR, MS together with elemental analysis.

Key words: spiroheterocycle; 1,3-dipolar cycloaddition; nitrile oxide; isoxazole

1 前 言

吡唑衍生物具有良好的除草、杀菌、抗肿瘤和抗真菌活性，并且高效、低毒，是钠氢离子交换器 NHE-1 的抑制剂[1]、HIV-1 逆转录酶[2]、二肽基肽酶 IV(DPP-IV)[3]、COX-2 抑制剂[4]及腈吡螨酯(Cyenopyrafen)[5]、吡螨胺[6]等医药和农药的重要中间体。异噁唑啉衍生物因其独特的结构和生物活性，具有消炎[7]、止痛、抗菌[8]等作用，已应用于药物、杀菌剂、除草剂、杀虫剂等产品[9]。例如，既具有很好的止痛和抗炎活性，又是引起毒副作用的 COX-2(cyclooxygenase-2)的抑制剂 3-甲基异噁唑啉化合物[10]，杀菌剂啶菌噁唑[11]，色素抑制类芽前除草剂异噁草酮[12]，具有很好的杀虫活性的

基金项目：国家自然科学基金青年项目（21602054）。

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收稿日期：2017-03-06

波 谱 学 杂 志

第34卷第1期 Chinese Journal of Magnetic Resonance Vol. 34 No. 1

2017年03月 Mar. 2017

Chinese J Magn Reson, 2017, 34(1): 69-77 doi:10.11938/cjmr20170109

取代基效应对二芳基硝酮CH=N(O)桥基^{1}H NMR化学位移的影响

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摘　要：合成一系列取代二芳基硝酮XArCH=N(O)ArY化合物, 测定其核磁共振氢谱（^{1}H NMR）, 指认出桥基CH=N(O)上质子的化学位移$\delta_{\mathrm{H[CH=N(O)]}}$，定量研究取代基效应对$\delta_{\mathrm{H[CH=N(O)]}}$的影响. 得到一个4参数定量方程，标准偏差（$S$）为0.020，较好地表达了$\delta_{\mathrm{H[CH=N(O)]}}$的变化规律. 结果表明，该类化合物的$\delta_{\mathrm{H[CH=N(O)]}}$主要受4个因素影响：X基团的场/诱导效应[$\sigma_\mathrm{F}$(X)]；Y基团的共轭效应[$\sigma_\mathrm{R}$(Y)]；基团X和Y之间的特殊交叉作用（$\Delta\sigma^2$）；以及基团X和O$^-$之间的特殊交叉作用[$\Delta\sigma^2_{(\mathrm{X\text{-}O^-})}$]. 其中，$\Delta\sigma^2_{(\mathrm{X\text{-}O^-})}$对$\delta_{\mathrm{H[CH=N(O)]}}$变化的贡献超过70%. 通过$\delta_{\mathrm{H[CH=N(O)]}}$与二芳基希夫碱XArCH=NArY桥基CH=N上质子化学位移的$\delta_{\mathrm{H(CH=N)}}$比较发现，这两类化合物桥基上质子的化学位移之间没有良好的线性关系. 因而，在应用NMR谱图解析有机化合物分子结构时，不能简单地用$\delta_{\mathrm{H(CH=N)}}$的变化去类比$\delta_{\mathrm{H[CH=N(O)]}}$的变化.

关键词：核磁共振（NMR）；^{1}H NMR化学位移；取代基效应；二芳基硝酮；二芳基希夫碱；基团特殊交叉作用

中图分类号：O482.53　　**文献标识码**：A

Substituent Effects on the ^{1}H NMR Chemical Shifts of CH=N(O) Bridge Group in Diaryl Nitrone

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Abstract: A series of substituted diaryl nitrones XArCH=N(O)ArY were synthesized, and their ^{1}H NMR spectra were measured. The ^{1}H chemical shift of the CH=N(O) bridge groups, $\delta_{\mathrm{H[CH=N(O)]}}$, in each compound was determined. The effects of substituents X and Y on $\delta_{\mathrm{H[CH=N(O)]}}$ were investigated quantitatively. A four parameters correlation equation was constructed to model the changes of $\delta_{\mathrm{H[CH=N(O)]}}$ with substituents, yielding a standard error of 0.020. The result indicated that $\delta_{\mathrm{H[CH=N(O)]}}$ in substituted diaryl nitrones are mainly affected by four factors: field/inductive effect (S) of substituent X [σ_F(X)], conjugative effect of substituent Y [σ_R(Y)], substituent specific cross-interaction effect between X and Y ($\Delta\sigma^2$) and substituent specific crossinteraction effect between X and O$^-$ [$\Delta\sigma^2_{(\mathrm{X\text{-}O^-})}$]. Among these factors, the contribution of $\Delta\sigma^2_{(\mathrm{X\text{-}O^-})}$ to $\delta_{\mathrm{H[CH=N(O)]}}$ was more than 70%. A comparison of $\delta_{\mathrm{H[CH=N(O)]}}$ in substituted diaryl nitrones to $\delta_{\mathrm{H(CH=N)}}$ of the CH=N bridge group in diaryl Schiff base XArCH=NArY revealed no good linear relationship between $\delta_{\mathrm{H[CH=N(O)]}}$ and $\delta_{\mathrm{H(CH=N)}}$. Therefore it should be noted that one cannot simply use the change of $\delta_{\mathrm{H(CH=N)}}$ to deduce the change of $\delta_{\mathrm{H[CH=N(O)]}}$ when carrying out organic molecule structure elucidation with NMR spectra.

Key words: nuclear magnetic resonance (NMR), ^{1}H NMR chemical shift, substituent effect, diaryl nitrone, diaryl Schiff base, substituent specific cross-interaction effect

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收稿日期：2016-01-27；**收修改稿日期：**2017-01-05

基金项目：国家自然科学基金资助项目(21272063)，湖南省教育厅科研资助项目(14C0466)和湖南省自然科学基金资助项目(14JJ3112).

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第33卷第2期 分析科学学报 2017年4月
Vol.33 No.2 JOURNAL OF ANALYTICAL SCIENCE Apr. 2017

DOI:10.13526/j.issn.1006-6144.2017.02.011

聚乙烯吡咯烷酮保护的纳米银可视化检测三聚氰胺

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摘 要:本文在聚乙烯吡咯烷酮(PVP)保护下制得银纳米粒子(AgNPs),当在pH为8.69的B-R缓冲溶液条件下,向AgNPs溶液中加入三聚氰胺后,AgNPs在392 nm波长处的吸光度降低,并在长波处出现新的吸收峰,且AgNPs在392 nm处的吸光度降低值(△A)与三聚氰胺的浓度呈现良好的线性关系。基于此,建立了一种灵敏检测三聚氰胺的方法,线性范围为$5.0\times10^{-8}\sim2.0\times10^{-6}$ mol/L(相关系数$r=0.9951$)。三聚氰胺的浓度在$0.1\times10^{-6}\sim2.0\times10^{-6}$ mol/L范围,AgNPs溶液的颜色变化可以直接用肉眼分辨,由此可以建立一种三聚氰胺的可视化半定量检测方法。建立的方法能用于合成样品和牛奶中三聚氰胺含量的检测。

关键词:银纳米粒子;吸光度;三聚氰胺

中图分类号:O657.32 **文献标识码**:A **文章编号**:1006-6144(2017)02-207-05

三聚氰胺是一种三嗪类含氮杂环有机化合物,其氮含量高达66%,将其添加到食品及饲料中可以提高蛋白质的虚高含量[1]。因此,食品中三聚氰胺的检测具有现实意义。目前,常用的三聚氰胺检测方法有高效液相色谱法[2]、气相色谱-质谱法[3]、电化学方法[4]以及同位素法[5]等。这些方法中大多操作比较繁琐,有些需要昂贵的仪器,不适于现场检测。因此,开发简单并能应用于现场分析的三聚氰胺检测方法,是该领域的重要发展方向。基于金属纳米粒子聚集而导致颜色变化的比色分析法引起了人们越来越多的关注[6],该方法已广泛用于检测金属离子[7]、小分子[8]和蛋白质[9]。其中,金纳米粒子(AuNPs)由于具有容易制备、稳定、生物相容性好、尺寸可调及高的消光系数等特性而被广泛应用于比色分析[10]。银纳米粒子(AgNPs)和AuNPs相比,拥有更高的吸光系数,因而在比色分析中也具有自身的优势。但是由于银表面容易氧化[11],使其在比色分析中存在稳定性相对较差的缺点,界面功能化和选择合适的稳定剂对提高AgNPs比色分析结果稳定性具有很好的效果。比如用适当配体稳定的功能化AgNPs已成功的用于氨基酸[12]、DNA[13]的比色分析。

利用目标分析物与纳米粒子表面分子之间的相互作用,引起纳米粒子聚集并导致颜色变化已用于检测2,4,6-三硝基甲苯[14]、含巯基的氨基酸和肽[15]。Han等[16]用对硝基苯胺稳定的纳米银,可视化检测出0.1 mg/kg含量的三聚氰胺。本文采用低毒的聚乙烯吡咯烷酮(PVP)稳定的AgNPs为探针,通过富电子的三聚氰胺和AgNPs表面上的缺电子PVP发生相互作用后,引起AgNPs团聚,导致吸收光谱的变化和溶液颜色的变化,从而建立了可视化检测三聚氰胺的方法,该方法具有更好的应用前景。

1 实验部分

1.1 仪器与试剂

Lambda35型紫外-可见分光光度计(美国,铂金埃尔默仪器公司);Tecnai G20型透射电子显微镜(美

收稿日期:2016-04-16 **修回日期**:2016-05-20

基金项目:国家自然科学基金(No.21275047)

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DOI：10.13526/j.issn.1006-6144.2017.03.018

电还原氧化石墨烯-金纳米棒修饰电极对酒石黄的测定

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摘　要：本文制备了氧化石墨烯-金纳米棒复合物（GO-GNRs）。利用滴涂法制备了修饰电极（GO-GNRs/GCE），通过循环伏安法，还原了 GO-GNRs 复合物中的 GO，制得电化学还原的石墨烯-金纳米棒修饰电极（ERGO-GNRs/GCE）。研究了酒石黄在不同电极上的电流响应，结果表明，ERGO-GNRs/GCE 对酒石黄的氧化有很好的电催化作用，其浓度在 0.05～6.0 μmol/L 范围内与氧化峰电流呈良好的线性关系，检出限为 15 nmol/L。利用 ERGO-GNRs/GCE 可完成样品中酒石黄含量的测定。

关键词：金纳米棒；氧化石墨烯；酒石黄；电化学还原

中图分类号：O657.1　　**文献标识码**：A　　**文章编号**：1006-6144(2017)03-383-04

酒石黄是广泛使用的人工合成色素之一。它主要用于食物、饮料、酸奶、冰淇淋、糖果等的着色，但由于其分子中含有偶氮官能团和芳环结构[1]，对人体可产生毒性，过量食用可能会引发哮喘、过敏以及儿童多动症[2]，因此，高灵敏的检测、监控柠檬黄在食品中的添加量是非常重要的。目前，酒石黄主要的检测方法有色谱法[3]，毛细管电泳法[4]、光度法[5]和电化学方法[6-7]。

本方法利用电化学还原的氧化石墨烯-金纳米棒复合物（ERGO-GNRs），通过带负电的氧化石墨烯（GO）与带正电的金纳米棒（GNRs）之间的静电作用，获得 GNRs 均匀、稳定分散于 GO 的纳米复合材料，再通过电化学法还原 GO，制得具有高度电催化活性的纳米复合物。此外，研究了该材料对酒石黄的电催化行为，并建立了对酒石黄的高灵敏的电化学检测方法。该检测方法性能优良，与大多数已报道的文献方法[8-9]有可比的检测性能。

1　实验部分

1.1　仪器与试剂

CHI 760C 型电化学工作站（上海辰华公司）；JSM-5610L 型扫描电子显微镜（SEM）（日本，JEOL 公司）；KQ50E 型超声波清洗器（昆山市超声仪器有限公司）。三电极系统：修饰的玻碳电极（GCE）为工作电极，饱和甘汞电极为参比电极，铂电极为对电极。

$HAuCl_4$、十六烷基三甲基溴化铵（CTAB）、$AgNO_3$、抗坏血酸，均购于 Sigma-Aldrich 公司；氧化石墨烯（GO，南京先丰纳米材料科技有限公司）；$NaBH_4$、酒石黄均购自上海化学试剂公司。0.1 mol/L 磷酸盐缓冲溶液（PBS）和 0.2 mol/L KCl 支持电解质溶液。其他试剂均为分析纯，水为二次蒸馏水。

1.2　金纳米棒（GNRs）与氧化石墨烯-金纳米棒（GO-GNRs）纳米复合物的制备

金纳米棒按文献方法[10]制备，步骤如下：1 mL 0.2 mol/L CTAB 与 1.0 mL 0.50 mmol/L $HAuCl_4$ 充分混合，然后加入新制的 120 μL 10 mmol/L 冰浴的 $NaBH_4$ 溶液，搅拌 2 min 后，把得到的金种溶液于温度 27 ℃下静置 2 h；将 0.2 mL 4 mmol/L $AgNO_3$ 加入 5.0 mL 1.0 mmol/L $HAuCl_4$ 与 5.0 mL 0.2 mol/L CTAB 的混合溶液中，室温下缓慢搅拌，逐滴加入 1.0 mL 0.1 mol/L 抗坏血酸后，加入 0.1 mL 金种溶

收稿日期：2016-05-27　　修回日期：2016-04-14
基金项目：国家自然科学基金(No.21471052)；湖南省教育厅项目(No.16B088)；教育部重点实验室开放课题(No.LKF1607)

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第34卷第3期 应用化学 Vol. 34 Iss. 3
2017年3月 CHINESE JOURNAL OF APPLIED CHEMISTRY Mar. 2017

新型2-(芳氨基乙基氨基)苯甲醇的合成及其杀菌活性

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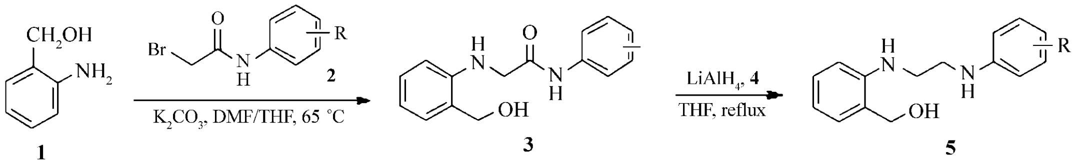
摘 要 2-氨基苯甲醇及其衍生物是一类很重要的具有双官能团的化合物,在有机化学和药物合成中具有广泛的用途。本文主要提供了一种简单、有效合成2-(芳氨基乙基氨基)苯甲醇类化合物的方法,同时测定了目标化合物的杀菌活性。溴乙酰芳胺与2-氨基苯甲醇经*N*-烷基化反应生成2-[(2-羟甲基苯基)氨基]乙酰芳胺类化合物3,然后经$LiAlH_4$还原生成了一系列结构新颖的2-(芳氨基乙基氨基)苯甲醇类化合物5a~5i,产率为76%~95%。用IR、^{1}H NMR、^{13}C NMR和元素分析等对产物结构进行了表征。目标化合物的杀菌活性结果表明,在测试浓度下,大部分显示中等至良好的活性,化合物5e对辣椒疫霉病菌的抑制活性达73.0%。

关键词 (芳氨基乙基氨基)苯甲醇;烷基化;合成;杀菌活性
中图分类号:O622 **文献标识码**:A **文章编号**:1000-0518(2017)03-0345-09
DOI:10.11944/j.issn.1000-0518.20176.03.160236

2-氨基苯甲醇及其衍生物是一类很重要的具有双官能团的化合物,在有机化学和药物合成中具有广泛的用途。一是可以作为多齿配体和过渡金属形成多核结构的金属有机配合物,有些配合物具有很强的抗铁磁性[1-3],有些具有杀菌活性[4],有些具有抗氧化活性[5]。二是可以用来合成具有生物活性的喹啉类化合物[6-10]、喹唑啉类化合物[11-12]、3,1-苯并噁嗪类化合物[13-15]、3,1-苯并噻嗪类化合物[16]、稠合的吲哚啉缩醛胺类化合物[17]等。2-氨基苯甲醇还可以用来合成手性试剂,用于不对称合成[18]。另一方面,2-氨基苯甲醇还可以诱导叙利亚地鼠胚胎(SHE)细胞的形态变换,并且产生剂量依赖性[19]。因此,2-氨基苯甲醇及其衍生物的合成受到广泛关注。Yoshida等[20-21]利用苯炔、胺基硅烷和醛或酮的三组分反应合成这类化合物,这种方法产率高、步骤少。格氏试剂与邻氨基苯酮或邻氨基苯甲酸酯的反应也是合成该类化合物的常用方法[13-15]。当前,国内生产2-氨基苯甲醇的方法主要是化学还原法,但是该方法工艺繁琐,废水量大。汪宏杰等[22]利用负载型Ni为催化剂,2-硝基苯甲醇为原料,采用液相催化加氢制备2-氨基苯甲醇,获得了很好的结果。这里,我们合成了一类新型*N*-(芳氨基乙基)取代2-氨基苯甲醇类化合物5(Scheme 1),因为它是合成1-氨基取代-3,1-苯并噁嗪类化合物[13-14]的重要中间体,化合物5中之所以引入芳氨基,是因为很多事实表明,氨基的引入可以提高化合物的生物活性[23-24]。同时,化合物5还可作为三齿配体,和过渡金属反应可以形成多核结构的金属有机配合物。本文主要研究了化合物5的合成方法和抑菌活性。



R=*o*-CH_3, *m*-CH_3, *p*-CH_3, *m*-OCH_3, *p*-OCH_3, H, *o*-Cl, *m*-Cl, *p*-Cl

Scheme 1 Synthesis of 2-[2-(arylamino)ethylamino]benzyl alcohol **5**

2016-06-06收稿,2016-08-25修回,2016-09-18接受

国家自然科学基金(21372070)、国家科技支撑计划项目子课题(2011BAE06B01)、湖南省高校创新平台开放基金(13K089)、理论有机化学与功能分子教育部重点实验室开放基金(LKF1302)资助

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文章编号: 1004-1656(2017)07-0980-06

基于硫氰酸铵增敏可视化检测微量铜离子

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摘要: NH_4SCN 能将三角形银纳米片(TAg-NPs)腐蚀。利用微量 Cu^{2+} 与抗坏血酸(Vc)发生反应生成的 Cu^{+} 进而被歧化为铜原子后,能有效覆盖在 TAg-NPs 活性银原子的表面,该覆盖层能阻止 NH_4SCN 对 TAg-NPs 的腐蚀。导致 TAg-NPs 的形貌、颜色、最大吸收波长等特性随 Cu^{2+} 浓度($6.0\times10^{-8}\sim1.0\times10^{-6}$ mol·L^{-1} 范围)的改变而改变。基于 TAg-NPs 最大吸收波长的变化值与铜离子浓度之间存在的定量关系,建立了检测微量 Cu^{2+} 的快速、简便的分光光度分析法。且基于 Cu^{2+} 浓度不同引起的溶液颜色不同,建立了更为快速、简便的可视化半定量检测铜离子方法。

关键词: 三角形银纳米片;铜离子;紫外-可见吸收光谱

中图分类号: O657.3 **文献标志码:** A

Visual detection of trace copper ions based on the sensibilization of ammonium thiocyanate

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Abstract: In this study,we found that the triangle silver nanoplate(TAg-NPs) could be etched by NH_4SCN. As a result,the TAg-NPs transform from triangle to circle,the color of TAg-NPs turned from blue to yellow by the corrosive effect of NH_4SCN,and the maximum absorption peak of the TAg-NPs blue-shift. However,extremely low concentration of Cu^{2+} could be reduced into Cu^{+} by ascorbic acid(VC). Subsequently,Cu^{+} could produce disproportionation reaction to generate copper deposited on the surface of TAg-NPs,which could prevent TAg-Nps from the corrosion by NH_4SCN. When the concentration of NH_4SCN was constant,it is confirmed that the color was turned from yellow to blue,and the morphology transformed by nanodisc gradually into trangles,and the plasmon absorption of TAg-NPs changed with the change of the concentration of Cu^{2+}. The change values of the plasmon absorption of TAg-NPs were proportional to the concentrations of Cu^{2+} in the range of $6.0\times10^{-8}\sim1.0\times10^{-6}$ mol·L^{-1}. According to these phenomena, we demonstrated a novel method for Cu^{2+} detection by either UV-visible spectrophotometric detection or naked-eye observation successfully.

Key words: triangular silver nanoplates; copper ions; UV-visible spectrophotometry

铜是生物体生长发育不可缺少的微量营养素元素之一,铜离子在人体许多生理功能中起着重

收稿日期: 2016-12-05;**修回日期:** 2017-05-03
基金项目: 国家自然科学基金项目(21275047)资助

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第 23 卷 第 6 期
2017 年 12 月
电化学
JOURNAL OF ELECTROCHEMISTRY
Vol. 23 No. 6
Dec. 2017

DOI: 10.13208/j.electrochem.161104
Cite this: *J. Electrochem.* **2017**, *23*(6): 708-717
Artical ID:1006-3471(2017)06-0708-10
Http://electrochem.xmu.edu.cn

Electroactivities of Pd/Fe_3O_4-C Catalysts for Electro-Oxidation of Methanol, Ethanol and Propanol

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Abstract: Development of palladium (Pd) catalysts with high electroactivity for alcohol oxidation is significant for alcohol fuel cells. In this work, Pd nanoparticles were formed by sodium borohydride ($NaBH_4$) reduction method and subsequently deposited on the surface of carbon supported ferriferrous oxide (Fe_3O_4/C) composite to obtain the Pd/Fe_3O_4-C catalysts with different Fe_3O_4 loadings. Their transmission electron microscopic (TEM) images show that the Pd nanoparticles were uniformly dispersed on the Fe_3O_4/C. Electroactivities of the prepared Pd/Fe_3O_4-C catalysts towards oxidation of C1-C3 alcohols (methanol, ethanol, *n*-propanol and iso-propanol) in alkaline media were investigated by cyclic voltammetry (CV), chronoamperometry and electrochemical impedance spectroscopy. Among the prepared catalysts (Pd/Fe_3O_4(2%)-C, Pd/Fe_3O_4(5%)-C, Pd/Fe_3O_4(10%)-C and Pd/C), the Pd/Fe_3O_4(5%)-C catalyst presented the highest electro-oxidation current density for oxidation of C1-C3 alcohols. According to the CV data, the anodic peak current densities for oxidation of methanol, ethanol, *n*-propanol and iso-propanol on the Pd/Fe_3O_4(5%)-C catalyst were over 1.7, 1.4, 1.7 and 1.3 times larger than that on the Pd/C catalyst, respectively. Furthermore, the charge transfer resistance of ethanol oxidation on the Pd/Fe_3O_4(5%)-C catalyst was much lower than that on the Pd/C catalyst. For all of the prepared catalysts, the decreases in electro-oxidation current density of the tested C1-C3 alcohols followed the order of *n*-propanol > ethanol > methanol > iso-propanol. In addition, the presence of Fe_3O_4 nanoparticles in the carbon powder improved the electrochemical stability of the Pd nanoparticles.

Key words: Pd catalyst; Fe_3O_4; alcohol oxidation; electrocatalyst

CLC Number: O646 **Document Code**: A

Direct alcohol fuel cells (DAFCs) are of significant interest from both energy and environmental considerations. Anode reaction in DAFCs is electro-oxidation of alcohols, which has been extensively investigated in recent decades[1-7]. It has been recognized that platinum (Pt) and Pt-based catalysts are the best electro-catalysts for alcohol oxidation. Unfortunately, practical application of the Pt-based catalysts is seriously limited because of the high cost and rare resources of Pt. In addition, poisoning effect of Pt surface, caused by the intermediate product like carbon monoxide (CO) produced during the alcohol electro-oxidation, also results in the decline of the electroactivity. Ferriferrous oxide (Fe_3O_4) has been reported to present unique catalytic and environmental friendly properties[8], and has been therefore used to improve the electroactivity of Pt-based catalysts. Huang et al has prepared a novel yolk/shell Fe_3O_4-polydopaminee-graphene-Pt (Fe_3O_4@PDA/RGO/Pt) nanocomposite that exhibited lower over-potential, higher electrocatalytic activity and notably stability for methanol oxidation than Pt/graphene[9]. Hong has syn-

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Received: 2016-11-04, Revised: 2017-03-17 *Corresponding author, (86-731)58290045, E-mail: yqfyy2001@hnust.edu.cn

This work was financially supported by the National Natural Science Foundation of China (No.21376070) and the Hunan Provincial Natural Science Foundation of China (No.14JJ2096).

第32卷 第2期 湖南科技大学学报(自然科学版) Vol.32 No.2
2017年 6月 Journal of Hunan University of Science & Technology(Natural Science Edition) Jun. 2017

doi:10.13582/j.cnki.1672-9102.2017.02.013

质谱双探针法对食品中N-亚硝胺化合物的全检测

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摘　要: 食品中亚硝胺化合物的种类达300种,当前的亚硝胺检测国标只检测代表性的4种亚硝胺化合物.选择亚硝胺类化合物在EI源质谱中电离出的亚硝酰胺基(N_2O)和亚硝酰(NO)2个独特碎片离子作双探针信号,以市售腊肉为检测对象,探索出一种亚硝胺类化合物全检测的方法,大幅度减少了现有国家标准对食品中亚硝胺类化合物的漏检.该检测方法原理简单、实验操作方便、测试成本低.

关键词: N-亚硝胺; 电子轰击质谱; 离子探针; 食品安全

中图分类号: O656.3　　**文献标志码:** A　　**文章编号:** 1672-9102(2017)02-0078-07

Determination of N-nitrosamine compounds in food by using double-ion probe method of electron impact mass spectrometry

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Abstract: There are over 300 N-nitrosamine compounds found in food, but the current national standards only detect four representative nitrosamine compounds. N-nitrosamine compounds can be ionized and produce two unique fragment ions, nitroso amide (N_2O) and nitrosyl (NO), in electron impact (EI) mass spectrometry ionization, and this property is used to determine the existence of nitrosamine compounds and quantify these compounds by selecting the two ions as double-probe signals. The commercially available preserved meat was selected as test objects. A method of determination of N-nitrosamine compounds in food was explored. This method can greatly reduce the missed detection of nitrosamine compounds existing in food. The method is simple in principle and the experiment operation involved is convenient, it greatly cut down the cost of testing.

Keywords: N-nitrosamines; electron impact mass spectrometry; ion probe; food safety

N-亚硝胺类化合物[1]属于亚硝基化合物,为剧毒有机化合物,具有致癌[2]、致畸[3]和致突变性[4]等作用,是现今4大食品污染物之一.新鲜的食品中,亚硝胺类化合物的含量很低,但在运输、加工、储存等过程中很容易因缺氧、积热、微生物、霉变等因素产生各种各样的N-亚硝胺化合物.迄今已发现的N-亚硝胺化合物有300多种,资料显示,食品的来源不同、微生物种类不同、存放的时间不同,产生的N-亚硝胺化合物种类也会不同[5].亚硝胺化合物种类的多样给食品的相关检测带来了很大的麻烦,另外,食品中的其他

收稿日期:2016-12-07

基金项目:国家自然科学基金资助项目(21372069,21602054);教育部新世纪优秀人才支持计划资助项目(NCET-13-0784)

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DOI:10.19603/j.cnki.1000-1190.2017.01.009

第51卷第1期　　华中师范大学学报(自然科学版)　　Vol. 51　No. 1
2017年2月　　JOURNAL OF CENTRAL CHINA NORMAL UNIVERSITY(Nat. Sci.)　　Feb. 2017

文章编号： 1000-1190(2017)01-0052-04

2,3-二芳基-1,3-苯并噁嗪的合成及对利什曼原虫CYP51活性的初步研究

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摘　要： 首次对2-(2-硝基苯基)-3-(4-甲基苯基)-1,3-苯并噁嗪(1)与利什曼原虫CYP51的相互作用进行了初步研究，发现化合物1对利什曼原虫CYP51表现出较强的抑制活性，且作用方式类似于底物与利什曼原虫CYP51的Ⅰ型结合方式. 该研究不仅发现了一种新型非唑类针对利什曼原虫CYP51的抑制剂：1,3-苯并噁嗪，而且也为创制新型作用方式的CYP51抑制剂研究提供了依据.

关键词： 2,3-二芳基-1,3-苯并噁嗪；利什曼原虫；CYP51；活性

中图分类号： O626　　　**文献标识码：** A

1,3-苯并噁嗪衍生物是一类重要的含氮杂环化合物，具有抗癌[1-3]、抗血小板聚集[4]、抗细菌和真菌[5-6]、抗结核病[7-8]、杀虫[9]等广泛的生物活性[10-12]. 本课题组曾报道2-(2-硝基苯基)-3-(4-甲基苯基)-1,3-苯并噁嗪(1)具有良好的抑制水稻纹枯病菌的活性(100%，500 μg/mL)[13]，同时对蚜虫也具有一定的活性[14]. 这里将报道化合物1(见图1)对利什曼原虫(Leishmania infantum)的杀虫活性. 文献对1,3-苯并噁嗪类化合物的杀虫活性虽有报道[9,14]，但是相对较少，特别是对利什曼原虫的杀虫活性还未见报道. 利什曼原虫是引起利什曼病的病原体. 利什曼病的临床特征主要表现为长期不规则的发热、脾脏肿大、贫血、消瘦、白细胞减少和血清球蛋白的增加，如不予合适治疗，患者大都在病后1～2 a内因并发其他疾病而死亡. 本病多发于地中海国家及热带和亚热带地区，大约危及世界上90多个国家[15]，我国主要发生在新疆、甘肃、四川、陕西、山西和内蒙古等地区. 至今，利什曼病几乎没有防治的疫苗，只有少量中等治疗效果的药物. CYP51(甾醇14α-去甲基化酶)是生物甾醇合成过程中的关键酶，当其活性和功能受到抑制，就不能有效供给生物甾醇C-14α甲基羟基化所需氧原子，导致C-14α位去甲基化反应受阻，生物甾醇合成减少或被完全阻断，最后导致菌体细胞死亡[16-17]. 因此，利什曼原虫所含CYP51成了化学药物治疗利什曼病的潜在靶标[15]. 所以，为了寻找杀利什曼原虫的高活性化合物，获得治疗利什曼病的高效药物，本文研究了化合物1对利什曼原虫CYP51的抑制活性以及二者的作用方式.

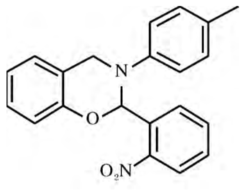

图1　化合物1的结构
Fig. 1　Structure of compound 1

1　实验部分

1.1　仪器与试剂

NMR用Bruker Avance Ⅱ-500 M核磁共振仪测定；红外(IR)用PE-2000型傅里叶变换红外光谱仪测定；熔点用WRS-1B数字熔点仪测定(未校正)；元素分析用PE 2400 Ⅱ元素分析仪测定；质谱使用Thermo Finnigan LCQ质谱仪测定；双光束紫外-可见分光光度计(Perkin Elmer，UV-Lamb-

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收稿日期： 2016-09-28.

基金项目： 国家自然科学基金项目(21372070)；国家科技支撑计划项目子课题(2011BAE06B01)；理论有机化学与功能分子教育部重点实验室开放基金项目(LKF1402).

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