Integrative self-assembly of covalent organic frameworks and fluorescent molecules for ultrasensitive detection of a nerve agent simulant

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ABSTRACT Binding of fluorescent molecules to the porous matrix through noncovalent interactions will synergistically expand their application spectrum. In this regard, we report an integrative self-assembly of molecule 1 with benzothiadiazole and 9,9-dihexyl fluorene units, and covalent organic frameworks (COFs) via an emulsion-modulated polymerization process, within which molecules of 1 are able to interact with the scaffolds of COFs through CH- π interactions. Thus the π - π interactions between the fluorescent molecules are largely suppressed, giving rise to their remarkable monomer-like optical properties. Of particular interest is that, given by the specific interaction between COFs and a nerve agent simulant diethyl chlorophosphite (DCP), these assembled composites show the ability of ultrasensitive detection of DCP with a detection limit of ~40 ppb. Moreover, the present integrative assembly strategy can be extended to encapsulate multiple fluorescent molecules, enabling the assemblies with white light emission. Our results highlight opportunities for the development of highly emissive porous materials by molecular self-assembly of fluorophores and molecular units of COFs.

Keywords: covalent organic frameworks, sensor, noncovalent interactions, nerve agent, self-assembly

INTRODUCTION

Nerve agent is a colorless and highly toxic gas. It has unique toxicological concerns owing to the existence of an unpredictable asymptomatic latent phase that takes place prior to the onset of lifethreatening pulmonary edema. Therefore, the development of sensitive and selective sensors for this chemical has attracted considerable

attention [1–3]. Fluorescence sensing, on the basis of fluorescence enhancement or fluorescence quenching induced by the target analytes, has attracted intensive attention because it features with high sensitivity, anti-interference ability, cost-effectiveness and portability, etc. [4–13]. The development of methods for signal amplification and discrimination remains critical and is of great value in practical use [14–18]. High-luminous-efficiency porous materials with specific recognition ability have advantages of sensitive and selective detection due to large surface areas. To meet these challenges, various strategies and sensing systems have been developed, among which porous matrices hold great promise because their porous structures facilitate the accessibility of target analytes to the binding sites by decreasing the diffusion resistance [19–22]. Particularly, the immobilization of fluorophores within the porous matrix through either covalent or noncovalent interactions can largely reduce the undesired molecular aggregation that degrades the signal detection.

Compared with other porous materials, as a newly emerging type of crystalline porous materials, covalent organic frameworks (COFs) incorporated with fluorophores have shown some potentials in fluorescence sensing, benefiting from the combination of large surface areas, good thermal and chemical stability, adjustable porosity and tunable organic functional groups [23–36]. On one hand, some progresses have been achieved by integrating designated luminescent units into COFs for detecting gaseous hydrogen chloride, ammonia vapor, formaldehyde and arene vapors [37–40]. Normally, mo-

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lecules are loaded into the porous materials through a diffusion-adsorption method. The diffusion of molecules can block the pores of COFs and would result in inhomogeneous loading of molecules. Moreover, the adsorbed molecules within the matrices cannot avoid the aggregation of molecules in the porous material. However, highly emissive COFs are rarely achieved because the aggregation-caused quenching (ACQ) between π - π stacked layers exists, which largely suppresses their detection limitations. On the other hand, the detection sensitivity of the fluorescence probes is also determined by the “active site” capable of trapping target analytes, which requires the integration of specific receptors into organic units prior to the synthesis of COFs.

Herein, we demonstrate a concept of integrative self-assembly of highly emissive fluorescent molecules with COFs (from 1,3,5-tris(4-aminophenyl)benzene (TAPB) and terephthalaldehyde (PDA)) through noncovalent interactions (Fig. 1 and Fig. S1). This synthetic strategy mainly relies on the synchronized interfacial polymerization of monomers of COFs with localized fluorescent molecules trapped at the liquid-liquid interface. As a proof of concept, we first design and synthesize molecule 1 (7,7'-(9,9-dihexyl-9H-fluorene-2,7-diyl)bis(4-(7-(4-(sec-butoxy)phenyl)-9,9-dimethyl-9H-fluoren-2-yl)benzo[c][1,2,5]thiadiazole)) with benzothiadizole and 9,9-di-

hexyl fluorene units (Fig. 1). An important feature of such molecule is that its π -conjugated units are expected to interact with TAPB-PDA-COFs through supramolecular self-assembly, capable of locking molecule 1 within the pores of TAPB-PDA-COFs.

The resultant integrative assemblies 1CTAPB-PDA-COFs have several remarkable features including: (i) facilitated accessibility of target analytes through porous matrix; (ii) highly emissive fluorescence probes without self-aggregation and (iii) target specific on-demand synthesis, which are likely to be beneficial for the ultra-sensitive and selective fluorescence sensing of diethyl chlorophosphate (DCP), which is considered as a nerve agent simulant or as a chemical analogue of cholinesterase inhibiting organophosphate pesticides [41,42].

RESULTS AND DISCUSSION

The detailed procedures for synthesis of Molecule 1 and fabrication of 1CTAPB-PDA-COFs are provided in the Supplementary information. Loading of molecule 1 (~3 wt%) into TAPB-PDA-COFs is enabled by a two-step polymerization-crystallization process, as illustrated in Fig. S2. After the removal of oil and crystallization in acetic aqueous solution, colloidal particles of 1CTAPB-PDA-COFs were produced.

The morphology, crystallinity and the porous structure

Figure 1 Conceptual design of integrative assemblies of 1CTAPB-PDA-COFs for amplified ratiometric fluorescence detection of DCP.

of 1CTAPB-PDA-COF colloids were characterized by transmission electron microscope (TEM), scanning electron microscope (SEM), X-ray diffraction (XRD) and nitrogen sorption experiments. Electron microscopy images in Fig. 2a, b, Figs S3 and S4 reveal that the resulting composites are hollow capsules with diameters and shell thicknesses of (400 ± 200) nm and (50 ± 10) nm, respectively. XRD pattern in Fig. 2c reveals that these capsules are well crystallized in the presence of molecule 1, in consistent with the simulated XRD pattern of the eclipsed-AA stacking model (inset in Fig. 2c). The nitrogen sorption isotherm is identified as type IV mode, with a Brunauer-Emmett-Teller (BET) surface area of $101.8 \text{ m}^2 \text{ g}^{-1}$ (Fig. 2d).

The UV-Vis spectrum of molecule 1 in chloroform solution exhibits two absorption peaks at 335 and 435 nm, respectively, and the photoluminescence (PL) spectrum of molecule 1 displays green luminescence with one emissive peak at 550 nm (Fig. S5). The fluorescence quantum yield of molecule 1 is measured to be $\sim 38\%$. The UV-vis spectrum of 1CTAPB-PDA-COFs (~ 3 wt% of molecule 1) exhibits an absorption peak centered at 385 nm (Fig. S6). Upon excitation, 1CTAPB-PDA-COFs

emitted luminescence with peak maxima at 552 nm (Fig. 2e), which is similar to that of solubilized molecule 1 (551 nm), while it differs from that of aggregation 1 (537 nm) (by injection of the chloroform solution of molecule 1 into methanol and aged for 48 h, Fig. S7). It is worth noting that the PL peak positions of 1CTAPB-PDA-COFs are nearly kept constant (552 nm) upon the increase of loading of molecule 1 from 0 to 10 wt% (Fig. S8). Time-resolved PL spectra in Fig. 2f reveal that the lifetime of 1CTAPB-PDA-COFs (1.8 ns) is similar to that of isolated molecule 1 (1.6 ns), whereas it is much shorter than that of aggregation 1 (3.5 ns). These results clearly reveal that molecule 1 trapped in TAPB-PDA-COFs has non-aggregated monomer-like optical properties. The spatial distribution of molecule 1 in TAPB-PDA-COF colloids was further examined by using confocal laser scanning microscopy (CLSM) coupled with fluorescence emission spectroscopy. A fluorescence microscopy image in Fig. 2g reveals that all the colloidal particles of 1CTAPB-PDA-COFs exhibited brilliant luminescence with the same color. The fluorescence emission spectroscopy of a single particle shows a single emissive peak centered at ~ 550 nm (Fig. 2h), in consistent with the

Figure 2 (a) SEM and (b) TEM images of crystalline 1CTAPB-PDA-COFs. (c) The XRD pattern of crystalline 1CTAPB-PDA-COFs and its simulated XRD pattern with AA-stacked model. (d) N_2 adsorption-desorption isotherms of 1CTAPB-PDA-COFs before and after crystallization. The BET surface areas of 1CTAPB-PDA-COFs before and after crystallization are 101.3 and $31.5 \text{ m}^2 \text{ g}^{-1}$, respectively. (e, f) The fluorescence spectra and delay lifetimes of monomer 1, aggregation 1 and 1CTAPB-PDA-COFs. (g, h) CLSM image and spatially resolved fluorescence spectra of crystalline 1CTAPB-PDA-COFs. (i) 3D CLSM image of hollow sphere 1CTAPB-PDA-COFs.

measurement from PL spectra of 1CTAPB-PDA-COFs. Moreover, excellent spectral reproducibility is obtained at multiple particles, revealing that all the particles have similar loading density of molecule **1** (Fig. 2h). Reconstructed three-dimensional (3D) CLSM image in Fig. 2i confirms that the luminescence was homogeneous across the shell of TAPB-PDA-COFs capsules. All the above results indicate that molecule **1** is uniformly distributed throughout the TAPB-PDA-COFs with monomer-like optical properties.

In order to understand the specific interactions between molecule **1** and TAPB-PDA-COFs, we performed molecular dynamics (MD) simulations of molecule **1** within TAPB-PDA-COFs. The MD simulation results indicate that molecules of **1** are laterally attached to the

columnar pores across the interlayer of TAPB-PDA-COFs within 5 ns (Fig. 3a, Fig. S9 and Movie S1).

Among various noncovalent interactions, we found that the CH- π interactions between π -conjugated units of molecule **1** and TAPB-PDA-COFs are the main contributor that immobilize molecule **1** within TAPB-PDA-COFs. The proposed CH- π interaction is also confirmed by independent gradient model (IGM) diagram, in which favorable interaction between the highlighted fragments can be clearly seen from the green oval (Fig. 3b and Fig. S10). This result indicates that the specific CH- π interactions are of particular importance to trap molecule **1** into TAPB-PDA-COFs to produce the monomer-like optical properties of molecule **1**. The interactions between molecule **1** and TAPB-PDA-COFs are further unveiled by

Figure 3 (a) MD snapshots of 1CTAPB-PDA-COFs. The MD simulations indicate that **1** monomer attached to the walls of TAPB-PDA-COFs. (b) IGM analysis of 1CTAPB-PDA-COFs shows CH- π interaction between **1** and TAPB-PDA-COFs. (c) The fluorescence decay lifetimes for different amounts of molecules **1** from 0 to 10 wt%. (d) Lifetime quenching and k_{ET} values for different amounts of molecules **1** from 0 to 10 wt%. (e) Normalized absorption spectra of molecule **1** in chloroform (red line) and normalized fluorescence spectra of TAPB-PDA-COFs spheres. (f) Illustration of the process that 1CTAPB-PDA-COFs generates a singlet exciton, such as the antenna effect and excited-state intramolecular proton transfer.

probing the fluorescence decay kinetics of TAPB-PDA-COFs at 450 nm with different loading amounts of molecule **1** (Table S1). As shown in Fig. 3c, the bare TAPB-PDA-COFs exhibited a triple-exponential emission decay with 0.07 ns (47.6%), 1.19 ns (31.8%) and 5.17 ns (20.5%), whereas loading of molecule **1** into TAPB-PDA-COFs can remarkably accelerate the decay process. For instance, 1CTAPB-PDA-COFs (3 wt% of molecule **1**) exhibit a fast decay with averaged time constants of 0.03 ns (73.9%), 0.52 ns (12.1%) and 2.86 ns (14.0%). Fig. 3d quantitatively reveals that the fluorescence lifetime of 1CTAPB-PDA-COFs decreases upon the increase of the amount of molecule **1**, which alternatively results in the increase in the effective energy-transfer rate k_{ET} . Both nonlinear variation of fluorescence lifetime and effective energy-transfer rate k_{ET} indicate that significant exciton migration from TAPB-PDA-COFs (donor) to molecule **1** (acceptor) takes place upon light irradiation. In addition, such a progressive shortening of the emission decay time of the donor indicates a nonradiative energy transfer process and rules out the possibility of trivial radiative energy transfer (emission-reabsorption) mechanism (Fig. 3e). Such exciton migration mechanism ensures its high luminous efficiency despite the fact that molecule **1** is shielded by a layer of COFs. For AA stacked TAPB-PDA-COFs, it is reasonable that a singlet exciton hops from one layer to the other before it reaches to molecule **1**

and decays by fluorescence (Fig. 3f). In addition, the fluorescence intensity of 1CTAPB-PDA-COFs in PL spectra did not show any detectable decrease after light irradiation for 2.5 h, which reveals high photostability against photo bleaching of the composites (Fig. S11).

Encouraged by the above characterization results of highly luminous and photostable molecule **1** after being trapped in TAPB-PDA-COFs, we set out to investigate the detection sensitivity and discriminatory capability of 1CTAPB-PDA-COFs. A home-built optical chamber coupled with a fluorometer (Ocean Optics USB4000) was applied to detect various organics, such as DCP, benzene hexachloride, chlorothalonil, hydrogen chloride, diethylcyanophosphonate and common organic solvents (Fig. S12). Colloidal particles of 1CTAPB-PDA-COFs were cast into a quartz tube and were exposed to the gaseous analytes to detect the fluorescence responses. As shown in Fig. 4a, exposure of 1CTAPB-PDA-COFs to trace DCP vapors gave rise to fluorescence quenching behavior. Notably, the 1CTAPB-PDA-COFs sample exhibits ratiometric fluorescence responses with a detection limit to be as low as ~40 ppb for DCP (Fig. 4a), which is much lower than that with aggregation **1** (~320 ppb). Importantly, the fluorescence quenching response of 1CTAPB-PDA-COFs is very fast, i.e., ~1.1 s (Fig. 4b), which is promising for their practical application. Moreover, trace DCP can be detected multiple times until

Figure 4 (a) Time-dependent fluorescence quenching profile of 1CTAPB-PDA-COFs and aggregation **1** upon exposure to DCP vapors at different concentrations. (b) The response time of 1CTAPB-PDA-COFs to trace DCP vapor. (c) Fluorescence responses of 1CTAPB-PDA-COFs to various potential interferences. Error bars represent the standard deviation of five measurements. (d) Density functional theory-calculated P-Cl bond length of isolated DCP and DCP activated by COFs. (e) The schematic diagrams showing intramolecular charge transfer-excited state. (f) Schematic diagram of the fluorescence quenching of synergistic effect between fluorescent molecules and porous matrix.

a drop of fluorescence intensity to its half, despite the fact that DCP-induced fluorescence quenching responses were irreversible.

The quenching constant (KSV) of 1CTAPB-PDA-COFs to DCP is $0.5 \times 10^{10} \text{ L mol}^{-1}$ (Fig. S13). One step further, 1CTAPB-PDA-COFs also exhibits high selectivity for DCP against the potential interfering agents, as demonstrated in Fig. 4c and Fig. S14, where exposure of 1CTAPB-PDA-COFs to various volatile organic compounds produces negligible fluorescence responses in comparison with the remarkable fluorescence quenching caused by DCP vapor (0.16 ppm). The ultrasensitive and selective detection of DCP for 1CTAPB-PDA-COFs can be attributed to the synergistic effect between fluorescent molecules and porous matrix. On the one hand, given the benzothiadiazole units in molecule 1, molecule 1 can interact with DCP to form a complex by dipole-dipole interactions, resulting in the fluorescence quenching behavior. On the other hand, the imine group of TAPB-PDA-COFs can attack DCP to “activate” it, which synergistically contributes to the fluorescence quenching of molecule 1. The interaction between TAPB-PDA-COFs and DCP was verified by theoretical calculations, from which one can observe an elongated P–Cl bond in DCP/TAPB-PDA-COFs (2.18 Å) compared with that in individual DCP molecule (2.05 Å) (Fig. 4d). The “activated” DCP favors to break into $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}^+=\text{O}$ and Cl^- . The excited molecule 1, upon light irradiation, can form a complex with $(\text{CH}_3\text{CH}_2\text{O})_2\text{P}^+=\text{O}$, which gives rise to fluorescent quenching (Fig. 4e). Overall, the TAPB-PDA-COFs can accommodate and activate DCP molecules respectively by mesopores and imine bonds, which allows complexation between “activated” DCP and fluorescent molecules to take place (Fig. 4f), thereby giving rise to the irreversible fluorescent quenching behavior, as shown in Fig. 4a.

Given the promising sensing ability of the composite from integrative assembly of COFs and fluorescent molecules, we envision that the present strategy can be extended for trapping other one or multiple fluorescent molecules into COFs to broaden the application spectrum. Toward this goal, molecules 2 and 3 with emissive blue-emission and orange-emission, respectively, were designed and synthesized (Fig. 5a, Figs S15 and S16). PL spectra show that both 2CTAPB-PDA-COFs and 3CTAPB-PDA-COFs composites have non-aggregated monomer-like optical properties with an emissive peak at 430 and 540 nm, respectively (Fig. 5c). Moreover, the PL spectra of the composites can be strictly modulated by mixing molecules 2 and 3 with a desired molar ratio

Figure 5 (a) The chemical structures of molecules 2 and 3. (b) The optical microscopic images and optical images of samples by mixing different ratios of molecules 2 and 3 in TAPB-PDA-COFs under the excitation of 365 nm. (c) Solid-state fluorescence spectra of TAPB-PDA-COFs with different ratios of molecules 2 and 3 under the excitation of 385 nm. (d) The corresponding CIE chromaticity coordinates of TAPB-PDA-COFs with different ratios of molecules 2 and 3.

(denoted as (2, 3)CTAPB-PDA-COFs). The emissive colors of the composite can be tuned by simply tuning the molar ratio between molecules 2 and 3 within the TAPB-PDA-COFs, as shown by optical images under UV light and fluorescence microscopy images (Fig. 5b). Of particular interest is that, under a molar ratio of 100:1 white light emission (WLE) of (2, 3)CTAPB-PDA-COFs is achieved, as indicated by corresponding International Commission on Illumination (CIE) chromaticity coordinates (0.30, 0.29) in Fig. 5d. The above results suggest that systematic color tunability can be achieved by trapping multiple fluorescent dyes into COFs, which may offer a novel and efficient approach to producing functional molecules/COFs composites.

CONCLUSIONS

In summary, we have developed a simple, yet robust approach to encapsulate fluorescence molecules into TAPB-PDA-COFs through a two-step polymerization-crystallization strategy. The specific noncovalent CH- π

interactions between TAPB-PDA-COFs give rise to the non-aggregated optical properties of fluorescent molecules. For illustration the application of this composite, 1CTAPB-PDA-COFs shows superior sensitivity and selectivity than the aggregation 1 toward the detection of a nerve agent simulant (DCP). The merits of ultralow detection limit (40 ppb) with rapid signal response (within 1.1 s) may facilitate their practical use. Moreover, the present work may bring new inspiration to the chemosensors in terms of the exploration of ultrasensitive sensors that combine the merits of both COFs and fluorescent probes.

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Author contributions Yang Z designed and engineered the samples; Gong Y, Guo Y, Qiu C, Zhang Z, Zhang F, Wei Y and Wang S performed the experiments; Che Y, Wei J and Yang Z wrote the paper. All authors contributed to the general discussion.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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共价有机框架和荧光分子的一体化自组装对神经毒模拟物的超灵敏检测

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摘要 荧光分子通过非共价键作用载入到多孔矩阵中能够拓展其应用范围. 本文报道了利用乳液限域的方法将带有苯并噻二唑和9,9-二己基芴基团的荧光分子**1**和共价有机框架(Covalent Organic Frameworks, COFs)一体化自组装, 使得分子**1**通过CH- π 作用固定在共价有机框架的骨架之上. 因此这会极大地抑制荧光分子之间的 π - π 作用, 使其表现出荧光分子单体的光学性质. 更有意思的是, 共价有机框架和神经毒剂模拟物(DCP)的特殊的作用, 使得一体化自组装的复合物能够实现对神经毒剂模拟物高灵敏度的检测(检测限为40 ppb). 而且, 当前的一体化组装策略能够被拓展用于装载多种不同发射波长的荧光分子来实现白光. 我们的结果提供了一种利用荧光探针分子和共价有机框架综合自组装来制备高发光效率多孔材料的新方法.