

Exploring fluorescent covalent organic frameworks for selective sensing of Fe³⁺

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Covalent organic frameworks (COFs) have been widely applied in gas capture and separation, but the fluorescent property of COFs with large π -conjugated system tends to be underexplored. Here we report the fluorescent properties of several COFs including TaTa, DhaTab, TRITER-1 and TzDa and the effect of metal ions of Na⁺, Mg²⁺, K⁺, Ca²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺, Cd²⁺ and Fe³⁺ on the fluorescence of these COFs. The results show that only Fe³⁺ significantly quenched the fluorescence of the studied COFs. The possibility of the four COFs for selective sensing of Fe³⁺ was demonstrated. The possible mechanism of the effect of Fe³⁺ on the fluorescence of the COFs was based on the absorption competition quenching.

fluorescence, covalent organic frameworks, iron ion, fluorescent probe

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1 Introduction

Covalent organic frameworks (COFs) with strong covalent bonds are an intriguing crystalline porous materials constructed by the ordered consecutive condensation of organic molecules [1,2]. The unique structures and properties make COFs promising applications in diverse fields such as gas capture and separation [3], catalysis [4], and chromatography [5–8]. However, the intrinsic luminescent property of crystalline COFs with large π - π framework tends to be underexplored.

To date, few luminescent crystalline COFs have been used to detect explosives and metal ions [9]. Dalapati *et al.* [10] demonstrated the potential of Py-Azine COF for selective fluorescent detecting of 2,4,6-trinitrophenol explosive in acetonitrile. Lin *et al.* [11] reported 3D-Py-COF COF for

luminescent sensing of picric acid in dimethyl formamide. Zhang *et al.* [12] utilized PI-COF as a luminescent probe for 2,4,6-trinitrophenol in ethanol. Ding *et al.* [13] synthesized sulfoether functionalized COF-LZU8 for fluorescent detecting of Hg²⁺ in acetonitrile. Li *et al.* [14] employed COF-JLU3 for fluorescent sensing Cu²⁺ in the tetrahydrofuran and water (9:1, *V/V*). Wang *et al.* [15] showed PI-COF 201 and PI-COF 202 had the rapid and selective sensing of Fe³⁺ in dimethyl formamide and acetonitrile, respectively. The investigation of luminescent property and luminescent COFs in the potential of sensing is of great significance for promoting their wide applications in analytical chemistry.

Herein, we reported the fluorescent properties of several COFs and their potential for fluorescent sensing of Fe³⁺. 1,3,5-tri-(4-aminophenyl) benzene (TaPb), terephthalaldehyde (TpTa), 1,3,5-tri-(4-aminophenyl) triazine (Tz) and 2,5-dihydroxyterephthalaldehyde (Da) were used to obtain the four COFs (TaTa, DhaTab, TRITER-1 and TzDa) via solvother-

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mal condition [16–19]. The four COFs had large surface area, good solvent and thermal stability and strong fluorescent emission. The effect of metal ions (Na^+ , Mg^{2+} , K^+ , Ca^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Ag^+ , Cd^{2+} and Fe^{3+}) on the luminescence of these COFs were studied, and the potential of these COFs for selective sensing of Fe^{3+} was demonstrated.

2 Experimental

2.1 Reagents and chemicals

1,3,5-Tri-(4-aminophenyl) benzene (TaPb), terephthalaldehyde (TpTa), 1,3,5-tri-(4-aminophenyl) triazine (Tz) and 2,5-dihydroxyterephthalaldehyde (Da) were obtained from Tongchuangyuan Pharmaceutical Technology Co. (China). *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF), ethanol (EtOH), acetic acid, sodium nitrate (NaNO_3), potassium chloride (KCl), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), *n*-butanol (*n*-BuOH), aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and ferric nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) were bought from Sinopharm Chemical Reagent Co. (China). Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), cadmium nitrate tetrahydrate ($\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and *o*-dichlorobenzene (*o*-DCB) were provided by Aladdin Chemistry Co. (China). Silver nitrate (AgNO_3) was given by Shanghai Chemical Reagent Co. (China). Ultrapure water was purchased from Wahaha Foods Co. (China). All chemicals and reagents used were at least of analytical grade.

2.2 Instrumentation

All fluorescence data were recorded on an F-7000 spectrofluorometer (Hitachi, Japan). The absorption spectra were recorded with a UV-3600 Plus spectrophotometer (Shimadzu, Japan). Powder X-ray diffraction spectrometry (PXRD) patterns were measured on a D2 Phaser diffractometer (Bruker AXS, Germany) using $\text{Cu K}\alpha$ radiation. Fourier transform infrared spectroscopy (FTIR) spectra were obtained on an IS10 spectrometer (Nicolet, USA). Thermo Gravimetric Analyzer (TGA, USA) data were acquired on a TG8121 thermal gravimetric analyzer (Rigaku, Japan). Scanning electron microscopy (SEM) images were performed on a Su1510 (Hitachi, Japan) instrument. Transmission electron microscope (TEM) images were carried out on a JEM-2100 transmission electron microscope (Hitachi, Japan). N_2 adsorption experiments were performed on a NOVA 2000e analyzer (Quantachrome, USA).

2.3 Synthesis of COFs TaTa, DhaTab, TRITER-1 and TzDa

TaPb (0.160 mmol, 56.2 mg) and TpTa (0.240 mmol,

32.2 mg) in the presence of acetic-acid (6 M, 0.6 mL) were mixed in *o*-DCB/*n*-BuOH (3/3 mL) under ultrasonication for 5 min. Then, acetic acid (6 M, 0.6 mL) was added into the mixed solution in the Teflon-lined autoclave (25 mL). The autoclave was sealed and heated at 120 °C for three days. The precipitate was refluxed with THF and EtOH in turn to remove the trapped molecules. The prepared TaTa powder was collected by centrifugation and dried under vacuum overnight. The DhaTab, TRITER-1 and TzDa were obtained in the same way as the TaTa by using their corresponding ligands instead of TaPb and TpTa.

2.4 Effect of metal ions on the fluorescence of the COFs

The synthesized COFs (TaTa, DhaTab, TRITER-1 and TzDa) (1.0 mg) were dispersed in DMF (10 mL). The aqueous solution of each individual metal ion (100 μL , 10 mM) was added into the COF DMF dispersion. The fluorescent spectra were obtained on an F-7000 fluorescence spectrophotometer (PMT voltage: 700 V; scan speed: 2400 nm/min; excitation slit: 5 nm; emission slit: 5 nm) within 1 min. 1.0 cm Quartz cell was used in all the fluorescent experiments.

3 Results and discussion

3.1 Preparation and characterization of TaTa, DhaTab, TRITER-1 and TzDa

The COF TaTa, DhaTab, TRITER-1 and TzDa were obtained under solvothermal conditions via Schiff base condensation catalyzed with acetic acid (Figure 1). The solvent was important for the synthesis of the COFs. A mixture *o*-DCB/*n*-BuOH (3/3 mL) was used to prepare the COFs with high surface area and crystallinity. Significantly, the TaTa with high crystallinity was firstly synthesized, though the structure of TaTa (A-B1) without crystal form was reported [16] (Figure 2(a)). The high intense peak at 2.9° and minor peaks at 4.9°, 5.8° and 7.5° of the PXRD patterns (Figure 2(a)) are consistent with the planes 100, 110, 200, and 120 reflection in the COF structures, respectively [17–19]. The PXRD patterns of the as-prepared TaTa, DhaTab, TRITER-1 and TzDa are in good agreement with those reported in literatures [16–19], indicating the successful synthesis of the COFs.

Though the obtained COFs possessed similar skeleton, the DhaTab and TzDa had higher degree of crystallinity than the TaTa and TRITER-1, respectively. It was proved that hydrogen bonding was critically important in the preparation of high crystallinity COFs [17,19]. The appearance of the C=N stretching vibration peak at 1660 cm^{-1} in the FTIR spectrum (Figure 2(b)) of the COF TaTa, DhaTab, TRITER-1 and TzDa further confirms the successful formation of the four

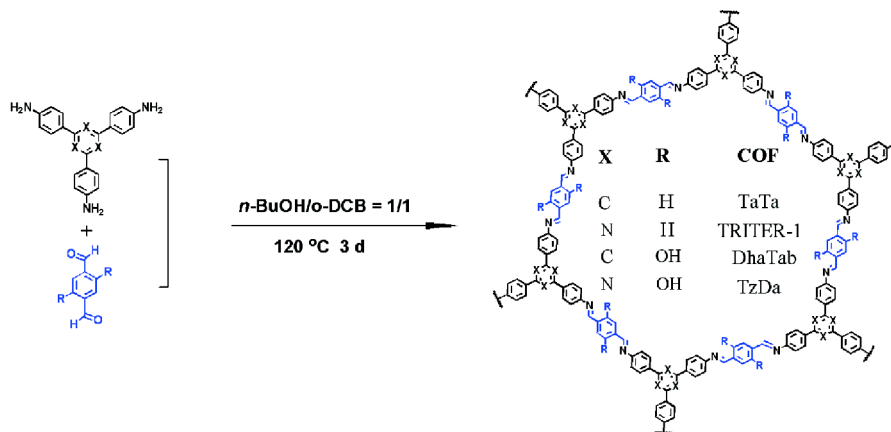


Figure 1 Synthesis routes for TaTa, DhaTab, TRITER-1 and TzDa (color online).

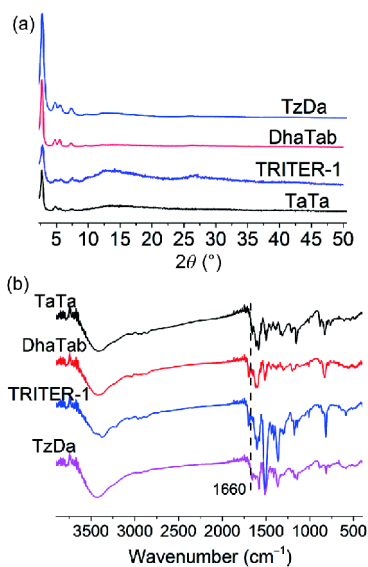


Figure 2 (a) PXRD patterns and (b) FTIR spectra of TaTa, DhaTab, TRITER-1, TzDa (color online).

COFs via the Schiff base reaction. TGA curves of the four COFs show no remarkable weight loss up to 400 °C, indicating their excellent thermal stability (Figure S1, Supporting Information online).

Both SEM and TEM were used to characterize the morphology of the as-prepared TaTa, DhaTab, TRITER-1 and TzDa (Figure S2). The TaTa, DhaTab and TRITER-1 were globular, but TzDa was fluffy clusterlike. The permanent porosity and Brunauer-Emmett-Teller (BET) surface areas of the four COFs were characterized via the N₂ adsorption-desorption analysis. The BET surface area of the as-prepared TaTa, DhaTab, TRITER-1 and TzDa (Figures S3–S6) were 605, 750, 497 and 703 m² g⁻¹, respectively. The DhaTab and TzDa had larger BET surface area than the TaTa and TRITER-1 respectively, due to the high crystallinity of the COF DhaTab and TzDa with the hydrogen-bond interaction. The mesoporous size of prepared four COFs was about 40 Å

(Figures S3–S6), in good consistent with that published [16–19].

3.2 Fluorescent property of TaTa, DhaTab, TRITER-1 and TzDa

The as-prepared COFs (TaTa, DhaTab, TRITER-1 and TzDa) are stable in DMF and water due to no significant change in the PXRD patterns (Figure S7) and the fluorescence intensity (Figure S8). The fluorescent excitation and emission spectra of TaTa, DhaTab, TRITER-1 and TzDa in the DMF/H₂O (9:1, *V/V*) are shown in Figure 3. The luminescent property of TaTa and DhaTab is similar to TRITER-1 and TzDa, respectively. TaTa and DhaTab show the emission peak of 473 and 445 nm, respectively, upon excitation at 310 nm. The emission peaks of TRITER-1 and TzDa are respectively located at 555 and 583 nm under excitation at 365 nm. The replacement of benzene ring with triazine ring from TaTa to TRITER-1 leads to a red-shift in the excitation peaks because the triazine ring enhances the conjugation of the COF system and further reduces the excitation energy of the TRITER-1 [20–22]. This is also the reason for the red-shift in the excitation peaks from DhaTab to TzDa. The fluorescent emission peaks show a slight red-shift from TRITER-1 to TzDa upon the same excitation wavelength because of intramolecular charge transfer (ICT) from phenyl group (donor) to the triazine ring (acceptor) [19,23]. The larger electronegativity of N than C results in the blue-shift of DhaTab emission peaks in comparison with TaTa.

3.3 Effect of metal ions on the fluorescence of TaTa, DhaTab, TRITER-1 and TzDa

Figure 4 shows the effect of metal ions on the fluorescence of TaTa, DhaTab, TRITER-1 and TzDa. Na⁺, Mg²⁺, K⁺, Ca²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺ and Cd²⁺ had no obvious influence on the fluorescence of the four COFs. Al³⁺ slightly enhanced the

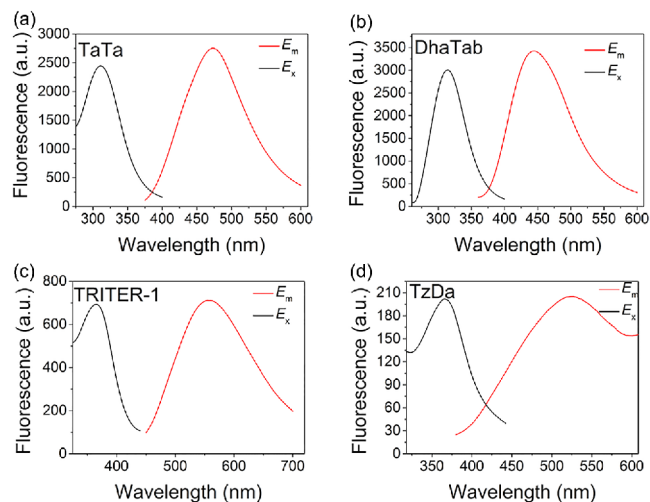


Figure 3 Excitation and fluorescence spectra. (a) TaTa; (b) DhaTab; (c) TRITER-1; (d) TzDa in the DMF/H₂O (9:1, *V/V*) (color online).

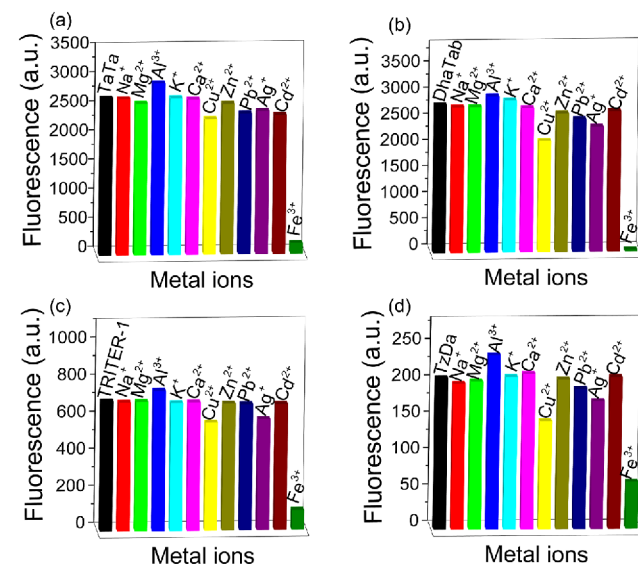


Figure 4 Effect of metal ions (1.0 mM each) on the fluorescence of the COFs. (a) TaTa, (b) DhaTab, (c) TRITER-1 and (d) TzDa in the DMF/H₂O (9:1, *V/V*) (color online).

fluorescence of the four COFs. Interestingly, only Fe³⁺ obviously quenched the fluorescence of the four COFs.

To further study the effect of Fe³⁺, the values of the quenching coefficient (K_{SV}) of Fe³⁺ on the fluorescence of the COFs were evaluated based on the Stern-Volmer equation [24]: $I_0/I = 1 + K_{SV} M$ (where I and I_0 are the fluorescent intensities of the COF in the presence and absence of metal ions, respectively; M is the concentration of metal ions) (Table 1). The K_{SV} values for TaTa, DhaTab, TRITER-1 and TzDa were 1.4×10^4 , 1.0×10^5 , 5.6×10^3 and $3.3 \times 10^3 \text{ M}^{-1}$, respectively. Obviously, DhaTab exhibited the most sensitive quenching response to Fe³⁺.

The effect of Fe³⁺ on the fluorescence of TaTa, DhaTab,

TRITER-1 and TzDa is likely due to the absorption competition quenching (ACQ) [25,26]. Fe³⁺ has an obvious and strong UV-Vis absorption in the range of 250–400 nm while other metal ions (Na⁺, Mg²⁺, Al³⁺, K⁺, Ca²⁺, Cu²⁺, Zn²⁺, Pb²⁺, Ag⁺, Cd²⁺) have no UV-Vis absorption (Figure 5(a)). The UV-Vis absorption spectra of all these COFs overlap with that of Fe³⁺ (Figure 5(b)). However, there is no significant overlap between the UV-Vis absorption spectra of Fe³⁺ and the emission spectra of TaTa, DhaTab, TRITER-1 and TzDa (Figure 5(c)), indicating no possibility for energy transfer between these COFs and Fe³⁺. The overlapped extents between the UV-Vis absorption spectra of the COFs and Fe³⁺ follow an increasing order of DhaTab > TaTa > TRITER-1 > TzDa (Figure 5(b)), in good agreement with the order of K_{SV} . So, the fluorescence quenching of TaTa, DhaTab, TRITER-1 and TzDa likely resulted from the Fe³⁺ absorption competition.

Table 1 K_{SV} of TaTa, DhaTab, TRITER-1 and TzDa for Fe³⁺

	I (a.u.)	I_0 (a.u.)	K_{SV} (M ⁻¹)
TaTa	179	2692	1.4×10^4
DhaTab	27	2822	1.0×10^5
TRITER-1	106	702	5.6×10^3
TzDa	64	208	3.3×10^3

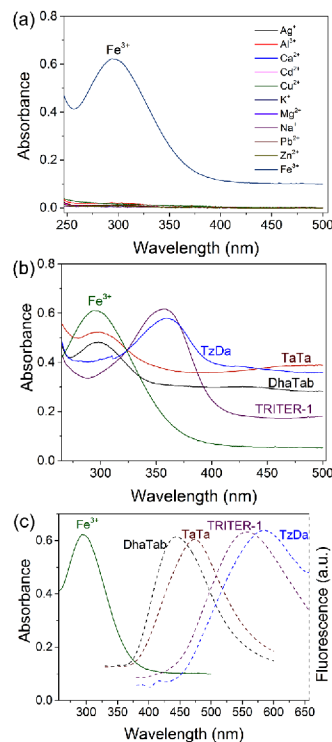


Figure 5 (a) UV-Vis absorption spectra of metal ions. (b) UV-Vis absorption spectra of TaTa, DhaTab, TRITER-1, TzDa and Fe³⁺. (c) UV-Vis absorption spectra of Fe³⁺ and the fluorescent emission spectra of TaTa, DhaTab, TRITER-1, TzDa. The concentration of the metal ions is 0.33 mM (color online).

3.4 Evaluation of DhaTab for selective sensing Fe³⁺

Further experiments were carried out to evaluate the possibility of DhaTab for sensing Fe³⁺. The effect of pH on the fluorescence of DhaTab was examined. The results show that the fluorescence of DhaTab is stable in a wide pH range of 4–11 (Figure S9). Study on the effect of the concentration of Fe³⁺ show that the fluorescence of DhaTab linearly quenched (Figure 6). A linear calibration function of $F=2369-4.38C_{\text{Fe}^{3+}}$ (where F is the fluorescence of DhaTab, while $C_{\text{Fe}^{3+}}$ is the concentration of Fe³⁺ in μM) in the range of 5–500 μM ($R^2=0.993$) with a detection limit (LOD) of 0.12 μM (Figure 6(b)). The precision for eleven replicate measurements of 30 μM Fe³⁺ was 2.6% (relative standard deviation, RSD). DhaTab gave better linear range of the calibration function and LOD than the other COFs such as PI-COF 201 and PI-COF 202 for fluorescent sensing Fe³⁺ [15].

4 Conclusions

We have investigated the fluorescence properties of the COF TaTa, DhaTab, TRITER-1 and TzDa and the effect of metal ions on their fluorescence. All of the four COFs exhibit significant quenching response to Fe³⁺ due to absorption competition quenching (ACQ). DhaTab shows the most sensitive quenching response to Fe³⁺ with the K_{SV} of $1.0 \times 10^5 \text{ M}^{-1}$. This article shows the potential of DhaTab for fluorescent sensing Fe³⁺ and expands the sensing application of fluorescent COF materials.

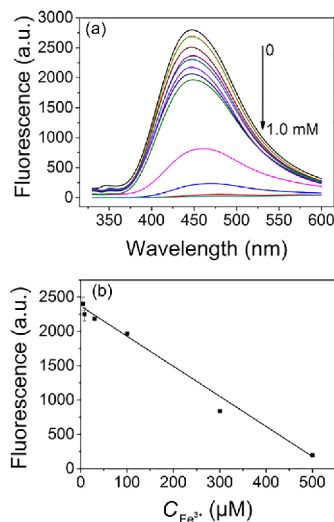


Figure 6 (a) Fluorescence spectra of DhaTab in the presence of different concentrations of Fe³⁺ in the DMF/H₂O (9:1, V/V). (b) Linear relationship between fluorescence and the concentration of Fe³⁺ (color online).

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

Supporting information The supporting information is available online at <http://chem.scichina.com> and <http://link.springer.com/journal/11426>. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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