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Thiadiazole-Based Covalent Triazine Framework Nanosheet for Highly Selective and Sensitive Primary Aromatic Amines Detection among Various Amines

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The primary aromatic amines (PAAs), as a class of persistent and highly toxic organic pollutants, have been posing a great threat to human health and the environment. Therefore, design and preparation of highly sensitive and selective luminescent probe to detect PAAs among various amines are important but challenging. In this work, by introducing electron-deficient monomer 4,4'-(benzo[c][1,2,5]thiadiazole-4,7-diyl)dibenzaldehyde (BTDD) with an aggregation-caused quenching behavior into the 2D framework, fluorescent ultrathin covalent triazine framework (F-CTF) nanosheet was constructed. Compared with aggregated BTDD monomer, the obtained F-CTF-3 nanosheet shows much high fluorescence quantum yield due to BTDD fragment is well dispersed in the 2D framework. The F-CTF-3 nanosheet exhibits high stability, high porosity, high fluorescence performance and has rich electron-deficient unit in the pore channel, making it ideal platform for sensing electron-rich PAAs molecules. In fact, the F-CTF-3 nanosheet shows high sensitivity and selectivity for PAAs detection by fluorescence quenching, among various amines, covering some classic aliphatic amines, heterocyclic amines, secondary aromatic amines and tertiary aromatic amines. To the best of our knowledge, it is the first reported fluorescent sensor for selective PAAs sensing from various amines. Moreover, F-CTF-3 exhibits the unprecedented low detection limit of 11.7 and 1.47 nM toward phenylamine (PA) and p-phenylenediamine (PDA), respectively, surpassing all the reported fluorescent sensors. The combination of experimental analysis and density functional theory (DFT) calculations demonstrate that the unique PAAs detection performance of the F-CTF-3 can be attributed to the static quenching process, which is confirmed by the formation of the ground-state fluorescence-quenched complex on account of the hydrogen bonding interactions between F-CTF-3 and PAAs. This work not only provides a thiadiazole-based 2D fluorescent organic framework nanosheet, but also an excellent fluorescent sensor with unexpected sensitivity and selectivity for PAAs detection.

Introduction

In recent years, amines have been widely applied to many domains including chemical, pharmaceutical, food and military industries.¹⁻³ In particular, primary aromatic amines (PAAs), such as phenylamine (PA), *p*-phenylenediamine (PDA) and 1-naphthylamine (NPA) are widely used in manufacturing dyes, rubber and agrochemicals, and exposure to PAAs is considered

to result in the damage to the respiratory system, central nervous system, cardiovascular system, and may even cause carcinogenicity.⁴⁻⁸ Meanwhile, the PAAs usually coexist with other amines in the fields of environmental and industrial monitoring, quality control of food, and medical diagnosis, thus the high selective and sensitive detection of PAAs pollutants have great significance.9-13 However, owing to the amines have the similar molecule structures, physicochemical properties, and interaction force, the selective detection of PAAs from the other amines is still a tough task. At present, numerous analytical procedures have been developed for the detection of PAAs and its derivatives, including spectrometry, chromatography, electrochemistry and fluorescent chemosensor methods.^{4,14-20} Among them, fluorescent chemosensor has great advantages due to its high sensitivity, easy operation and fast response that is capable for real-time monitoring.^{21,22} These fluorescent chemosensors are mostly based on fluorescence quenching or the active materials by interaction with analytes.^{23,24} Although many fluorescent sensors based on polymers or organic small molecules as active materials for fluorescence detection of PAAs have been

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developed, the specific sensor material can selectively detect PAAs molecules from various amines has not yet been reported.

Strategically, it is very thrilling to design and synthesize fluorescent materials for discriminative recognition of amines through interactions between an electron-deficient unit and electron-rich amines, which can perturb the photoluminescence (PL) of the sensors.^{25,26} As electrondeficient fluorescent molecules that have been widely used in various optoelectronic fields, 2,1,3-Benzothiadiazole (BT) based molecules are ideal chromophores to construct fluorescent sensors for amines detection.^{27,28} However, the BT based molecules usually belong to a series of special fluorescent small molecule probes, called aggregation-caused quenching luminogens (ACQgens), which display luminescence property at the solution state.^{1,29-32} However, the aggregated ACQgens exhibit the energy loss of excited states via nonradiative pathways, thus they cannot fluoresce at solid state, limiting the practical application of the ACQgens.^{31,33,34} Therefore, by covalently immobilized onto the material skeleton, the aggregation of ACQgens can be effectively suppressed by the synergy of the anchoring and diluting effect, thus the obtained materials can possess strong fluorescent emission.35,36

Covalent triazine frameworks (CTFs) are a kind of new multifunctional materials with the triazine ring unit, which not only have stable and adjustable porous structure, but also are convenient for the functional group and performance design.³⁷⁻⁴² In consequence, CTFs with BT unit may be a promising candidate for the detection of amines in water. Compared with the small molecule fluorescent probe, the designed fluorescent CTF materials not only can greatly enhance the fluorescence performance because of the BT units with ACQ behavior are fully dispersed in the framework of the CTF material, but also have synergistic effect for the fluorescence detection as a result of the preconcentration effect of the abundant porous structure of F-CTF.^{37,43}

According to the above discussion, herein, we proposed the strategy to construct ACQgens into 2D fluorescence CTF materials to achieve highly luminescent fluorescent porous material for the selective detection of PAAs in water. As a proof-of-concept experiment, the fluorescent covalent triazine framework (F-CTF) was synthesized by the condensation reaction between 4,4'-(benzo[c][1,2,5]thiadiazole-4,7diyl)dibenzaldehyde (BTDD) monomer with ACQ behavior and phenamidine hydrochloride (PAHC). Compared with the BTDD monomer, the F-CTF-3 exhibits much higher luminous efficiency with the quantum yield of 33.3%, indicating that the dispersed ACQgens in 2D CTF framework nanosheet can efficiently and substantially tune the electronic transition energies and raise the luminous efficacy. Based on their outstanding water stability, porosity, and high fluorescent, the detection of selected amines was explored in the F-CTF-3. Fourteen amines of nine classes (Molecular structures of the various organic amines is shown in Fig. S3, ESI +): primary aliphatic amines (ethylamine, EA; n-propylamine, PPA),



Scheme 1. Schematic of the synthesis route of F-CTF-3 via the condensation reaction of PAHB and BTDD.

aliphatic amines (dimethylamine, secondary DMA: diethylamine, DEA), tertiary aliphatic amines (trimethylamine, TMA), primary aromatic amines (phenylamine, PA; pphenylenediamine, PDA; 1-naphthylamine, NPA), secondary aromatic amines (diphenylamine, DPA), tertiary aromatic amines (triphenylamine, TPA), heterocyclic amines (5-amino-1h-tetrazol, ATZ; Amitrole, ATL), pyridine amine (4dimethylaminopyridine, DMAP) and quaternary ammonium salt (tetramethylammonium chloride, TMAC) were studied. It has been found that F-CTF-3 represents high fluorescence quenching efficiency toward PA, PDA and NPA. The limit of detection (LOD) of F-CTF-3 toward PA, PDA and NPA are estimated to be 11.7, 1.47 and 26.2 nM, respectively. Particularly, the LOD values for PA and PDA sensing are much lower than that of any other reported fluorescence sensors, including MOFs, COFs, and POPs, such as DTPP (24 nM for PA), LVMOF-1 (55 nM for PA), BCP-Py-CHO (7 nM for PDA) and DTAF (50 for PDA). To our knowledge, the F-CTF-3 is the first fluorescent sensor that can selectively detect PAAs from various amine molecules. The experimental results and density functional theory (DFT) calculations demonstrate the static quenching mechanism, the guest PAAs molecules and the host F-CTF-3 are formed the ground-state non-fluorescent complex by the hydrogen bonding, which is able to collaboratively enforce for its specific recognition and detection of PAAs molecules. Therefore, the F-CTF-3 possesses high fluorescent selectivity and sensitivity towards PAAs among various amines.

Results and discussions

Synthesis and Characterization.

PAHB and BTDD monomers were used to preparation of the 2D F-CTF-3 nanosheet with irregular hexagonal (Scheme 1). The condensation reactions were conducted under solvothermal conditions in a mixed solvent of dimethyl sulfoxide and water with cesium carbonate catalyst at 120 °C for 3 days. The detailed synthesis methods can be seen in the ESI⁺. Fourier Transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), and X-ray photoelectron spectroscopy (XPS) spectra of the acquired solid were measured to confirm the structure of the F-CTF-3. The FT-IR spectra of the F-CTF-3 show the appearance of the

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Fig. 1 (a) FT-IR spectra and (b) XPS spectra of F-CTF-3. (c) N₂ adsorption/desorption isotherms of F-CTF-3 after treated in NaOH (6M) and HCI (6M) aqueous solution, respectively, at 77 K. (d) DFT pore size distribution for the corresponding F-CTF-3 evaluated by using N₂ adsorption data measured at 77 K.

characteristic peak for C=N in triazine ring at 1503 cm⁻¹ with the concomitant disappearance of the aldehydic group (2730 cm⁻¹) stretching vibrations of BTDD and the amidogen group (3500 cm⁻¹) stretching vibrations of PAHB, thus indicating the condensation reaction occurred (Fig. 1a). In addition, the peak assigned to the triazine ring at around 168.9 ppm in the ¹³C CP-MAS NMR spectra of F-CTF-3 (Fig. S4⁺) can be observed, further verifying the formation of the triazine ring. The XPS spectrum of F-CTF-3 obviously revealed the nitrogen signal of the amidine group, thiophene ring and triazine ring at a binding energy of 398.6, 399.1 and 399.7 eV, respectively, which also demonstrate the triazine ring successful formed. (Fig. 1b) The powder X-ray diffraction (PXRD) patterns of F-CTF-3 indicate that the sample is amorphous structure (Fig. S5 +). Additionally, the theoretical structure of F-CTF-3 was built with Materials Studio modelling software and optimized with Forcite module based on Universal force field. As shown in Fig. S6⁺, F-CTF-3 possesses hexagonal geometry with P6/mmm space groups. The optimized lattice parameters for F-CTF-3 are $a = b = 34.6196 \text{ Å}, c = 3.4582 \text{ Å}; \alpha = \beta = 90, \gamma = 120$.

The porosity and specific surface area of F-CTF-3 were investigated through nitrogen adsorption/desorption isotherm measurements at 77 K. (Fig. 1c) The Brunauer-Emmett-Teller (BET) surface area and total pore volume of F-CTF-3 were calculated to be 425 m²/g and 0.44 cm³/g, respectively. The pore size distribution was calculated by using the density functional method (DFT) method resulted in a pore size of 1.8 nm (Fig. 1d). It should be noted that F-CTF-3 should possess two different pore structure in theory while only one pore size of 1.8 nm is observed by N2 adsorption data since the obtained F-CTF-3 is amorphous structure.^{39,44,45} To demonstrate the chemical durability, the F-CTF-3 samples were dispersed in different solutions, including aqueous HCl (6 M) and NaOH (6 M) solutions at room temperature for 3 days. After soaking in those harsh conditions, the treated F-CTF-3 samples were separated by filtration, and rinsed with water, THF and

acetone and then activated at 120 °C under vacuum for 24 h. Obviously, the nitrogen adsorption/desorption isotherms, the XRD patterns and FT-IR spectra of the treated F-CTF-3 retained essentially unchanged in those harsh conditions, verifying excellent chemical durability of F-CTF-3 (Fig. 1c and S7⁺). The mass loss before 200 °C at thermogravimetric (TGA) curve is observably apparent because of the solvent volatilization from the pore of F-CTF-3. Obviously, F-CTF-3 has a pore structure capable of storing these solvents, further indicating that F-CTF-3 is porous material (Fig. S8⁺). In addition, the framework of F-CTF-3 can remain until about 500 °C, demonstrating that the outstanding thermostability of the F-CTF-3 (Fig. S8⁺). The TEM image of F-CTF-3 manifests the stratified morphologies with extended porous network structure (Fig. S9 +). By carefully observing the TEM images, we can see that F-CTF-3 shows stacking of layer structures on the particle edges. To further confirm the obtained nanosheet structure of F-CTF-3, we conducted Atomic Force Microscopy (AFM) test. AFM image shows that F-CTF-3 has lamellar layers with thickness of 1.12 nm, also verifying the 2D structure of F-CTF-3 nanosheet (Fig. S9†).

Optical property of F-CTF-3.

In order to explore the luminescence effect of building ACQ molecule into 2D F-CTF-3 nanosheet, the fluorescence performance of ACQ monomer and F-CTF-3 were studied. Firstly, the fluorescence behavior of BTDD monomer in the solvent was analyzed. As shown in Fig. 2a, the fluorescence emission intensity of the BTDD monomer increases gradually by adding the THF fraction in the THF/H₂O mixture. Because of the BTDD can be completely dissolved in THF, the aggregated BTDD molecules are well dispersed and can release energy with a radiative transition, causing the fluorescence to appear and increase.³⁰ The solid state photoluminescence (PL) showed that the BTDD monomer exhibits fluorescence emission at 505 nm upon excitations at 374 nm while intense emission bands can be observed at 523 nm (λ_{ex} = 416 nm) for F-CTF-3. (Fig. S10 †) The absolute quantum yield of the BTDD and F-CTF-3 are 8.32% and 33.6% upon excitation at 374 and 416 nm, respectively (Fig. 2b). Interestingly, the quantum yield of BTDD monomer was improved about four times by constructing this ACQgens into 2D F-CTF-3 nanosheet. Fig. 2c shows timeresolved PL lifetime measurements, which reveals that the lifetimes of BTDD monomer and F-CTF-3 are 2.44 and 1.67 ns. respectively. Combined with the lifetime and quantum yield data, the radiative rate constant of BTDD and F-CTF-3 are calculated to be 3.41×10^7 s⁻¹ and 2.02×10^8 s⁻¹, respectively, indicating that the radiative rate constant of F-CTF-3 has more than 1 order of magnitude than that of the BTDD monomer. These results demonstrate that the orderly construction of ACQgens molecule (BTDD) into 2D F-CTF-3 nanosheet can greatly increase its luminescence performance. We noticed that, owing to the rigidity effect, building aggregation-induced emission (AIE) molecules into 2D or 3D skeletons can observably enhance their luminescence performance.31,33 Interestingly, because of ACQgens molecules are highly dispersed in the skeleton of F-CTF-3 by the synergy of the



Fig. 2 (a) Fluorescence emission spectra of BTDD monomer with varying fraction of tetrahydrofuran (THF)/water mixtures. (b) Fluorescence quantum yield and (c) transient fluorescence spectrum of the BTDD and the F-CTF-3.

anchoring and diluting effect, this work shows that the building ACQgens into 2D CTF ultrathin nanosheets can also greatly improve the luminescence performance. Moreover, F-CTF-3 is readily dispersed in water and other organic solvents, making it promising candidate for the pollutant detection in water (Fig. S11 ⁺). Fig. S12 ⁺ exhibits that F-CTF-3 still maintains its fluorescence emission intensity for twenty cycles tests in water system, implying that F-CTF-3 possesses the stable fluorescence properties.

PAAs detection and selectivity.

Considering the outstanding luminescence properties and high porosity, F-CTF-3 may be able to act as potential fluorescent sensors for detecting amines. Herein, fourteen kinds of commonly-used amines, primary aliphatic amines (EA and PPA), secondary aliphatic amines (DMA and DEA), tertiary aliphatic amines (TMA), primary aromatic amines (PA, PDA and NPA), secondary aromatic amines (DPA), tertiary aromatic amines (TPA), heterocyclic amines (ATZ and ATL), pyridine amine (DMAP) and quaternary ammonium salt (TMAC) were selected. In order to examine the detection ability of F-CTF-3 towards micro-quantity of amines in aqueous solution, fluorescence-quenching titrimetries were adopted by gradually adding quantitative amines solution into the dispersed F-CTF-3 suspensions. As shown in Fig. 3a-d and S13-17⁺, the emission intensity decreased monotonically and drastically when the PAAs concentration increased, while the other non-PAAs scarcely show this tendency. Fig. S18 + exhibits that PAAs, including PA, PDA and NPA, possess the highest quenching efficiencies of 96.36, 99.53 and 92.17 % for F-CTF-3 while non-PAAs showed very weak quenching efficiencies. To the best of our knowledge, the F-CTF-3 is the first fluorescent sensor that can distinguish PAAs from various amines solution in water system. The fluorescent quenching efficiency can be quantitatively explained by the Stern-Volmer (SV) equation: $(I_0/I) = 1 + K_{sv}$ [Q], where K_{sv} is the quenching constant (M⁻¹), [Q] is the molar concentration of the analyte, Io and I are the luminescence intensities before and after addition of the analyte, respectively. As indicated in Fig. 3a-e and S13–17⁺, F-CTF-3 has the high K_{sv}



Fig. 3. The emission spectra of F-CTF-3 dispersed in water upon incremental addition of four representative amines (a. PA, b. DEA, c. DPA and d. ATZ) (3 μ M, 20 μ L addition each time; inset: SV plots of selected amines). (e) Stern-Volmer plots of 14 various amines in F-CTF-3. (f) Selective detection of PA on F-CTF-3 the presence of the other non-PAAs in water. (g) Regeneration of the F-CTF-3 for PA quenching in water (The black bars represent the initial fluorescence intensity and the red bars represent the intensity upon addition 30 μ M PA solution).



Fig. 4. (a) Spectral overlap between normalized absorption spectra of organic amines and the normalized excitation spectra of F-CTF-3 in water. (b) The bimolecular quenching constant (K_a) of F-CTF-3 for PAAs detection. (c) ¹H-NMR (CDCl₃) spectra of PA, PA@BTDD and BTDD. (d) FT-IR spectra of F-CTF-3 and PA@F-CTF-3. XPS spectra of (e) N_{1s} and (f) S_{2p} in F-CTF-3 and PA@F-CTF-3.

values of 6.36×10^6 M⁻¹ toward PDA, 8.01×10^5 M⁻¹ toward PA, and 3.57×10^5 M⁻¹ toward NPA, respectively (Table S1⁺). The LOD values of F-CTF-3 toward PA, PDA and NPA are calculated to be 11.7, 1.47 and 26.2 nM, respectively. As shown in Table S2 and S3⁺, we have listed all the reported fluorescence sensors towards PA and PDA sensing. Surprisedly, the F-CTF-3 exhibits record low LOD values for PA and PDA sensing among reported fluorescence sensors, including MOFs, COFs, and POPs, such as DTPP (24 nM, PA), LVMOF-1 (55 nM, PA), BCP-Py-CHO (7 nM, PDA) and DTAF (50 nM, PDA). (Table S2 and S3⁺).⁴⁶⁻⁴⁹ The results demonstrate the extremely high sensing sensitivity of F-CTF-3 towards PAAs.

The selectivity of F-CTF-3 toward the PAAs detection was then investigated by testing the fluorescence change in the presence of other amines. Therefore, the competition experiments were conducted by alternate addition of PAAs solutions (3 μ M, 20 μ L) and the competitive non-PAAs solutions (Saturation concentration, 20 μ L). As shown in Fig. 3f and S19-31⁺, neither of the competitive non-PAAs showed an appreciable influence on the PAAs detection. These results further confirm that F-CTF-3 exhibits a satisfactory selectivity toward PAAs detection.

In addition, we explored the sensing ability of regenerated F-CTF-3 toward PAAs. It is found that the quenching efficiencies of generated F-CTF-3 toward PAAs are basically unchanged up to five cycles, indicating its excellent recyclability and stability for the sensing application (Fig. 3g and S32⁺). **Mechanism for probing PAAs.**

To better understand the fluorescence-quenching effect of F-CTF-3 toward PAAs, the guenching mechanism was proposed. Normally, the quenching on fluorescent sensor by organic molecules are mainly explained the follow three mechanisms: fluorescence resonance energy transfer (FRET), photoinduced electron transfer (PET), and dynamic/static quenching mechanism.³⁰⁻³³ FRET occurs only when the absorption spectrum of the analyte overlaps with the emission spectrum of the sensor. As shown in Fig. 4a, we can see that the absorption band of PAAs, DPA, DMAP and TPA are completely covered the excitation band of F-CTF-3, which means the existence of energy transfer from the F-CTF-3 to the PAAs, DPA, DMAP and TPA. Furthermore, to explore the PET process between F-CTF-3 and analytes, we calculated the orbital energies of the lowest unoccupied molecular orbitals (LUMOs) and highest occupied molecular orbitals (HOMOs) of amines and F-CTF-3 by DFT calculations using Gaussian 09

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Fig. 5. (a) Schematic representation of the mechanism for the selective fluorescence response of F-CTF-3 to PA. (b) The optimized geometric structure of the excited-state PA@F-CTF-3. Selected fragments highlighting the hydrogen bonding interactions in PA@F-CTF-3 (Color code: H, white; C, gray; N, blue; and S, yellow).

software. As shown in Fig. S33 and Table S4⁺, the LUMO levels of these amines and F-CTF-3 are arranged in descending order, and we can foresee how easily an electron can be transferred to an electron-deficient assay during fluorescence quenching. The LUMO orbital energy levels of the amines are higher than that of F-CTF-3, indicating that the electron transfer from excited F-CTF-3 to the amine molecules is thermodynamically forbidden. Therefore, the FRET and PET mechanism is insufficient to elucidate the mechanism of quenching F-CTF-3 by PAAs.

To further explore the quenching mechanism of F-CTF-3 toward PAAs, we analyzed the possibility of dynamic/static quenching mechanism. Both two types of quenching process need contact between the fluorophore and the analyte. Dynamic quenching process occurs when there is a collision between the guest analyte and the fluorophore in the fluorescent host. Static quenching holds ground-state non-fluorescent complex formation between the fluorophore and the analyte. To investigate the quenching process of F-CTF-3, we can calculate the rate constant in the process of double molecules quenching (K_q value) by Stern-Volmer equation based on the K_{sv} value and the average lifetime data. As shown in Fig. 4b and Table S5⁺, the k_q values of F-CTF-3 for

PA, PDA and NPA detection is 4.80×10¹⁴, 3.81×10¹⁵ and 2.14× 10¹⁴ mol/s, respectively. Owing to the dynamic quenching usually depend on the collision, the maximum of its K_a value is not more than the classic intermolecular collision frequency of 2.0 \times 10¹⁰ mol/s, thus demonstrating that the static quenching mechanism is followed for the analyte detection of F-CTF-3. To further confirm the static quenching process, we examined the relationship between K_{sv} values and temperature. For dynamic quenching, owing to the increment temperature is beneficial to the molecule collision in dynamic quenching process, thus the K_{sv} value of the sensor will be increased. On the contrary, for static quenching, the rising temperature is not conducive to the stability of the ground-state non-fluorescent complex, thus the value of K_{sv} is reduced for the complex. Fig. S34 and Table S5⁺ exhibit that the K_{sv} values at 0 $\,\,^\circ\text{C}$ of F-CTF-3 (1.82×10⁶, PA; 2.62×10^7 , PDA; 8.33×10^5 , NPA) is much larger than the values at 25 °C (8.01×10⁵, PA; 6.36×10⁶, PDA; 3.57×10⁵, NPA) of F-CTF-3, further proving that the quenching process is static quenching one.

According to the above discussion, the static quenching mechanism for PAAs sensing in F-CTF-3 is caused by formation of the ground-state non-fluorescent complex between the host F-CTF-3 and the guest analyte. Therefore, in order to deeply understand the formation of ground-state non-fluorescent complex, we investigated the binding abilities of the analyte with the F-CTF-3 by evaluating the binding constant (K_b) and the corresponding stoichiometry (n). As shown in Fig. S35 and Table S6⁺, the binding abilities (K_b) of the different analytes to the F-CTF-3 decrease in the following order: PDA>PA>NPA>DPA>DMAC>TPA. Besides, it should be noticed that the Kb values of the PAAs are much larger than that of DPA, DMAC and TPA and the huge difference is beneficial to distinguish and detect for these analytes. Meanwhile, it is observed the stoichiometry (n) of the binding interactions varied as the analytes and multiple binding sites are active for PAAs, which resulted in strong and stable binding with the F-CTF-3 in the ground-state nonfluorescent complex. In contrast, for the DPA, DMAC and TPA, there are only a few binding sites between F-CTF-3 and the analytes and thus only the unstable complex can form.

Motivated by these findings, the formation of ground-state non-fluorescent complex was investigated by taking PA sensing in F-CTF-3 as an example. The PA-treated F-CTF-3 (PA@F-CTF-3) was tested by ¹H-NMR, FTIR and XPS spectra. Firstly, to investigate the role of BTDD units in F-CTF-3 on the PA detection, the interactions between BTDD and PA were analyzed by ¹H-NMR spectra. The comparison of ¹H-NMR spectra of PA, BTDD and PA@BTDD in CDCl₃-d₁ reveals that the chemical shift of hydrogen in the -NH₂ group shifted observably from 3.57 ppm in PA to 3.63 ppm in PA@BTDD (Fig. 4c and S36⁺). In addition, the chemical shift of hydrogen in the benzene ring of PA also changed.⁵⁰ In FT-IR spectra, the peak at 3550 cm⁻¹ of PA@F-CTF-3 indicates the PA is adsorbed in F-CTF-3. (Fig. 4d). Moreover, the interactions between PA and F-CTF-3 can be confirmed by FT-IR spectra analysis. For instance, the C=N bonds in thiadiazole ring of F-

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CTF-3 at 1420 cm⁻¹ shifted to 1416 cm⁻¹, while the N-S bonds of the thiadiazole ring shifted from 842 cm⁻¹ to 839 cm^{-1,51} For XPS spectra in Fig. 4e, it can be seen that the N_{1s} peaks of the thiadiazole ring and triazine ring in F-CTF-3 and PA@F-CTF-3 are shifted from 400.3 and 398.8 eV to 400.0 and 398.3 eV, respectively. The S_{2p} peak of BTDD in F-CTF-3 obviously shifts from 166.8 and 165.6 eV to 166.0 and 165.2 eV after PA adsorption. (Fig. 4f) All those shifts suggest the strong interactions between -NH₂ group in PA and thiadiazole ring in F-CTF-3, as illuminated in the Fig. 5a.

To further confirm the formation of non-fluorescent complex induced by the hydrogen bonding between the F-CTF-3 and PA, we calculated the interactions of PA and F-CTF-3 in the excited-state complex by using time-dependent density functional theory (TDDFT) with CAM-B3LYP functional and 6-31G(d,p) basis set. As shown in Fig. 5b, the distance between H atoms of -NH₂ in PA and the N atoms of the thiadiazol ring in F-CTF-3 is 2.176 Å, which is within the range of classic hydrogen bond length, indicating that F-CTF-3 has the hydrogen bond interaction with PA in the excited-state PA@F-CTF-3 complex. Moreover, Fig. 5b shows that the binding energy between PA and F-CTF-3 in the excited-state complex is -211.44 kJ/mol, further suggesting that F-CTF-3 possesses the strong interaction with PA in the nonfluorescent complex. Therefore, the strong interactions between PA and F-CTF-3 can be attributed to the formation of the non-fluorescent complex induced by the hydrogen bond interactions between PA and F-CTF-3.

In order to elucidate the difference of quenching efficiency between PAAs and aliphatic amines, DFT calculations were performed to access optimized geometries for the interactions of F-CTF-3 with PAAs and aliphatic amines, respectively. As shown in Fig. S37-S40⁺, the binding energies of F-CTF-3 toward PAAs molecules (-60.21 KJ/mol, PA; -83.62 KJ/mol, PDA; -92.54 KJ/mol, NPA) are larger than those of aliphatic amines molecules (-44.47 KJ/mol, EA; -48.82 KJ/mol, PPA; -47.46 KJ/mol, DMA; -50.49 KJ/mol, DEA; -48.34 KJ/mol, TMA; -56.16 KJ/mol, TMAC), suggesting much stronger interactions between F-CTF-3 with PAAs. The larger binding energies indicate that PAAs could more easily form the ground state non-fluorescent complex structure with F-CTF-3, which is the precondition for the fluorescence detection of PAAs in F-CTF-3.

Besides, the fluorescence detection experiments show that the fluorescence quenching efficiency of PDA molecules with two amino groups is higher than that of PA and NPA with only simple amino group, implying that the multiple amino groups in PAAs molecules are beneficial to guench the fluorescence of F-CTF-3. In order to verify the conjecture, we investigated the detection ability of F-CTF-3 towards 1.3.5triaminobenzene (TAB) molecules. Since 1,3,5triaminobenzene trihydrochloride was used in this work, TAB solution was neutralized before the fluorescence quenching experiment. As shown in Fig. S41 and Table S7⁺, the K_{sv} and LOD values of F-CTF-3 toward TAB are 2.13×10⁴ M⁻¹ and 440 nM, respectively, and the fluorescence detection ability of F-CTF-3 toward TAB is observably lower than that of PA in this

condition. It should be noticed that the TAB molecule is relatively stable in hydrochloride state. However, it will immediately deteriorate in the neutral or basic solution, thus resulting in poor detection performances of F-CTF-3 toward TAB. In fact, the distinct colour change of TAB solution was also observed in the neutralization process. To compare the real quenching ability of TAB and PA for F-CTF-3, the fluorescence detection experiments were performed in aqueous solution of pH=1. As shown in Fig. S42 +, the fluorescence detection performance of F-CTF-3 toward TAB is observably higher than that of PA in pH=1 aqueous solution, proving that more amino groups of PAAs are conductive to the fluorescence detection of F-CTF-3 in the same conditions. More significantly, although F-CTF-3 shows excellent fluorescence detection abilities towards PA under the nearly neutral conditions, only weak fluorescence-quenching effect was observed in acid aqueous solution of pH=1, further confirming that the hydrogen bond interactions between PA molecules and F-CTF-3 plays a key role in fluorescence detection process. Owing to the presence of a large number of H⁺ disrupts the hydrogen bond interactions between PA and F-CTF-3 in the acid solution, the formation of stable ground state non-fluorescent complex between F-CTF-3 and PA will be unfavourable, thus significantly suppressing the fluorescence detection of F-CTF-3 toward PA.

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To explain the difference of the fluorescence detection toward PA and NPA, the adsorption kinetics of PA and NPA were studied. As shown in Fig. S43⁺, the adsorption of F-CTF-3 toward PA reaches equilibrium within 2 mins, while that of F-CTF-3 toward NPA still does not reach equilibrium even in 30 mins, indicating that F-CTF-3 has higher adsorption rate for PA because of the molecular dimension of PA is smaller than that of NPA. To further verify this conclusion, the adsorption kinetics data was fitted with pseudo-first-order kinetic model and pseudo-second-order kinetic model. Remarkably, as shown in Fig. S44 and Table S8⁺, the pseudosecond-order kinetic model is more precise, and the derived kinetic rate constant k_2 of F-CTF-3 toward PA is 34.53 g mM⁻¹ min⁻¹, which is 2 orders of magnitude higher than that of F-CTF-3 toward NPA. Owing to the faster adsorption rate and adsorption induced preconcentration effect, 37,43 the fluorescence detection ability of F-CTF-3 toward PA is higher than that of NPA.

The binding energy and the equilibrium absorption capacity of NPA in F-CTF-3 are higher than that of PA since the larger molecule usually possesses higher affinity for its stronger van der Waals interactions with adsorbent.⁵²⁻⁵⁴ However, in comparison with PA, the larger molecule size of NPA results into the slower diffusion rate of NPA to access to the pore of F-CTF-3, as confirmed by the above adsorption kinetic data. Therefore, although F-CTF-3 has the larger binding energy and equilibrium absorption capacity towards NPA, the detection ability of F-CTF-3 toward PA is higher than that of NPA because of the slower adsorption rate of NPA. To verify this conclusion, the time-depended fluorescence detection of F-CTF-3 toward PA and NPA were performed. As shown in Fig. S45⁺, the detection of F-CTF-3 toward PA reaches quenching

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equilibrium within 1 min, while 10 min are needed to reach quenching equilibrium for NPA in F-CTF-3, indicating that F-CTF-3 has faster response for PA detection. These results are in line with the adsorption kinetic data in Fig. S43, S44 and Table S8 + . It should be noticed that even at 20 mins of contacting time between the F-CTF-3 and two amines, the quenching ability of NPA is still inferior to that of PA, as shown in Fig. S46⁺. This inconformity may be attributed to fluorescence emission overlap of NPA with F-CTF-3. To confirm this conclusion, the emission spectra of PA, NPA and F-CTF-3 were tested in water system at the excitation wavelength of 372 nm. Fig. S47⁺ shows that the fluorescence emission spectra of NPA and F-CTF-3 has overlapping parts, while that of PA and F-CTF-3 does not. The result indicates that NPA has the fluorescence compensation effect for the quenched F-CTF-3. Based on these findings, the low detection rate and K_{sv} values of F-CTF-3 toward NPA than that of PA can be attributed to the slower diffusion rate of NPA and its fluorescence compensation effect.

In addition, to further evaluate the molecular size screening effect of F-CTF-3 toward PAAs, four PAAs with incremental molecular sizes (PA, NPA, Amino anthracene (AAT) and 4amino-P-triphenyl (APT)) were selected. Since APT and AAT are insoluble in water, the selected amines for fluorescence quenching experiments were measured in DMF system. As shown in Fig. S48⁺, it can be preliminarily found that the detection performances of the PAAs analytes with different molecule size in F-CTF-3 decrease in the following order: PA>NPA>AAT>APT. Furthermore, the SV equation and K_{sv} value were utilized to further quantify the quenching ability. As illustrated in Fig. S49 and Table S9⁺, the K_{sv} values of F-CTF-3 toward PA, NPA, AAT and APT are 2.69×10⁴, 1.74×10⁴, 4.22×10^3 and 4.13×10^3 M⁻¹, respectively, in which the K_{sv} value of F-CTF-3 toward PA with smallest molecule is 1 order of magnitude higher than that of F-CTF-3 toward APT with largest molecule. Therefore, the results indicate that F-CTF-3 has an obvious screening effect on the PAAs analytes with different molecule size.

It should be noticed that the Eddaoudi group developed a luminescent Zr(IV)-based MOF (Zr-BTDB-fcu-MOF) in which the thiadiazole unit can freely rotate in the 3D framework. ¹¹ This MOE exhibits excellent turn-on fluorescent detection of aliphatic amines on account of the restricted rotation of the thiadiazole core in the 3D framework, reducing nonradiative recombination pathways and subsequently enhancing emission intensity. In stark contrast, the rotation of the thiadiazole ring in F-CTF-3 is limited because of the thiadiazole units are dense stacking in the 2D framework, thus the detection mechanism of F-CTF-3 toward amines is quite different from that of Zr-BTDB-fcu-MOF. The turn-off model of F-CTF-3 toward PAAs detection is attributed to the static quenching process, which derived from the formation of the ground state non-fluorescent complex induced by the hydrogen bonds interactions between PAAs and thiadiazole ring of F-CTF-3. In addition, although some nonporous polymers containing thiadiazole units were also reported for PAAs detection, their performances are inferior than that of F-CTF-3,^{3,23,24,55} suggesting that adsorption induced preconcentration effect is also beneficial to the PAAs detection.

Conclusions

In summary, by constructing the BTDD monomer with ACQ effect into the framework of 2D ultrathin covalent triazine framework nanosheet, the thiadiazole-based F-CTF-3 with irregular hexagonal pore structure was synthesized. Owing to the synergy of the anchoring and diluting effect, F-CTF-3 possesses the much higher fluorescence quantum yield and radiative rate constant than those of the BTDD monomer. Interestingly, the F-CTF-3 is the first fluorescent probe that exhibits excellent selectivity and sensitivity for PAAs sensing among various amine molecules in water system. Moreover, the LOD values of F-CTF-3 for PA and PDA are estimated to be 11.7 and 1.47 nM, respectively, which are much lower than any reported sensing materials. Experimental analysis and DFT calculations demonstrated that the highly selective and sensitive PAAs detection in F-CTF-3 can be ascribed to the static quenching process, which derived from the formation of the ground state non-fluorescent complex induced by the hydrogen bonds interactions between PAAs and F-CTF-3. Given its outstanding sensitive and selective for PAAs detection as well as the high thermal and chemical stability, F-CTF-3 has great prospects as a fluorescent sensor for practical applications.

Conflicts of interest

The authors declare no competing financial interest.

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The thiadiazole-based covalent triazine framework nanosheet is the first fluorescent sensor that can selectively detect PAAs from various amines.