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荧光三维共价有机框架的研究进展

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摘要 共价有机框架(covalent organic frameworks, COFs)是一种由有机分子构筑单元通过共价组装形成的二维或三维晶态有机多孔材料, 是当前化学和材料科学领域的前沿研究方向. 其中, 荧光COF因其具有较高结晶性、固有的开放多孔结构及稳定性等特点, 在荧光传感领域中的应用受到广泛关注. 目前, 荧光COF的研究主要集中于层状堆积的荧光二维COF, 荧光三维COF的报道则较少. 事实上, 三维COF中分子构筑单元通过共价键连接在三维空间延伸扩展, 可有效抑制荧光基团因堆积引起的荧光猝灭过程, 是一种构筑发光材料的理想平台, 引起研究者的关注. 本文首先综述了近年来荧光三维COF的合成方法, 包括直接合成法及后合成修饰法. 其次, 总结了荧光三维COF在爆炸物检测、挥发性有机物检测及金属离子检测方面的传感应用. 此外, 简要介绍了荧光三维COF在发光器件和成像方面的研究进展. 最后, 还对荧光三维COF所面临的挑战及未来的发展前景进行了讨论, 旨在为荧光三维COF的设计、合成和应用提供参考.

关键词 共价有机框架, 三维共价有机框架, 荧光, 发光材料

共价有机框架(covalent organic frameworks, COFs)是一种由分子构筑单元通过共价键连接形成的新型多孔材料, 属于晶态有机多孔聚合物[1~5]. COF具有比表面积大、骨架密度小、稳定性高、结构高度有序、功能可定制等特点, 在分子吸附与分离[6~9]、催化[10~13]、能源[14~17]、传感[18~21]等领域存在广阔的应用前景. 其中, 荧光COF在传感领域中的应用受到广泛关注[18,19,22~29], 展现出以下独特优势: (1) COF是晶态材料, 可通过目标导向构筑荧光COF并实现精准识别; (2) COF固有的开放多孔结构可方便客体分子进入孔道并与功能基元结合, 实现高效传感; (3) 其优良的稳定性有利于传感过程中保持结构完整, 方便重复利用; (4) 通过建立构效关系, 可指导设计性能更优的荧光COF. 因此, 自2008年报道第一例荧光COF(triphenylene COF, TP-COF)以来[30], 荧光COF的研究愈发受到重视.

当前, 荧光COF的研究主要集中于层状堆积结构的二维COF[18,19,22~33], 在化学检测[18,19,22~27]、生物传感[28,29]和成像[31~33]等方面展示出应用潜力. 然而, 由于二维COF层层之间存在着强相互作用(如π-π堆积), 而大部分荧光团具有荧光猝灭现象[34], 引入之后难以构筑荧光较强的发光材料, 有时甚至没有荧光. 相比之下, 具有较高比表面积、贯穿孔道结构及大量开放功能位点的三维COF[4,35]是一种构筑荧光材料的理想平台. 首先, 三维COF的空间网络结构可有效减少荧光团之间的相互作用, 从而减弱可能由堆积引起的荧光猝灭过程, 进而构筑荧光COF[36]; 其次, 三维COF具有丰富的孔道结构和更大的比表面积, 有利于分析物与功能位点充分作用, 提高检测灵敏度, 并潜在用于荧光信号的集成和放大. 因此, 荧光三维COF的研究引起了关注[36~42], 极具应用潜力.

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但需指出, 三维COF的合成难度很大[4,35,43,44]. COF采用动态共价成键方式构筑, 存在共价键生成、断裂及重组的自纠错行为. 相对于在平面共价成键过程中存在π-π堆积作用的二维COF, 三维COF是三维空间共价成键组装, 其合成主要依赖于共价键的形成[43,44]. 由于共价键键能高, 可逆成键组装能力弱, 很难从原子层面对三维框架成键过程进行精准控制, 结晶难度更大. 同时, 三维COF在结构设计和表征方面还存在一系列挑战[4,35]. 因此, 荧光三维COF的构筑难度很大, 但值得高兴的是, 在研究者的努力下取得了一些进展[36~42]. 本文详细论述了荧光三维COF的合成及应用, 并对其面临的挑战和未来的发展方向进行总结和展望, 以期对荧光三维COF这一极具潜力研究领域的发展提供新思路.

1 荧光三维COF的合成

目前, 根据连接键种类, 三维COF可分为硼酸酯三维COF、亚胺三维COF、碳碳双键连接三维COF等. 然而, 荧光三维COF的键连方式主要是席夫碱键和碳碳双键, 构筑荧光三维COF的方法包括直接法及后合成修饰法. 荧光三维COF可通过相应分子前体直接合成, 也可先合成框架, 再通过后合成修饰的方式构筑(表1).

1.1 直接法

直接法即通过相应分子前体直接合成荧光三维COF的方法. 目前, 大部分荧光三维COF的合成均采用此方法. 2016年, Lin等人[36]利用[4+4]缩合反应, 将作为四面体节点的四(4-氨基苯基)甲烷(TAPM)与具有平面四边形的1,3,6,8-四(4-甲酰苯基)芘(TFPPy)分子反应, 通过溶剂热法构筑了第一例荧光三维COF(3D-Py-COF)(图1(a)). 不同于荧光较弱或不具有荧光的相应类似二维COF, 该三维COF粉末在紫外灯照射下表现出明亮的黄绿色荧光. 该研究表明, 将荧光分子引入到三维COF的网状结构中, 可有效抑制荧光团之间的聚集猝灭效应, 进而构筑荧光三维COF. 随后, Ding等人[37]采用相同的合成策略, 设计、合成了含有四苯乙烯基元的荧光三维COF(3D-TPE-COF). 相关研究显示, 该COF在450 nm蓝光激发下具有黄色荧光, 荧光量子产率高达20%, 高于相应的模型化合物(6.6%). 2022年, Wei等人[38]也通过直接法构筑了一例本身无荧光但吸附不同有机溶剂分子时产生荧光的三维COF.

除通过以上直接引入发光分子构筑荧光三维COF, 在形成三维COF过程中还可形成特殊连接键(如碳碳双键), 进而获得荧光三维COF. 2022年, Liao等人[39]以四(4-甲酰基苯基)硅烷(TFS)为四面体节点, 分别与1,4-苯二乙腈(PDAN)和4,4′-联苯二乙腈(BPDAN)通过Knoevenagel反应合成了碳碳双键连接的三维COF(JUC-580与JUC-581)(图1(b)). 实验发现, 在363和365 nm光源的照射下, JUC-580和JUC-581产生绿色荧光, 荧光量子产率分别为3%和6%. 然而, 结构类似但由亚胺键连接的两个三维COF(COF-300和COF-320)在固态下几乎不具有荧光. 该结果表明, 通过直接法构筑碳碳双键连接三维COF也是一种获得荧光三维COF的策略.

1.2 后合成修饰法

直接合成三维COF[36~38]是目前构筑荧光三维COF的主要方法. 但由于三维COF的结构解析困难[45,46], 功能基团引入还可能造成拓扑结构改变[47]等问题, 通过直接法构筑荧光三维COF有时难度较大. 后合成修饰法作为一种迂回的策略[48~51], 可在确定结构三维COF的基础上快速引入发光基元, 进而构筑荧光三维COF.

镧系金属具有良好的发光性能, 可通过后合成修饰方式引入三维COF框架中, 进而构筑荧光三维COF. 2020年, Li等人[40]采用多步后合成修饰的策略, 将Eu(III)引入三维COF, 成功构筑了具有发光性能的荧光三维COF(Eu-3D-COF). 首先, 使用四(4-甲酰基苯基)甲烷(TFPM)和3,3′-二羟基-4,4′-联苯二胺(DHBD)构筑了OH-3D-COF. 随后, 他们利用OH-3D-COF与丙二酸环(亚)异丙酯的无溶剂酯化反应, 制备了羧基功能化修饰的COOH-3D-COF, 进一步通过羧基与Eu(III)的配位引入发光中心, 合成了具有发光性能的Eu-3D-COF(图1(c)). 相关光谱表征结果表明, Eu(III)成功修饰到COF框架中且其最大负载量为386 mg/g. 荧光测试表明, COOH-3D-COF无荧光, Eu-3D-COF在325 nm紫外光照射下产生红色荧光, 荧光量子产率约为38.2%.

2 荧光三维COF的应用

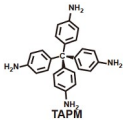
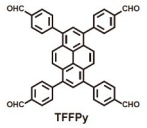
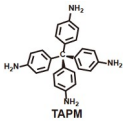
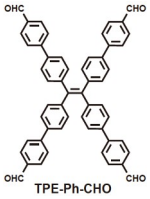
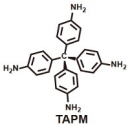
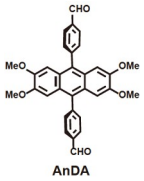
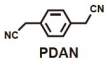
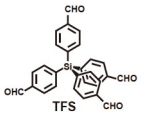
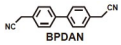
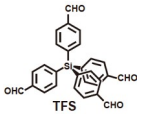
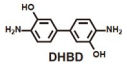
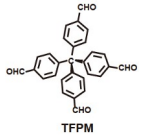
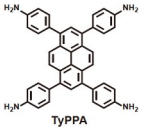
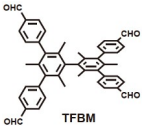
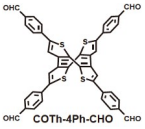
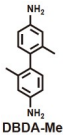
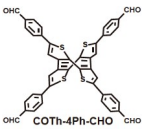
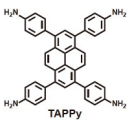
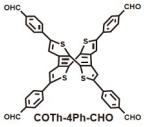
基于其丰富的孔道结构及荧光性质, 荧光三维COF已在荧光检测、发光二极管及荧光成像方面取得了应用.

2.1 荧光检测

当分析物进入孔道中与三维COF框架发生作用, 使三维COF的荧光发生改变, 即可实现目标分析物的

表 1　荧光三维COF[a)]

Table 1　Fluorescent 3D COFs

COF名称	连接方式	合成类型	前体分子		拓扑类型	发光特点			参考文献
						λ_{ex}(nm)	λ_{em}(nm)	荧光量子产率(%)	
3D-Py-COF	[4+4]	直接法	 TAPM	 TFFPy	**pts**	408	484(DMF)	–	[36]
3D-TPE-COF	[4+4]	直接法	 TAPM	 TPE-Ph-CHO	**pts**	450	543	20	[37]
dynaCOF-330	[4+2]	直接法	 TAPM	 AnDA	**dia**	420	490~550	–	[38]
JUC-580	[4+2]	直接法	 PDAN	 TFS	**dia**	363	585	3	[39]
JUC-581	[4+2]	直接法	 BPDAN	 TFS	**dia**	365	583	6	[39]
Eu-3D-COF	[4+2]	后修饰	 DHBD	 TFPM	–	325	614	38.2	[40]
3D-LCOF	[4+4]	直接法	 TyPPA	 TFBM	**pts**	365	498(乙醇)	29(乙醇)	[41]
COF-NUST-11	[4+2]	直接法	 DBA-Me	 COTh-4Ph-CHO	**dia**	360	610	–	[55]
COF-NUST-12	[4+2]	直接法	 DBDA-Me	 COTh-4Ph-CHO	**dia**	360	610	–	[55]
COF-NUST-13	[4+4]	直接法	 TAPPy	 COTh-4Ph-CHO	**pts**	360	610	–	[55]

a) “–”表示相关文献中无该数据; Py, Pyrene, 芘; DMF, *N*,*N*-二甲基甲酰胺; TPE, 四苯乙烯; dynaCOF, 动态COF; JUC, 吉林大学COF; LCOF, 荧光COF; NUST, 南京理工大学

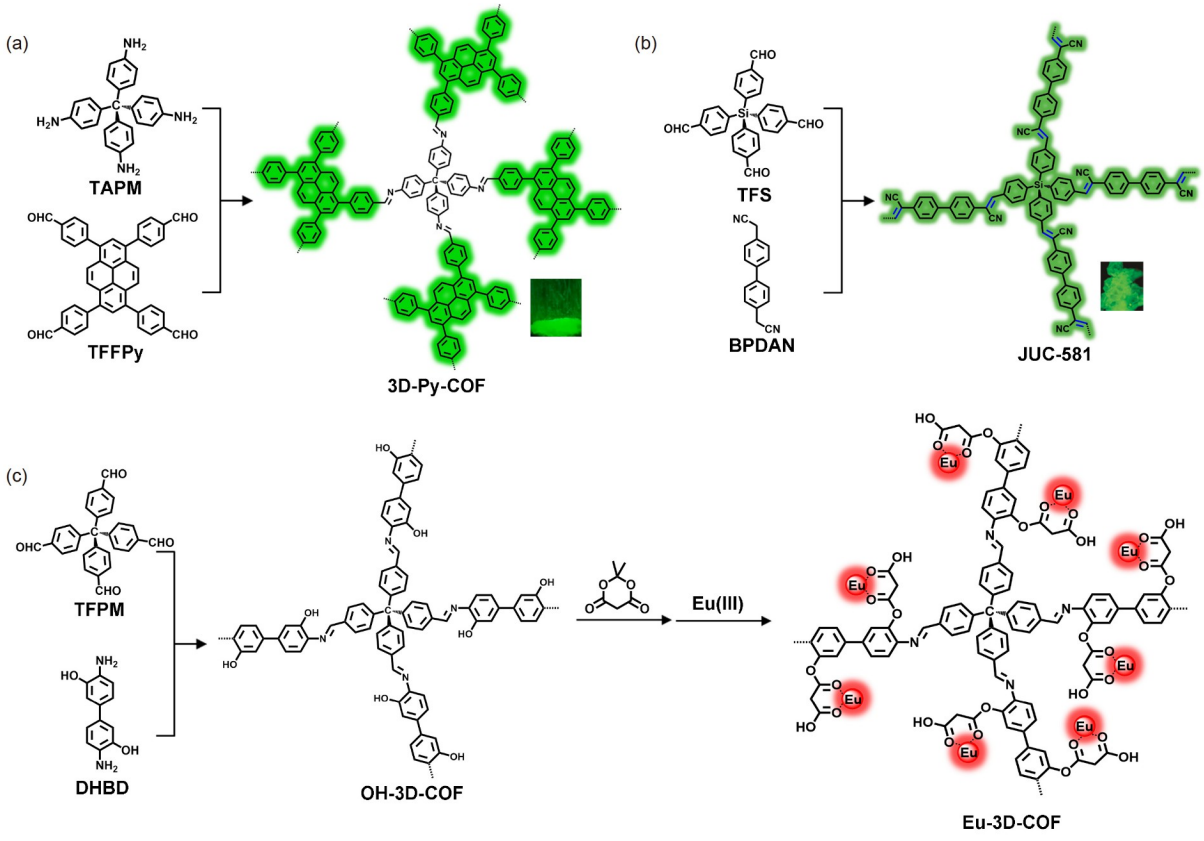


图 1 荧光三维COF的合成. (a) 通过荧光分子前体TFFPy直接合成荧光3D-Py-COF及其粉末在紫外灯照射下的荧光照片[36]; (b) 通过形成碳碳双键合成荧光三维COF(JUC-581)及其荧光照片[39]; (c) 通过后合成修饰引入Eu(III)合成荧光Eu-3D-COF[40]

Figure 1 The synthesis of fluorescent 3D COFs. (a) The synthesis of fluorescent 3D-Py-COF from fluorescent precursor[36]; (b) the synthesis of fluorescent 3D COF (JUC-581) via the formation of C=C bond[39] and its fluorescence microscopic image; (c) the construction of fluorescent Eu-3D-COF via post-synthetic modification of 3D COF with luminescent Eu(III)[40]

检测. 目前, 荧光三维COF已用于爆炸物[36,37]、挥发性有机物[38,41]和重金属离子检测[42].

硝基芳烃类爆炸物是军用炸药的主要成分, 其快速、灵敏的检测对维持社会稳定具有重要意义. 2016年, Lin等人[36]首次将荧光三维COF(3D-Py-COF)用于爆炸物检测. 实验结果表明, 当苦味酸(picric acid, PA)这一模型爆炸物加入含有3D-Py-COF的悬浮液后, 3D-Py-COF的荧光逐渐被淬灭, 当PA的浓度为20 ppm(1 ppm=1 μg/g)时, 荧光猝灭程度达到75%, 根据相应Stern-Volmer曲线计算, 得到猝灭常数(K_{sv})为3.1×10^4 L/mol(图2(a)~(c)). 3D-Py-COF的荧光被PA猝灭可能的原因是二者之间发生电子转移和共振能量转移. 2018年, Ding等人[37]也研究了3D-TPE-COF对PA的荧光检测性能. 他们将PA水溶液(1.0×10^{-2} mol/L)逐渐加入3D-TPE-COF粉末的水相悬浮液中, 结果发现, PA可有效猝灭3D-TPE-COF的荧光. 根据相应的Stern-Volmer曲线, 他们计算得到K_{sv}约为3.3×10^4 L/mol (图2(d)~(f)).

挥发性有机物(volatile organic compounds, VOCs)是空气污染物的一种, 识别VOCs对环境监测具有较大的意义. 与荧光分子筛相比, 荧光三维COF孔道结构更加多样, 在识别和检测多种挥发性有机物方面更具优势[38,41]. 根据荧光三维COF的多孔特性, 其也可用于挥发性有机物的检测[38,41]. 2020年, Liu等人[41]通过[4+4]缩合反应合成了可用于VOCs识别的三维COF(3D-LCOF, 图3). 该三维COF粉末不发光, 但分散在乙醇中时, 3D-LCOF富含π电子的芘基团与缺电子的VOCs之间相互作用, 其悬浮液表现出明显的黄绿色荧光. 相关实验结果表明, 当3D-LCOF分散在其他常见的VOCs溶剂中时, 悬浮液在紫外光激发下发射不同波长的荧光. 随着溶剂的给电子能力增加, 3D-LCOF的悬浮液荧光从蓝色变为浅蓝色; 此外, 随着溶剂极性的增加, 3D-

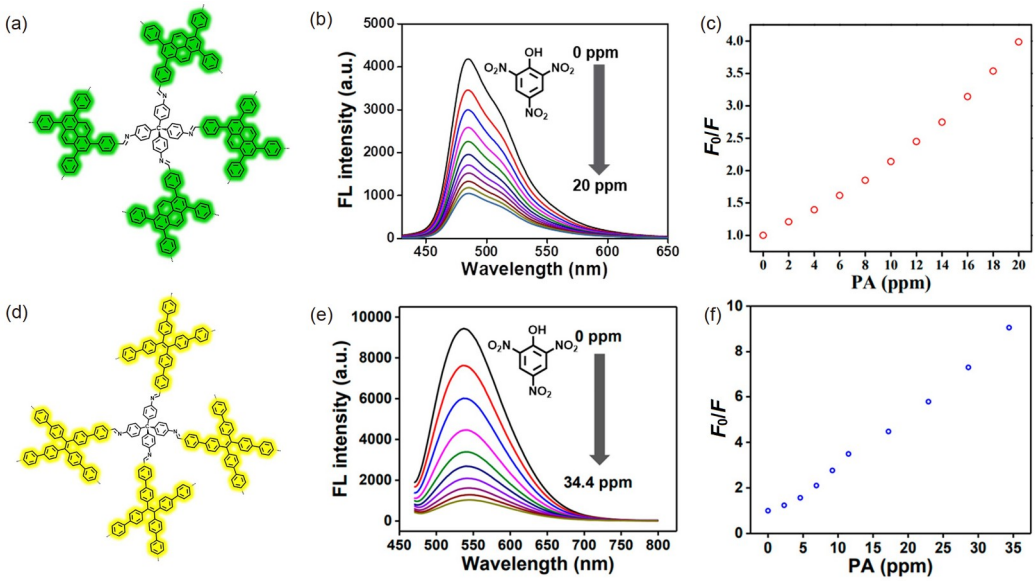


图 2 荧光三维COF对苦味酸的检测. 3D-Py-COF的结构示意图(a)、苦味酸PA对3D-Py-COF悬浮液的荧光猝灭(b)及Stern-Volmer曲线(c)[36]; 3D-TPE-COF的结构示意图(d)、苦味酸PA对3D-TPE-COF悬浮液的荧光猝灭(e)及Stern-Volmer曲线(f)[37]

Figure 2 Fluorescent 3D COF for the detection of picric acid. The structure presentation of 3D-Py-COF (a), the fluorescence quenching of 3D-Py-COF suspension by picric acid (b) and its Stern-Volmer curve (c)[36]; the structure presentation of 3D-TPE-COF (d), the fluorescence quenching of 3D-TPE-COF suspension by picric acid (e) and its Stern-Volmer curve (f)[37]

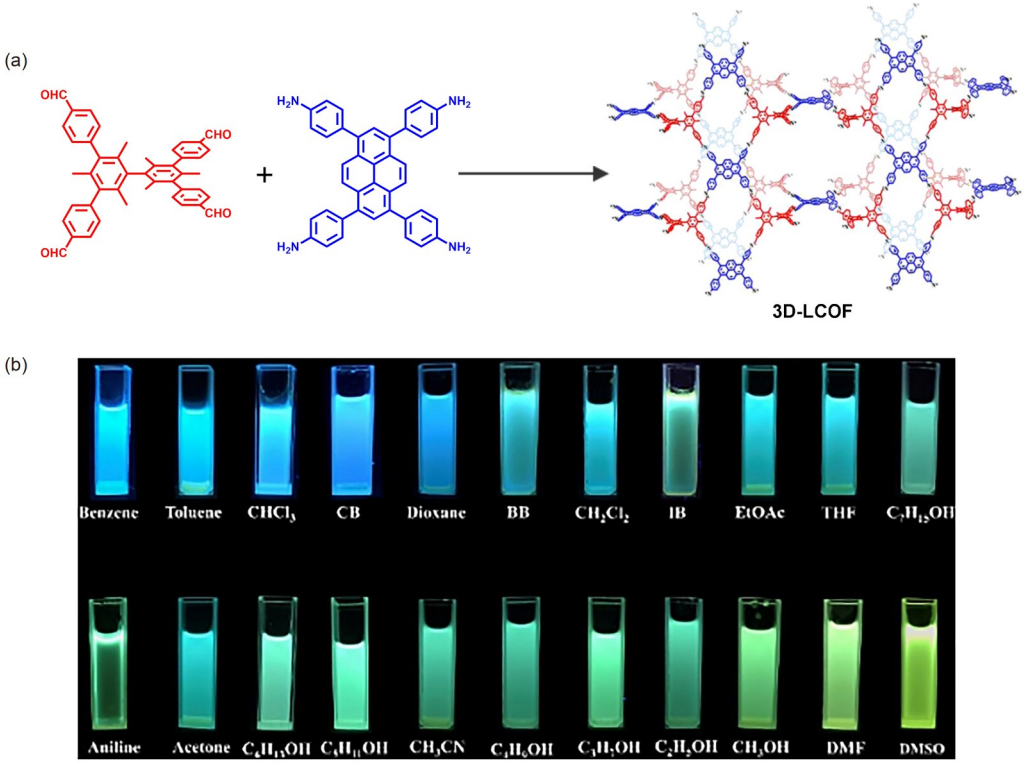


图 3 3D-LCOF的合成(a)及分散在不同VOCs中的荧光照片(λ_{ex}=365 nm)(b)[41]

Figure 3 Schematic presentation the synthesis of 3D-LCOF (a) and the fluorescence microscopic image of the suspension of 3D-LCOF in different VOCs (λ_{ex}=365 nm) (b)[41]

LCOF的悬浮液荧光从蓝色变为黄绿色. 根据以上特征, 该三维COF可用于VOCs的荧光检测. 2022年, Wei等人[38]系统研究了各种VOCs对含蒽功能基元三维COF的荧光点亮行为. 研究结果显示, 该三维COF也可用于VOCs的荧光检测.

此外, 荧光三维COF还可用于重金属离子检测[42]. Co^{2+}是维生素B_{12}的组成部分, 在人体内铁的代谢和血红蛋白的合成中起着关键作用, 然而高含量钴的接触会引起严重的健康问题[52]. 2021年, Wang等人[42]利用TAPM、联苯(BPDA)和联吡啶(Bpy)通过直接法构筑了可检测Co^{2+}的荧光三维COF, 并将其用于Co^{2+}的检测. 相关实验表明, 在324 nm波长照射下, 该COF在406 nm处有一个强荧光发射峰, 随着Co^{2+}浓度的增加, 该荧光峰被逐渐猝灭. 当Co^{2+}浓度在0.01~0.25 μmol/L范围内时, 所得COF的荧光猝灭度(F_0-F)与分析物浓度具有良好的线性关系. 根据该线性关系, 此荧光三维COF对Co^{2+}的检测限为2.63 nmol/L. 当加入相同浓度的其他金属离子时, COF的荧光变化不明显, 对Co^{2+}具有选择性和一定的抗干扰检测性能. 与相应的分子前体Bpy相比, 该荧光三维COF对Co^{2+}的线性检测范围更宽, 选择性更好.

2.2 发光器件

白色发光二极管(white light emitting diodes, WLED)灯由于使用寿命长、节能环保、安全性高等优点, 已取代传统白炽灯和荧光灯等成为新一代固态照明光源[53]. 制造WLED的一种常规方法是在蓝色发光二极管(light emitting diodes, LED)芯片上涂覆可产生黄色光的荧光粉. 目前, 商用WLED产品主要使用含稀土元素的荧光粉[54], 随着高科技产品对稀土元素需求的增加, 寻找可替代的无稀土荧光粉具有重要意义. 荧光三维COF具有无金属、可设计的特点, 在WLED发光器件方面具有较大的应用潜力. 2018年, Ding等人[37]首次成功将具有黄色荧光的3D-TPE-COF均匀涂覆在蓝色发光二极管(峰值约为450 nm)表面(图4(a)), 获得了非常接近纯白光(Commission International de I'Eclairage, CIE坐标为(0.30, 0.35))的WLED灯(图4(b)). 此外, 鉴于该COF的稳定性, 他们进一步测试了该灯的稳定

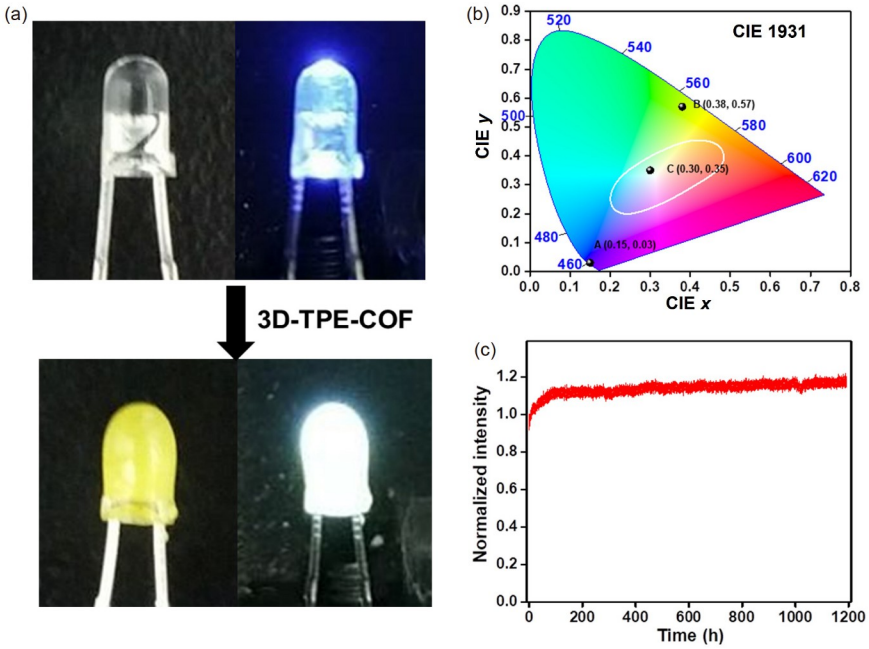


图 4 基于3D-TPE-COF WLED的制备及性质[37]. (a) 市售蓝光LED和涂覆薄层3D-TPE-COF LED在未点亮(左)和点亮(右)下的照片; (b) CIE-1931坐标图及蓝光LED(A点)、3D-TPE-COF(B点)和COF涂覆制备WLED(C点)发光在坐标图中的位置; (c) 3D-TPE-COF涂覆制备WLED长时间2 mA电流点亮下的归一化发光强度

Figure 4 The fabrication and characterization of 3D-TPE-COF based WLED[37]. (a) The photographs of the commercial blue LED and the same LED coated with a thin layer of 3D-TPE-COF before (left) and after being turned on (right); (b) CIE-1931 chromaticity diagram and the positions marked for the emission of blue LED (A), 3D-TPE-COF (B) and COF-coated WLED (C); (c) normalized luminescence intensity vs. time curve of the 3D-TPE-COF-coated WLED driven at 2 mA for long time

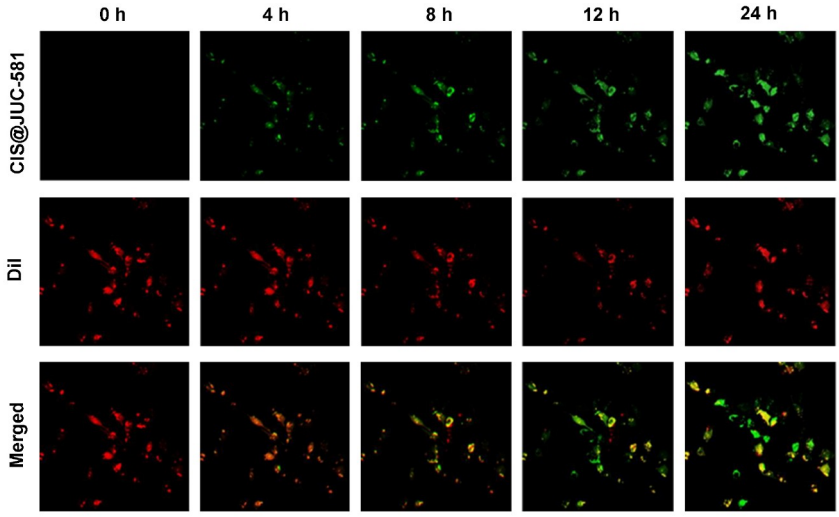


图 5 不同时间下JUC-581(上)、商用染色剂DiI(中)和两者混合物(下)对细胞染色后的细胞荧光成像[39]
Figure 5 Cell fluorescence imaging of JUC-581(top), DiI(middle), and merged (bottom) at different times[39]

性. 结果显示, 在连续发光1200 h后, 该WLED灯发光稳定, 无明显衰减(图4(c)). 该工作表明, 荧光三维COF在制备稳定、无金属WLED方面具有较大应用潜力.

2.3 荧光成像

荧光三维COF相较于荧光MOF, 存在稳定性高及无金属等特点, 也可用于生物成像. 2022年, Liao等人[39]同时利用了荧光三维COF的发光特性和多孔结构, 探究了荧光三维COF在药物装载与成像示踪方面的应用. 他们利用碳碳双键连接三维COF(JUC-581)骨架中的氰基与顺铂(cisplatin, CIS)上氨基的相互作用, 将JUC-581用于抗癌药物顺铂的负载. 相关实验结果表明, JUC-581对细胞几乎无伤害, 而CIS@JUC-581对细胞具有较高的毒害性. 此外, 由于JUC-581具有绿色荧光可同时作为细胞的染色剂, 可实现从药物转运到细胞裂解的全过程可视化跟踪, 与商用染色剂1,1′-双十八烷基-3,3,3′,3′-四甲基吲哚菁高氯酸盐(DiI)相比, JUC-581可以更有效地实现细胞染色(图5).

3 总结与展望

作为一种新兴的荧光材料, 荧光三维COF具有比表面积大、贯穿孔道结构及大量开放功能位点的特点和较稳定的光致发光特性, 已在多个领域展现出应用潜力. 本文综述了荧光三维COF的设计、合成及其在荧光检测、发光器件、生物成像等领域中的研究进展. 然而, 尽管荧光三维COF在上述领域中展现出良好的可设计性、较高的灵敏度等优势, 但不可否认荧光三维COF的研究仍处在起步阶段, 还存在众多问题待解决. 目前, 荧光三维COF主要通过相应功能分子直接合成, 适用功能分子较少, 合成难度大, 结构解析困难, 荧光量子产率不够理想, 构效关系研究较少, 难以定向设计、合成. 根据当前荧光COF的相关研究, 席夫碱键引起的非辐射能量耗散及荧光构筑单元之间可能存在的聚集诱导猝灭是造成荧光COF发光强度较弱的重要原因. 因此, 采用碳碳双键构筑三维COF以及抑制荧光单元之间的聚集猝灭或通过聚集诱导发光(aggregation-induced emission, AIE)分子构筑荧光三维COF等, 是合成具有强发光性能三维COF的潜在策略. 总之, 荧光三维COF作为一种有潜力的新兴荧光材料, 目前仍面临诸多挑战, 但相信随着三维COF设计、合成和结构解析的突破, 荧光三维COF将取得快速发展.

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Summary for “荧光三维共价有机框架的研究进展”

Recent advances in fluorescent 3D covalent organic frameworks

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Covalent organic frameworks (COFs) represent an emerging class of crystalline porous organic materials constructed by covalently linking organic molecules into two-dimensional (2D) or three-dimensional (3D) structure, which is the cutting-edge research in chemistry and material science. Due to their large surface areas, low density, high stability and ordered frameworks, COFs are promising materials for adsorption and separation, catalysis, energy storage, sensing and so on. Among them, the application of fluorescent COFs in the field of sensing has attracted a lot of attention with the following advantages: (1) Specific molecular recognition can be achieved based on the tailor-made structure of fluorescent COFs; (2) the inherent porous structure of COFs can achieve efficient sensing by facilitating the interaction between the guest molecule and the functional unit; (3) their excellent stability can maintain the structure intact during the sensing process, which is important in recycling; and (4) the structure-property-function relationships can guide the design of fluorescent COFs with superior performance. Up to now, most of the reported fluorescent COFs were fluorescent 2D COFs and few fluorescent 3D COFs have been reported. In fact, 3D COFs, in which the molecular building blocks are extended in three dimensions by covalent self-assembly connections, can efficiently avoid the fluorescence quenching caused by the stacking of fluorescent units. Therefore, 3D COFs are considered as an ideal candidate for the construction of luminescent materials. In this review, we summarized the recent research progress in fluorescent 3D COF, including the methods used to construct fluorescent 3D COFs and their applications in chemical sensing, light-emitting materials and bioimaging. In addition, the challenges and prospects of fluorescent 3D COF are also discussed.

In the first part, we discussed the synthetic strategies used to construct fluorescent 3D COFs. In general, fluorescent 3D COFs can be obtained by direct synthesis of the corresponding fluorescent building blocks or by post-synthetic modification of the pre-prepared frameworks. Many fluorescent units, including pyrene, tetraphenylene, and anthracene have been successfully incorporated into 3D COFs to construct fluorescent 3D COFs. Besides, fluorescent 3D COFs can also be synthesized directly via the formation of conjugated C=C bond. In addition, luminescent ions could also be successfully immobilized into the framework via post-synthetic modification method to construct fluorescent 3D COFs. Then we summarized the applications of these fluorescent 3D COFs in detection (e.g., explosive detection, volatile organic compounds sensing and metal ions detection), fabricating optoelectronics, and cell imaging.

In the last part, we give the conclusion about the review, including a summary of the construction methods of fluorescent 3D COFs and their applications in sensing, optoelectronics, and imaging. However, there are still few studies on fluorescent 3D COFs due to the problems that hinder the development. First, the fluorophores suitable for the construction of fluorescent 3D COFs are quite limited. Second, the synthesis and structure determination of fluorescent 3D COFs are very challenging. Third, there are rather few studies on structure-property-function relationships, which makes their target design and synthesis very challenging. Since the excitation energy dissipation caused by Schiff base and the aggregation caused fluorescence quenching are the main reasons for the weak fluorescence of 3D COFs, constructing 3D COFs with C=C bonds and suppressing the aggregation quenching between fluorescent units or constructing 3D COFs with AIE molecules are potential strategies for the synthesis of fluorescent 3D COFs with strong fluorescence. We believe with the efforts from all the researchers worldwide, fluorescent 3D COFs will develop rapidly as the design, synthesis and structure determination of 3D COFs continue to evolve.

covalent organic framework, 3D covalent organic framework, fluorescence, luminescent materials

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