太阳光照下酞菁类有机半导体光催化C-H活化合成联芳基功能材料

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摘要 有机共轭功能材料由于具有优异的光学和电学性能在有机光电子学领域备受关注和研究. 发展简单、高效、绿色的有机功能材料合成方法是该领域研究中的一个重要课题. 本研究发展了一种通过酞菁类有机半导体材料作为催化剂光催化C-H活化合成联芳基类功能材料的绿色方法. 以酞菁类半导体材料为光催化剂, 采用日常生活中最常见的清洁能源太阳光为光源, 实现了室温下通过光催化直接C-H活化的方式合成联芳基化合物. 研究发现, TiOPc(酞菁氧钛)半导体材料的催化活性最高, 且对不同的芳基功能团展现了良好的催化活性. 并以TiOPc作为光催化剂, 合成了具有常见蒽类骨架结构的半导体功能材料, 拓展了有机半导体功能材料的合成途径.

关键词 有机半导体, 酞菁, 光催化, 联芳化合物, C-H活化

有机共轭功能材料由于在光学和电学上的优异表现以及兼具质轻、价廉、易于加工等方面的独特性能组合, 一直备受关注和研究. 经过几十年的不断研究, 该领域取得了重要进展, 一方面表现为有机共轭功能材料体系的不断丰富, 另一方面表现为相关器件性能的不提高. 譬如, 目前, 基于有机共轭功能材料的有机发光二极管(OLED)^[1,2]、有机场效应晶体管(OFET)^[3,4]、有机太阳能光伏(OPV)^[5]、有机发光晶体管(OLET)^[6]、有机场效应光波导(OFEW)^[7]等器件均获得了显著发展, 其在很多应用领域均展示了重要的应用前景. 此外, 发展有机功能材料的合成方法也是重要

的研究方向之一, 其中通过芳基C-H键活化合成有机共轭分子是最直接有效的方法. 基于过渡金属催化C-H活化的合成方法被广泛地用来构筑有机共轭功能材料^[8,9]. 例如, 高希珂课题组^[10,11]利用Pd催化的Suzuki偶联实现了萘2/6-位化学衍生物的合成; 耿延侯课题组^[12,13]采用Herrmann催化剂通过C-H活化合成了并吡咯类共轭功能材料, 这类功能材料表现出优良的双极性、N-型电荷传输特性.

然而, 相较于过渡金属催化的反应方式而言, 光催化反应条件温和, 不需要高温, 更加绿色环保^[14]. 近年来发展的利用有机半导体催化剂在光照条件下直接催

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化C-H活化法是合成联芳基有机功能材料的一种简单有效的方法. 半导体材料的带隙通常落在太阳光能谱范围内, 因而作为催化剂被广泛应用于光催化研究^[15]. 太阳光是一类广泛存在的可持续清洁能源, 太阳光谱主要集中在可见光部分, 紫外光仅占4%, 其他为红外光, 所以发展具有可见光波长吸收的光催化材料具有重要的意义. 基于无机半导体CdS, ZnO, TiO₂等的光催化C-H的研究也逐渐被报道^[16-19], 而有机半导体材料往往对可见光具有良好的吸收性, 但基于有机半导体材料的光催化C-H的研究还鲜有报道^[20-25]. 例如Burkhard Konig课题组^[24]以有机染料Eosin Y作为光催化剂在绿光波长下实现了C-H活化; Dorota Gryko研究团队^[25]以卟啉作为光催化剂在455 nm波长下构筑联芳基功能材料. 但是, 该领域的研究目前还不够系统化, 需要进一步扩展有机半导体光催化种类, 开发具有高效率 and 稳定性的光催化系统.

植物中的叶绿素是对太阳光有效利用的一种天然化合物, 大部分的植物通过叶绿素对太阳光进行催化吸收, 如何利用叶绿素结构构筑有机的光催化剂有可能是发展高效光催化材料的有效途径. 酞菁(Pc)是一种常用的半导体染料分子, 与叶绿素中的卟啉环结构相似, 吸光性能好、电学性能优异^[26], 相较于卟啉类、花酞亚胺类等半导体材料具有优异的光吸收特性, 预示其在光催化实现C-H活化方面的潜在应用. 本研究发展了一种基于酞菁类半导体材料太阳光下光催化C-H活化合成功能材料的绿色方法. 室温条件下以有机半导体材料酞菁作为催化剂, 在清洁能源太阳光照射下, 通过C-H活化实现了芳烃与杂环芳烃的直接偶联; 通过筛选不同种类的酞菁类半导体材料, 证明酞菁氧钛(TiOPc)的光催化活性最高. 最后以TiOPc为催化剂, 在太阳光条件下, 实现了具有常见蒽类骨架结构的有机共轭功能材料的绿色合成. 这一研究可进一步拓展到其他有机半导体功能材料的合成, 在有机光电子学领域具有重要的意义.

1 实验

(i) 试剂和仪器. 所有反应在氮气气氛下进行, 反应底物按照本研究所示方法制备, 其他所有试剂购自Alfa Aesar, 阿拉丁试剂或百灵威. 酞菁类衍生物购买纯度为98%, 经过气相沉积2次提纯, 纯度为99.5%, 其中TiOPc主要为Phase II^[27]. ¹H NMR谱以四甲基硅烷(TMS)为内标, CDCl₃作溶剂, 使用Bruker Avance 400核磁.

(ii) 反应步骤. 重氮盐与杂环芳烃摩尔比为1:10, 催化剂按照1%摩尔当量加入密封瓶, 放入磁子, 加入氮气气氛, 注入10 mL DMSO作为溶剂, 太阳光照下搅拌反应2 h. 反应结束后, 用二氯甲烷稀释, 再经水洗、干燥、浓缩后采用柱层析法, 以乙酸乙酯/石油醚(1:5, v:v)作淋洗剂分离提纯.

(iii) 材料表征. 2-(4-硝基苯基)噻吩(**4a**): 产率60%, 淡黄色固体. ¹H NMR(400 MHz, CDCl₃) δ =8.27(d, J =8.7 Hz, 2H), 7.85(d, J =8.7 Hz, 2H), 7.58(dd, J =3.7, 0.9 Hz, 1H), 7.49(dd, J =5.3, 0.9 Hz, 1H), 7.16(dd, J =5.3, 3.7 Hz, 1H) ppm. 可参考文献^[28]查阅已报道的核磁数据.

2-(4-硝基苯基)呋喃(**4b**): 产率62%, 淡黄色固体. ¹H NMR(400 MHz, CDCl₃) δ =8.27(d, J =9.4 Hz, 2H), 7.85(d, J =9.4 Hz, 2H), 7.60(d, J =1.8 Hz, 1H), 6.92(d, J =3.2 Hz, 1H), 6.59(dd, J =3.2, 1.8 Hz, 1H) ppm. 可参考文献^[29]查阅已报道的核磁数据.

N-叔丁氧羰基-2-(4-硝基苯基)-1-氢-吡咯(**4c**): 产率84%, 淡黄色固体. ¹H NMR(400 MHz, CDCl₃) δ =8.26~8.24(m, 2H), 7.55~7.53(m, 2H), 7.43~7.40(dd, J =3.3 Hz, J =1.8 Hz, 1H), 6.34~6.32(dd, J =3.4 Hz, J =1.8 Hz, 1H), 6.29~6.26(t, J =3.3 Hz, 1H), 1.43(s, 9H) ppm. 可参考文献^[30]查阅已报道的核磁数据.

2-(4-甲氧基苯基)噻吩(**4d**): 产率50%, 透明油状物. ¹H NMR(400 MHz, CDCl₃) δ =7.54(d, J =8.7 Hz, 2H), 7.24~7.21(m, 2H), 7.50(dd, J =5.3, 3.4 Hz, 1H), 6.94(d, J =8.7 Hz, 2H), 3.85(s, 3H). 可参考文献^[28]查阅已报道的核磁数据.

2-(4-溴苯基)噻吩(**4e**): 产率60%, 白色固体. ¹H NMR(400 MHz, CDCl₃) δ =7.55~7.49(m, 4H), 7.32(d, J =4.3 Hz, 2H), 7.11~7.09(m, 1H). 可参考文献^[31]查阅已报道的核磁数据.

2-(3,5-二氯苯基)噻吩(**4f**): 产率64%, 白色固体. ¹H NMR(400 MHz, CDCl₃) δ =7.55(d, J =0.9 Hz, 2H), 7.42(d, J =5.3 Hz, 1H), 7.40(d, J =3.7 Hz, 1H), 7.32(m, 1H), 7.16(dd, J =5.3, 3.6 Hz, 1H). 可参考文献^[32]查阅已报道的核磁数据.

9-(4-甲氧基苯基)蒽(**9**): 产率20%, 白色固体. ¹H NMR(400 MHz, CDCl₃) δ =8.50(d, J =4.6 Hz, 1H), 8.10~8.02(m, 2H), 7.74(d, J =8.9 Hz, 2H), 7.50~7.32(m, 8H), 2.55(s, 3H). 可参考文献^[33]查阅已报道的核磁数据.

2 酞菁类半导体光催化C-H活化合成联芳基功能材料

芳烃重氮盐能有效地提供芳烃自由基, 著名的Meerwein芳基化反应就是采用芳烃重氮盐来实现芳烃偶联. 后续研究者们逐渐开发了基于 TiCl_3 , $\text{Ru}(\text{Bpy})_3^{2+}$, Eosin Y, 卟啉作为光催化剂的C-H芳基化反应^[24,25,34,35]. 为了研究有机半导体酞菁氧钛的光催化C-H性能, 采用在芳烃、杂环芳烃C-H活化领域应用广泛的芳烃重氮盐以及噻吩体系构筑反应体系. 图1为Eosin Y以及酞菁光催化活化芳基化反应图, 在已经报道的Eosin Y等光催化研究中, 往往根据催化剂的光吸收特性选用特定波长的光源来开展研究, 从而限制了这类催化反应的应用场景. 相对于卟啉、花酰亚胺类材料, 酞菁类半导体材料具有更宽的可见光吸收特性, 原则上可以采用日常生活中最常见的太阳光为光源进行催化, 因此其合成反应更加节能、环保.

2.1 不同类别酞菁类半导体材料光催化C-H活化效率研究

为了探究不同酞菁类有机半导体材料的反应活性, 首先以硝基苯重氮盐(1a)和噻吩(2a)作为反应底物(其中噻吩用量为重氮盐的十个当量, 溶剂采用超干的DMSO, N_2 氛围下), 直接太阳光照射进行反应. 实验中采用的酞菁类催化剂用量为重氮盐的1%. 通过对一系列酞菁类材料作为光催化剂反应条件的筛选, 结果表明酞菁类有机半导体均可以起到光催化C-H活化的效果, 但是不同的酞菁半导体作为光催化剂的催化效果

差异明显. 表1为在相同反应条件下所得芳基化产物(4a)的产率统计数据, 相关表征数据见实验部分. 对于不同金属的酞菁材料催化活性的对比研究结果表明, TiOPc 及 $\text{F}_{16}\text{-TiOPc}$ 的催化活性要高于 Pc , 且 TiOPc 的催化活性最高; CuPc / MnPc / NiPc / FePc / CoPc 等酞菁类材料的催化活性要低于 Pc . 这种有意思的现象或许与不同酞菁材料的带隙相关, 不同的金属将对带隙产生不同的影响. Pc 作为有机染料, 带隙为 1.40 eV ^[36], 本身具有吸光性能, 与卟啉^[25]表现出相似的催化性能. 金属酞菁, 如 CuPc 带隙为 $1.60\sim 1.70\text{ eV}$ ^[37,38], 带隙宽度大于 Pc , 吸收光谱蓝移, 减少了对太阳光的吸收, 从而表现出低于 Pc 的光催化效率. TiOPc 带隙在 $1.1\sim 1.2\text{ eV}$ ^[39], 小于 Pc 的带隙宽度, 吸收光谱红移, 光谱吸收范围拓宽, 对太阳光的吸收增加, 从而表现出高于 Pc 的催化效率. 而 $\text{F}_{16}\text{-TiOPc}$ 吸电子基团的引入, 对于带隙的影响有限, F 取代后的 TiOPc 材料可能减少激发态的电子转移给出, 从而使得 $\text{F}_{16}\text{-TiOPc}$ 的催化活性低于 TiOPc .

噻吩和重氮盐反应:

2.2 TiOPc 半导体材料光催化C-H活化合成联芳基功能材料

基于前面对不同酞菁作为光催化剂的研究, 证实

Eosin Y catalyzed direct C-H arylation of heteroarenes under blue LED

图1 (网络版彩色)Eosin Y及酞菁光催化C-H活化芳基化
Figure 1 (Color online) Eosin Y and Pcs catalyzed direct C-H arylation

表1 不同酞菁半导体材料光催化C-H活化效果

Table 1 C-H arylation efficiency of Pc semiconductors

编号	噻吩	酞菁催化剂	产率(%) ^{a)}
1	2a (10 equiv)	Pc	45
2	2a (10 equiv)	CuPc	44
3	2a (10 equiv)	NiPc	40
4	2a (10 equiv)	FePc	30
5	2a (10 equiv)	CoPc	32
6	2a (10 equiv)	MnPc	40
7	2a (10 equiv)	TiOPc	60
8	2a (10 equiv)	$\text{F}_{16}\text{-TiOPc}$	50
9	2a (10 equiv)	SnCl_2Pc	32

a) 产率为核磁产率

TiOPc具有更加优异的光催化效率,因此在接下来不同反应底物的研究中均采用TiOPc作为光催化剂. 本工作首先研究了**1a**与不同杂环**2**的光催化反应,分别采用了噻吩(**2a**)、呋喃(**2b**)、吡咯(**2c**)作为芳基化基团,催化效果如表2所示. 研究发现前三者均能获得良好的催化效果,并且以吡咯作为芳基化基团获得了最高的催化产率,效率可达84%. 后续进一步以噻吩(**2a**)作为芳基化基团,研究了不同取代基的重氮盐光催化效率. 我们分别选择了具有较强吸电子功能的-NO₂、给电子能力较强的-OCH₃,以及溴、氯等基团为取代基的重氮盐底物. 研究表明,具有吸电子基团的重氮盐的光催化产率要高于具有给电子基团的重氮盐的产率(表2). 这是因为吸电子基团的存在,重氮盐更加容易在TiOPc的催化下被活化. 对于卤素取代的重氮盐,在光催化芳基化后形成的产物由于芳环上卤素原子的存在,为后续进一步的功能化拓展提供了便利.

不同类别杂环芳烃与重氮盐芳基化反应:

表2 不同反应底物的TiOPc光催化C-H活化效果

Table 2 Substrate scope of heteroarenes with aryl diazonium salts

编号	底物	产物	产率(%) ^{a)}
1	1a (4-nitrophenyl diazonium tetrafluoroborate) + 2a (thiophene)	4a (4-nitrophenyl-thiophene)	60
2	1a (4-nitrophenyl diazonium tetrafluoroborate) + 2b (furan)	4b (4-nitrophenyl-furan)	62
3	1a (4-nitrophenyl diazonium tetrafluoroborate) + 2c (N-Boc-pyrrole)	4c (4-nitrophenyl-pyrrole)	84
4	1b (4-methoxyphenyl diazonium tetrafluoroborate) + 2d (thiophene)	4d (4-methoxyphenyl-thiophene)	50
5	1c (4-bromophenyl diazonium tetrafluoroborate) + 2a (thiophene)	4f (4-bromophenyl-thiophene)	60
6	1d (2,4-dichlorophenyl diazonium tetrafluoroborate) + 2a (thiophene)	4e (2,4-dichlorophenyl-thiophene)	64

a) 产率为核磁产率

2.3 TiOPc光催化C-H活化合成联芳基功能材料的机理推测

基于已报道的TiO₂^[16], TiCl₃^[19], Eosin Y^[24], 卟啉^[25], Ru(Bpy)₃²⁺^[33]等作为光催化剂的C-H活化研究. 我们对于TiOPc有机半导体材料光催化C-H活化的机理进行了推测,如图2所示. 首先, TiOPc在光照条件下形成激发态TiOPc*, 然后TiOPc*通过单电子转移过程, 将电子转移给重氮盐**1**, 重氮盐形成自由基**5**并生成氮气; 随后, 芳基自由基**5**与杂环芳烃**2**反应, 生成芳基化的中间产物自由基**6**, 之后中间产物**6**通过两种可能的途径得到芳基化的正离子产物**7**. 一条途径是通过TiOPc*氧化自由基产物**6**, 自由基**6**将电子转移给TiOPc*使其重新回到TiOPc, 同时自由基失去1个电子形成芳基化的正离子产物**7**; 另一条途径是芳基化中间产物**6**, 通过自由基链传递过程将自由基直接传递给重氮盐形成芳基自由基**5**. 最后芳基化的正离子通过去质子过程完成光催化C-H活化芳基化.

3 TiOPc光催化C-H活化合成有机半导体功能材料

在前期研究基础上, 我们进一步研究了TiOPc光催

图2 TiOPc光催化C-H活化芳基化机理推测

Figure 2 Suggested mechanism for direct C-H arylation of heteroarenes

化C-H活化在合成有机半导体功能材料中的应用。在有机半导体材料场效应研究中,化合物8是一类常见的骨架,并且基于此类骨架的有机半导体材料往往表现出优异的电荷传输性能^[1,6]。这里我们采用TiOPc作为光催化剂,在日光灯的照射下,实现了对于这类中间体的功能化,分别得到了带有功能化基团的产物9,如图3中所示,证实其在有机共轭材料合成方面的潜在应用。但需要指出的是,目前我们实验中得到的TiOPc对于上述蒽类材料的光催化C-H活化的产率很低,低于20%。造成这一结果的原因之一可能是由于蒽骨架分子在DMSO溶剂中溶解性较差,导致其有效浓度降低造成最终反应速率下降;另一方面可能是由于其光生

图3 TiOPc光催化C-H活化合成有机半导体

Figure 3 Synthesis of organic semiconductors by TiOPc photocatalysis

电荷分离还不够有效。我们相信,通过优化策略,可进一步提高该反应的催化活性,譬如引入外电场。半导体材料在电场作用下将会产生Franz-Keldysh效应,从而导致能量低于带宽的光子也能被吸收,展现出光谱吸收变宽以及红移,进而提高光的吸收率^[40]。同时,电场将会加速光生电荷的分离和调控^[7]。因而,我们推测TiOPc半导体材料,在光照条件下能够形成的光生电荷,通过外加电场或者构筑半导体异质结,在太阳光照下将加速积累并促进到重氮盐的转移,提高催化效率。

4 结论与展望

本工作研究了一种酞菁类半导体材料直接光催化C-H活化合成联芳基功能材料的绿色方法。C-H活化过程可以在太阳光、室温条件下进行。通过筛选发现TiOPc的光催化效率最高,且对于不同的芳基功能基团均能表现出良好的催化活性;并以TiOPc作为光催化剂,合成了具有常见蒽骨架结构的半导体材料。这一研究可以拓展到其他有机共轭功能材料体系,在有机光电子学领域具有重要意义。展望未来,我们推测可以通过外加电场或是构筑有机半导体异质结来提高半导体材料的光催化效率,关于这种半导体材料光催化方法的持续研究及其应用场景的拓展将适时开展。

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Summary for “太阳光照下酞菁类有机半导体光催化C-H活化合成联芳基功能材料”

Phthalocyanine-based organic semiconductors catalyzed C–H activation for heteroarenes functional materials in the sunlight

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Organic conjugated materials have attracted much attention in organic optoelectronics due to their excellent optical and electrical properties. In effort of continuous work, material system is continuously enriched, and the performance is rapidly improved. Currently, devices based on organic conjugate functional materials have achieved remarkable development, such as OLED, OFET, OPV, OLET, OFEW. Meanwhile, developing simple, efficient and green organic synthesis methods for these materials is a significant topic. And the most efficient synthesis method is the direct arylation of heteroarenes by C–H bond activation. Synthetic methods based on transition metal, for example, Ru and Ir complexes, catalyzed C–H activation are widely used to construct organic conjugated functional materials. Compared with the transition metal catalyzed reaction, photocatalytic reaction conditions are mild, low temperature and more environmentally friendly.

Recently, the direct C–H activation using semiconductor photo-catalysts, owing to good light absorption, is found to be a simple and effective method for organic functional materials. Lots of works based on inorganic semiconductors, such as CdS, ZnO, TiO₂, have been developed. Few works based on organic semiconductors, such as Eosin Y, porphyrin have also been reported. But, it is still not systematic enough, and necessary to further expand the kinds of organic semiconductor photocatalysis and develop a photocatalytic system with high efficiency and stability. In this paper, a green method for synthesizing heteroarenes functional materials via direct C–H activation has been developed. Phthalocyanine-based semiconductors are used as photocatalysts, and sunlight, the most common clean energy, is used as a light source at room temperature.

Firstly, the reaction conditions were optimized for the direct arylation of thiophene (**2a**) with diazonium salt (**1a**), 2 h sunlight irradiation, and 1 mol% phthalocyanine catalyst at room temperature. It's found that the desired product was obtained in all cases and titanium-phthalocyanine (TiOPc) semiconductor material exhibits the highest catalytic efficiency. The energy band structure of a photocatalytic material plays a key role in determining the performances of photocatalyst. According to the reported works, energy gaps of Pc, CuPc, TiOPc are respectively 1.40, 1.60–1.70, 1.10–1.20 eV. Narrower gaps response to better and wider light absorb.

Having optimized the reaction conditions, we examined the scope of the reaction of thiophene with different aryl diazonium salts. Among the aryl diazonium salts used for direct arylation of thiophene, electron-acceptor (–NO₂) diazonium salt is found to be more efficient for product formation than electron donor substituted ones (–OCH₃, Br, Cl). Notably, halogen-substituted aryl diazonium salts successfully underwent C–H bond arylation leaving the C–halogen bond intact, which is useful for further synthetic elaboration.

The C–H arylation of heteroarenes with aryl diazonium salts using TiOPc was expected to proceed through a radical mechanism. A mechanism for the photocatalytic, kinds of direct C–H arylation of heteroarenes with aryl diazonium salts catalyzed by TiO₂, TiCl₃, eosin Y, porphyrin were proposed. The crucial step involves generation of an aryl radical through single-electron transfer from the excited state of listed photocatalysts, to the aryl diazonium salt and its subsequent addition to a heteroarene to furnish an aryl radical intermediate. We reason that in our case a similar mechanism should operate. Under light irradiation, excited TiOPc proved to be efficient electron donors and acceptors.

Furthermore, semiconductor functional material with common anthracene-based structure is synthesized with TiOPc direct catalyzing C–H activation. For further optimized the catalytic efficiency, applying an external electric field or fabricating a semiconductor heterojunction should be considered. In summary, this green method could be further extended to the synthesis of other organic semiconductor functional materials, which is of great significance in organic optoelectronics.

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