View Article Online

Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Li, Z. Cui, S. Pang, L. Meng, D. Ma, Y. Li, Z. Shi and S. Feng, *J. Mater. Chem. C*, 2019, DOI: 10.1039/C9TC03265G.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/materials-c

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Luminescent Covalent Organic Framework as a Recyclable Turn-Off Fluorescent Sensor for Cations and Anions in Aqueous Solution⁺

Ming Li,ª Zhonghua Cui, *^b Shirui Pang,ª Lingkun Meng,ª Dingxuan Ma,^c Yi Li,ª Zhan Shi*a and Shouhua Feng ^a

Covalent organic frameworks (COFs) have shown great potential for use in ion sensing; however, applications of existing COFs are limited to sensing either cations or anions. In this study, a three-dimensional COF, COF-TT, is constructed by reacting the bis(tetraoxacalix[2]arene[2]triazine) core with tetra(p-aminophenyl)methane to provide a luminescent sensor. COF-TT exhibits ultrahigh thermal stability and exceptional chemical stability in aqueous solutions over a broad pH range from 2 to 14, which signifies immense practical potential for sensing applications. Excellent selectivity and high sensitivity of COF-TT toward Fe³⁺ cations and CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} anions are evident via luminescence quenching. COF-TT also exhibits excellent recyclability in terms of washing and re-exposure cycles. Both experimental data and theoretical calculations are employed to unveil the mechanisms of the quenching effect and sensing properties of COF-TT.

Introduction

Published on 09 September 2019. Downloaded by JAMES COOK UNIVERSITY on 9/9/2019 2:46:05 PM

Over the past decade, a large number of covalent organic frameworks (COFs)¹ have been synthesized due to their highly ordered structures, permanent porosities, and physicochemical stabilities against moisture. The structural features of COFs impart these new materials with immense potential for advanced applications. These COFs are structurally diverse and can be utilized as platforms in practical applications, such as gas storage² or separation,³ catalysis,⁴ drug delivery,⁵ fluorescence recognition,⁶ batteries,⁷ energy storage,⁸ and various other potential applications.⁹ Significant advancements have been made via attempts to use luminescent COFs as sensing materials in cationic and anionic solutions^{6b, 6e} as well as for medical diagnosis and monitoring (e.g., environmental and industrial manufacturing).

It is well recognized that Fe^{3+} , CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} play important roles in the field of life sciences. Fe^{3+} ions are essential for living organisms because they play a vital role in various biological processes, such as oxygen metabolism, oxygen absorption, and electron transfer, and they also find wide spread applications in industry.^{6b, 10} In addition, CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} ions are ubiquitous oxidants used both in the laboratory and in industry.¹¹ However, excess Fe³⁺ cations in biological systems can catalyze the production of reactive oxygen species (ROS) and harm nucleic acids and proteins. Uptake of Cr^{6+} in the human body can lead to serious cytotoxicity and carcinogenicity. KMnO₄ is a strong oxidizing agent, and is toxic and corrosive. Therefore, the design and manufacture of sensing materials with high selectivity and desired sensitivity with respect to Fe³⁺, CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻ ions are significant for biological and environmental safety.

COFs with luminescence properties were proposed by Liu and co-workers as materials to detect such toxic ions.^{6e} However, existing luminescent COFs probe either cations or anions, which greatly limits their commercial development. In this regard, the exploitation of luminescent COFs that can efficiently sense both cations (Fe³⁺) and anions (CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻) is essential for mass production. Furthermore, the majority of reported luminescent materials detect ions in organic solvents,^{6d, 6e} because development of sensors that operate in aqueous solutions remains challenging. Therefore, sensors that function in aqueous solution are desirable.

Herein, we report a highly porous and chemically stable luminescent covalent organic framework, denoted as COF-TT, derived from a flexible core consisting of bis(tetraoxacalix[2]arene[2]triazine) and the rigid tetra(paminophenyl)methane combined through a solvothermal preparation. The three-dimensional COF exhibited excellent sensitivity to detect Fe³⁺ cations and CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-1} anions based on a turn-off sensing mechanism. Moreover, the luminescence quenching mechanisms were investigated using

^{a.} State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

^{b.} Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, China

^c College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China

[†] Electronic supplementary information (ESI) available: Synthetic procedures, characterization details, reusability, and additionalanalytical results. See DOI: 10.1039/x0xx00000x

ARTICLE

both experimental studies and theoretical calculations. The luminescence properties of cations can be ascribed to the interactions of guest molecules with the COF skeleton, while the luminescent characteristics of anions are attributed to competitive adsorption of anions to the COF skeleton.



Figure 1. Schematic illustration of the synthesis of COF-TT.

Experimental

Synthesis of COF-TT

Published on 09 September 2019. Downloaded by JAMES COOK UNIVERSITY on 9/9/2019 2:46:05 PM

Tetra(p-aminophenyl)methane (152.1 mg, 0.3 mmol), extra dry DMAc (15 mL), and K₂CO₃ (166.0 mg, 1.2 mmol) were mixed well °C (Figure under nitrogen at 0 1). Bis(tetraoxacalix[2]arene[2]triazine) core (234.8 mg, 0.4 mmol) was dissolved in 5 mL DMAc and slowly added to the former mixture, then vigorously stirred at 120 °C for 2 days. The crude product was collected by filtration and subsequently washed with tetrahydrofuran (THF) and water, followed by Soxhlet extraction with THF (48 h). The final activated brown powder of COF-TT was obtained after vacuum drying overnight at 120 °C (317.6 mg, 82.1% yield).

Results and discussion

Structural characterization

The structural integrity of COF-TT was verified by Fourier transform infrared (FT-IR) spectroscopy (Figure 2). The disappearance of the tensile vibrations characteristic of C-Cl at 875 cm⁻¹ indicated that all the Cl atoms were replaced. The peak at 1565 cm⁻¹ was attributed to a C=N stretching vibration, which indicated that the triazine ring moiety was grafted in the framework. Furthermore, the peaks at 3396 and 1621 cm⁻¹, attributed to the N-H stretching vibration and primary amines, respectively, disappeared, confirming substitution of the amine groups in tetra-(4-anilyl)-methane.^{3e, 6b} Structural features of COF-TT were also characterized using solid-state ¹³C NMR spectroscopy (Figure 3). The signal at 62.5 ppm corresponded to the sp³ carbons of COF-TT. Seven distinct peaks ranging from 100 to 200 ppm were assigned to the sp² carbons associated with the cage-like structure of bis(tetraoxacalix[2]arene[2]triazine) and benzene rings.



Figure 2. FT-IR spectra of (a) the bis(tetraoxacalix[2]arene[2]triazine) core, (b) tetra(paminophenyl)methane, and (c) COF-TT.



According to the experimental structural characterization of COF-TT, we established a sound theoretical model based on Focite force-field calculations (Forcite Geometry Optimization-Convergence) using Accelrys' Materials Studio (MS) v. 8.0 software (Accelrys Software Inc., San Diego, CA, USA).⁵ The simulations offered an optimized structure of I-43D space group and a unit cell with a = b = c = 40.75 Å and α = β = γ = 90° (Fig. S1). The powder X-ray diffraction (PXRD) pattern displays three broad diffraction signals at $2\theta \approx 7^{\circ}$, 13°, and 19°, thus revealing a low degree of crystalline order for COF-TT powders (Fig. S2). The simulated and experimental PXRD patterns of the framework were in agreement. The morphology of COF-TT was observed by using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Fig. S3, the COF-TT solid consists of particles and nanoparticles. Thermogravimetric analysis (TGA) plots revealed that COF-TT was stable up to 400 °C (Fig. S4).

Porosity of COF-TT

To investigate the porosity, gas sorption of COF-TT was probed using CO₂ (3.30 Å), Ar (3.54 Å), and N₂ (3.64 Å) (The value in parentheses stand for the size of the molecule.). CO₂ adsorption of COF-TT at 195 K was highly consistent with typical type I gas adsorption isotherms, confirming that micropores exist in COF-TT (Figure 4). The Langmuir and Brunauer-Emmett-Teller (BET) surface areas of COF-TT were 736 and 528 m²·g⁻¹, respectively.

Page 2 of 7

Journal Name

Furthermore, the aperture size distribution was modeled using density functional theory (DFT), which revealed that the main aperture size of COF-TT is 5.2 Å. N₂ sorption isotherms at 77 K and Ar sorption isotherms at 87 K of COF-TT were obtained (Fig. S6); the BET surface areas calculated from these two isotherms were 446 m²·g⁻¹ and 451 m²·g⁻¹, respectively, different from those reported in a previous paper.^{3b}



Figure 4. CO_2 sorption isotherms of COF-TT at 195 K. Inset: Pore size distribution for COF-TT calculated using DFT.

Fluorescence sensing of cations

Published on 09 September 2019. Downloaded by JAMES COOK UNIVERSITY on 9/9/2019 2:46:05 PM

The cation recognition properties of COF-TT were measured and the luminescence response corresponding to the interaction of COF-TT with different cations in aqueous suspension was investigated using a series of spectroscopic methods. For comparison, an equal amount of solid COF-TT was ground and dispersed in separate aqueous solutions containing equal volumes of MCl_x (M = Mn²⁺, Ba²⁺, Na⁺, Ca²⁺, Pb²⁺, Li⁺, Mg^{2+} , K⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺, Al³⁺, Fe²⁺, Cr³⁺, Cu²⁺ and Fe³⁺; [M] = 10⁻² $mol \cdot L^{-1}$; x = 1–3, depending on the corresponding charge). The resultant mixtures were then immersed for 1 h in an ultrasonic bath to form uniform dispersion suspensions, then at r.t. to form Mn+@COF-TT (positive ion incorporated COF-TT) solutions for fluorescence studies. The fluorescence intensities of the Mn+@COF-TT solutions were recorded and compared (Figure 5). The detailed fluorescence quenching efficiencies of different metal ions for COF-TT are shown in Fig. S11. Interestingly, Mⁿ⁺@COF-TT suspensions show obviously different fluorescence intensities. The luminescence intensity of COF-TT at 490 nm (Figure 5) exhibits negligible enhancement or quenching upon addition of Mn²⁺, Ba²⁺, Na⁺, Ca²⁺, Pb²⁺, Li⁺, Mg²⁺, K⁺, Cd²⁺, Zn²⁺, Ni²⁺, Co²⁺, Al³⁺ or Fe²⁺, whereas marked fluorescence quenching was observed for Cr³⁺ and Cu²⁺. In sharp contrast, Fe³⁺ produced pronounced luminescence quenching, reducing the fluorescence intensity by 98.4% compared with that of the initial COF-TT in aqueous solution. More importantly, COF-TT immersed in an aqueous solution containing Fe³⁺ ions retained its characteristic luminescence after rinsing with H₂O (Fig. S12), enabling highly selective and repeated sensing of Fe³⁺.



Figure 5. Relative fluorescence intensities (excitation at 490 nm) of COF-TT dispersed in acidic aqueous solutions containing different cations (0.01 mol·L⁻¹).

To further investigate the sensitivity and quantitative sensitization of the quenching behavior, a concentration gradient experiment was carried out by changing the Fe³⁺ concentration. The titration of Fe³⁺ illustrated that the luminescence intensity of COF-TT gradually decreases with increasing Fe³⁺ concentration (Figure 6a), showing that the quenching process is diffusion-controlled (Figure 6b). When the Fe³⁺ concentration reached 0.9 mM, luminescence of the emulsion was hardly detected, demonstrating its obvious sensitivity for sensing Fe³⁺. The curve representing the relationship between the relative luminescence intensity and the Fe³⁺ concentration can be fitted using the formula: $I_0/I = 1.135 \exp([M]/0.265) + 0.223$ (where I₀ is the luminescence intensity of the H₂O@COF-TT suspension, I is the luminescence intensity of the Mn+@COF-TT suspension, and [M] (mM) is the concentration of the Fe³⁺ ion). For Fe^{3+} , using the Stern–Volmer (SV) equation $I_0/I = 1 + K_{SV}[M]$, the relationship between I_0/I and [M] can be fitted well. In the lowconcentration range, the SV curve is almost linear (Figure 6b, inset). The K_{SV} values are approximately 1.3×10^4 M⁻¹, which are comparable or even better than those for previously reported compounds for monitoring Fe^{3+} .^{10b-10e} The detection limit $(3\sigma/k_{sv})$ of COF-TT was calculated from the K_{sv} value and standard deviation of ten repeated luminescence measurements of the blank solution (Table S1, ESI⁺). For COF-TT, Fe³⁺ cations are the most effective guenchers with a detection limit of 3.69×10^{-4} M, similar to those of other reported compounds.^{10a-10c} The low detection limit indicates that COF-TT has extremely high detection sensitivity for Fe³⁺ ions.



Figure 6. (a) Luminescence spectra of the Fe³⁺@COF-TT suspensions upon addition of Fe³⁺ (0–1.2 mM) in acidic aqueous solution (Ex at 490 nm). (b) The plot of relative luminescence intensity vs. Fe³⁺ concentration. Inset: The linear correlation for the plot of I_0/I as a function of Fe³⁺ concentration.

ateria

ARTICLE

Nanu

C Accepted

ournal of Materials Chemistry (

Journal Name

ARTICLE

Mechanism for the luminescence quenching of cations

The luminescence quenching of cations for COFs is probably caused by three simultaneous behaviors: (i) collapse of the framework, (ii) competition between cations and COFs for absorption, and (iii) strong interactions between cations and COFs. Experimentally, interactions between Fe3+ and the COF-TT framework lead to luminescence quenching, further supported by the results of theoretical calculations. The PXRD spectra (Fig. S8) show that the framework of COF-TT remains unchanged after treatment with Fe³⁺ aqueous solution. The UV-visible absorption spectrum Fe³⁺ ions in aqueous solution has almost no overlap with the excitation spectrum of COF-TT (Fig. S13). Therefore, there is no competitive adsorption between Fe³⁺ and COF-TT. To elucidate the possible mechanism of the strong luminescence quenching from Fe³⁺, O 1s and N 1s X-ray photoelectron spectroscopy (XPS) and theoretical calculations were performed on COF-TT and some metal ions containing Mⁿ⁺@COF-TT. The O 1s peak for metal ion-free COF-TT changed from 513.65 to 534.42 eV upon Fe³⁺ addition (Figure 7a), and the bonding energy of N 1s in Fe³⁺@COF-TT increased by 0.76 eV compared to that of free COF-TT, which shifted to 399.94 from 399.18 eV (Figure 7b), representing weak interactions between Fe³⁺ and oxygen or nitrogen atoms. Strong interactions between oxygen or nitrogen atoms and Fe³⁺ ions led to changes in the electronic energy level of the ligand, resulting in inefficient energy transfer in COF-TT. As shown in Figure 7, the interactions of Mg²⁺, Mn²⁺, Ni²⁺, Fe²⁺, and Co²⁺ with nitrogen or oxygen atoms are negligible; therefore, the O 1s and N 1s peaks were not shifted in the XPS spectra. On the other hand, Cr³⁺ and Cu²⁺ ions shifted the bond energy of N 1s to 399.52 eV and 399.61 eV, respectively, while the O 1s peak remained unchanged probably due to weak interactions between Cr³⁺ or Cu²⁺ with COF-TT. Compared with other Mⁿ⁺@COF-TT, the XPS profiles of oxygen atoms showed the only obvious shift and the XPS spectra of nitrogen atoms have the most obvious shift in Fe³⁺@COF-TT. Therefore, the mechanism underlying the selective luminescent detection of Fe3+ involves the interaction between Fe³⁺ ions and Lewis bases in the COF-TT framework, which is stronger than that for other metal ions. Furthermore, the meraction between Fe³⁺ ions and oxygen atoms in the COF-TT framework is strong, while there is almost no interaction between other metal ions and COF. Optimized ground-state structures using the CAM-B3LYP methods combined with the def2SVP basis sets are displayed in Figure 8. In the case of calculations including solvent effects, the water was used in the polarizable continuum model (PCM).¹² The initial structures for the optimization process were taken from the crystal structures, and six oxygen and three nitrogen atoms were fixed during the optimization process for better geometrical prediction based on the crystal structures. All the calculations were carried out using the GAUSSIAN09 program packages. The Fe…O distance in the bis(tetraoxacalix[2]arene[2]triazine) core (2.118 Å) (Figure 8a), the Fe…N distance in the triazine unit (2.143 Å) (Figure 8b), and the Fe…N distance in the amine groups (2.309 Å) (Figure 8c) were used to determine the corresponding bond energies. The interaction energies of Fe³⁺@COF-TT in water corresponding to Figure 8a, b, c were -10.1, -21.8, -2.0 kcal·mol⁻¹, respectively, while the corresponding energies in gas phase were -24.0, -36.2, and 14.7 kcal·mol⁻¹. (Table S1) The interaction of Fe³⁺ with oxygen atoms in COF-TT was not a feature observed in other ions that consistent with the results shown in Figure 7a. The results of XPS analysis and the data in Figure 8 and Table S1 reveal that the ratio of the interaction of Fe-O to fluorescence quenching is larger than that to Fe…N in Fe³⁺@COF-TT. Although the O site is 10 kcal/mol lower than the energy required for adsorption at the N site, there is Cl…H adsorption at the N-position so that its energy is lower. In addition, the fact that COF-TT has many O layouts and almost no steric hindrance is also an important factor. The calculations further revealed the interaction of Fe³⁺ ions with nitrogen atoms of COF-TT. Both XPS experimental data and theoretical calculations show that quenching is mainly due to the exchange of electrons in the bis(tetraoxacalix[2]arene[2]triazine) core after bonding with Fe³⁺ ions through Lewis acid-base interactions.



Figure 7. (a) O 1s and (b) N 1s XPS spectra of the original COF-TT and $M^{n+}@COF-TT$.

Published on 09 September 2019. Downloaded by JAMES COOK UNIVERSITY on 9/9/2019 2:46:05 PM



Figure 8. Preferential Fe³⁺ ion bonding sites and the corresponding bonding energies, obtained by theoretical calculations (C, gray; N, blue; O, red; H, white; Fe, orange; Cl, green).

Fluorescence sensing of anions

Due to the prominent luminescence features of COF-TT, we also became interested in exploring the turn-off fluorescence sensing of anions. To investigate this potential application of COF-TT, equal masses of ground COF-TT materials were immersed in isometric K_nX aqueous solutions (X = ClO₃⁻, BrO₃⁻, CO₃²⁻, C₂O₄²⁻, OAc⁻, SCN⁻, IO₃⁻, Br⁻, ClO₄⁻, OH⁻, NO₃⁻, SO₄²⁻, I⁻, Cl⁻, PO₄³⁻, F⁻, CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻; [X] = 10⁻² mol·L⁻¹; n = 1-3, depending on the corresponding charge) for the luminescence study. The fluorescence intensities of the solutions were recorded and compared (Figure 9). Detailed fluorescence quenching efficiencies of COF-TT for different anions are shown in Fig. S14. The luminescence intensity at 490 nm increased negligibly after the addition of KClO₃, KBrO₃, K₂CO₃, K₂C₂O₄, KOAc, KF, KCl, KBr, KI, KNO₃, KOH, KSCN, K₂SO₄, K₃PO₄, KIO₃, and KCIO₄. However, addition of K₂CrO₄, K₂Cr₂O₇, and KMnO₄ showed significant luminescence quenching toward COF-TT. Furthermore, multiple cycles of experiments on COF-TT for detecting CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} anions indicated that COF-TT can regain its fluorescence intensity after washing with H₂O (Fig. S15–S17). These results indicated that COF-TT can be applied as a turn-off fluorescence sensor for sensing CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} ions with high sensitivity and excellent recyclability.



Figure 9. Relative fluorescence intensities (upon excitation at 490 nm) of COF-TT dispersed in acidic aqueous solutions containing different anions (0.01 mol·L⁻¹).

Sensitivity and quantitative sensitization of the quenching behavior are important criteria for a fluorescent sensor. Therefore, concentration gradient experiments were performed by varying the concentrations of $CrO_4^{2^-}$, $Cr_2O_7^{2^-}$, and MnO4⁻ ions. Titrations illustrated that the fluorescence intensity of COF-TT decreases with increasing concentration of $CrO_4^{2^-}$, $Cr_2O_7^{2^-}$, or MnO_4^- anions (Figure 10a–12a),

demonstrating that the quenching process is diffusion-controlled (Figure 10b-12b). Luminescence of the suspensions could not be detected when 0.8, 0.8, or 0.7 mM of CrO_4^{2-} , $Cr_2O_7^{2-}$, or MnO_4^{-} anions were present, respectively, indicating good sensitivity of COF-TT to detect K₂CrO₄, K₂Cr₂O₇, and KMnO₄ as a turn-off sensor. The variation in relative fluorescence intensity as a function of anion concentration (i.e., CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-}) is shown in Figures 10-12. The relative fluorescence intensity can be calculated as follows: $I_0/I = 1.281$ exp([X]/0.253) + 0.185, $I_0/I = 1.621 exp([X]/0.253) - 0.553$, and $I_0/I =$ 1.870 exp([X]/0.241) - 1.019, respectively (I₀ is the fluorescence intensity of H₂O@COF-TT and I is the fluorescence intensity of anion@COF-TT emulsions; [X] (mM) is the anion concentration). For CrO_4^{2-} , $Cr_2O_7^{2-}$ and MnO^{4-} , the curves of I_0/I vs. [X] can be readily applied to the Stern–Volmer equation $I_0/I = 1 + K_{SV}[X]$, with the SV curve being nearly linear in the low-concentration range (Figure 10b-12b, inset). The K_{SV} values for CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} were calculated to be approximately 1.4×10^4 M⁻¹, 1.4×10^4 M⁻¹ and 1.5×10^4 M⁻¹, respectively, comparable or superior to the reported as-synthesized materials for detecting CrO₄²⁻, Cr₂O₇²⁻, and MnO₄.¹¹ The detection limits $(3\sigma/K_{sv})$ of COF-TT were also determined based on the Ksv values and the standard deviations for ten repeated fluorescence measurements of H₂O@COF-TT solutions (Table S1). CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} are the most efficient quenchers of COF-TT, with detection limits of 3.43×10^{-4} M, 3.43×10^{-4} M, and 3.20×10^{-4} M, respectively, comparable to the values for other reported quenching materials.^{11b} The low detection limits suggest that COF-TT has very high detection sensitivity for CrO_4^{2-} , Cr₂O₇²⁻, and MnO₄⁻.



Figure 10. (a) Luminescence spectra of the CrO_4^{2-} @COF-TT suspensions upon addition of CrO_4^{2-} (0–1.2 mM) in acidic aqueous solution (Ex at 490 nm). (b) The plot of relative luminescence intensity as a function of CrO_4^{2-} concentration. Inset: The linear correlation for the plot of I_0/I as a function of CrO_4^{2-} concentration.

ARTICLE



Figure 11. (a) Luminescence spectra of the $Cr_2O_7^{2-}$ @COF-TT suspensions upon addition of $Cr_2O_7^{2-}$ (0–1.2 mM) in acidic aqueous solution (Ex at 490 nm). (b) The plot of relative luminescence intensity as a function of $Cr_2O_7^{2-}$ concentration. Inset: The linear correlation for the plot of I_0/I as a function of $Cr_2O_7^{2-}$ concentration.



Figure 12. (a) Luminescence spectra of the MnO₄ @COF-TT suspensions upon addition of different contents of MnO₄ (0–1.2 mM) in acidic aqueous solution (Ex at 490 nm). (b) The plot of relative luminescence intensity as a function of MnO₄ concentration. Inset: The linear correlation for the plot of I₀/I as a function of MnO₄ concentration.

Mechanism for the luminescence quenching byanions

Luminescence quenching by anions occurs due to structural collapse, interactions of anions with the COF skeleton, or competition of the excitation wavelength of the skeleton with the UV absorption by the anions. Consequently, the mechanisms of fluorescence quenching by CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻ anions were further explored. First, PXRD analysis confirmed that the structure of COF-TT remains intact even after immersion in aqueous solutions of anions (Fig. S8). Second, inductively coupled plasma (ICP) analysis reveals negligible amounts of 0.055%, 0.053%, and 0.045% in CrO42-, Cr2O72-, and MnO4-@COF-TT, respectively, verifying that CrO_4^{2-} , $Cr_2O_7^{2-}$, and MnO_4^{-} are not fixed in the channel of COF-TT. Therefore, the host-guest interaction is not the main factor governing luminescence quenching. Then, the excitation of COF-TT was studied by UV-vis absorption spectroscopy, and the absorption by various anions in pure aqueous solution was investigated to elucidate in detail the mechanism of luminescence quenching induced by CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻ (Fig. S18). Two wide absorption bands ranging from 310 to 413 nm for CrO_4^{2-} and $Cr_2O_7^{2-}$, and two other wide absorption bands ranging from 230 to 550 nm for MnO₄⁻ were observed, which almost overlapped with the adsorption band of COF-TT in the range 210–310 nm, while other anions showed no apparent absorption in this wavelength range. This observation testified that the strong competitive adsorption of excitation energy between COF-TT and CrO_4^{2-} , $Cr_2O_7^{2-}$, or MnO_4^{-} is the primary cause of luminescence quenching in the presence of these anions, which can suppress excitation energy transfer to an organic ligand of COF-TT by absorbing most of the excitation energy, resulting in a sharp decrease in the emission intensity or even quenching.

Conclusions

View Article Online DOI: 10.1039/C9TC03265G

In conclusion, COF-TT, a porous multifunctional luminescent COF sensor with high chemical and thermal stabilities, was prepared for the first time via a simple route. COF-TT showed high sensitivity and selectivity to Fe³⁺ cations, and CrO₄²⁻, Cr₂O₇²⁻, and MnO₄⁻ anions via luminescence quenching, indicating its immense potential for the qualitative and quantitative detection of these ions. Furthermore, the luminescent sensing mechanism was confirmed using both experimental and theoretical calculations. Our findings advance COFs as a functional platform for luminescent sensors, and expand the scope of materials designed to produce new COFs with unique luminescent sensing functions.

Acknowledgements

This work was supported by the Foundation of the Natural Science Foundation of China (no. 21771077, 21771084 and 21621001), the National Key Research and Development Program of China (no. 2016YFB0701100), the 111 Project (no. B17020)

Conflicts of interest

The authors declare no competing conflicts of interest.

Notes and references

- (a) Y. Xu, S. Jin, H. Xu, A. Nagai and D. Jiang, *Chem. Soc. Rev.*, 2013, **42**, 8012-8031; (b) S.-Y. Ding and W. Wang, *Chem. Soc. Rev.*, 2013, **42**, 548-568; (c) Z. Xiang, D. Cao and L. Dai, *Polymer Chem.*, 2015, **6**, 1896-1911; (d) S. Das, P. Heasman, T. Ben and S. Qiu, *Chem. Rev.*, 2017, **117**, 1515-1563.
- 2 (a) L. Li, K. Cai, P. Wang, H. Ren and G. Zhu, ACS Appl. Mater. Interfaces, 2015, 7, 201-208; (b) H. A. Patel, F. Karadas, J. Byun, J. Park, E. Deniz, A. Canlier, Y. Jung, M. Atilhan and C. T. Yavuz, Adv. Func. Mater., 2013, 23, 2270-2276; (c) S. Hug, M. B. Mesch, H. Oh, N. Popp, M. Hirscher, J. Senker and B. V. Lotsch, J. Mater. Chem. A, 2014, 2, 5928-5936; (d) Y. Liao, Z. Cheng, W. Zuo, A. Thomas and C. F. J. Faul, ACS Appl. Mater. Interfaces, 2017, 9, 38390-38400; (e) C. Pei, T. Ben, Y. Li and S. Qiu, Chem. Commun., 2014, 50, 6134-6136; (f) X. Zhang, J. Lu and J. Zhang, Chem. Mater., 2014, 26, 4023-4029.
- 3 (a) J. Lü and R. Cao, Angew. Chem. Int. Ed., 2016, 55, 9474-9480; (b) Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, Energy Environ. Sci., 2013, 6, 3684; (c) S. N. Talapaneni, D. Kim, G. Barin, O. Buyukcakir, S. H. Je and A. Coskun, Chem. Mater., 2016, 28, 4460-4466; (d) C. H. Lau, K. Konstas, A. W. Thornton, A. C. Y, Liu, S. Mudie, D. F. Kennedy, S. C. Howard, A. J. Hill and M. R. Hill, Angew. Chem. Int. Ed., 2015, 54, 2669-2673; (e) H. Zhao, Z. Jin, H. Su, J. Zhang, X. Yao, H. Zhao and G. Zhu, Chem. Commun., 2013, 49, 2780-2782.
- (a) D. Ma, K. Liu, J. Li and Z. Shi, ACS Sustainable Chem. Eng., 2018, 6, 15050-15055; (b) D. Ma, J. Li, K. Liu, B. Li, C. Li and Z. Shi, Green Chem., 2018, 20, 5285-5291; (c) Z.-J. Lin, J. Lü, L. Li, H.-F. Li and R. Cao, J. Catal., 2017, 355, 131-138; (d) Y.-X. Ma, Z.-J. Li, L. Wei, S.-Y. Ding, Y.-B. Zhang and W. Wang, J. Am. Chem. Soc., 2017, 139, 4495-4998; (e) H. Li, Q. Pan, Y. Ma, X. Guan, M. Xue, Q. Fang, Y. Yan, V. Valtchev and S. Qiu, J. Am. Chem. Soc., 2016, 138, 14783-14788; (f) M. Liras, M. Iglesias and F. Sánchez, Macromolecules, 2016, 49, 1666-1673; (g) J. Luo, X. Zhang and J. Zhang, ACS Catal., 2015, 5, 2250-2254; (h) P. Thomas, C. Pei, B. Roy, S. Ghosh, S. Das, A. Banerjee, T. Ben, S. Qiu and S. Roy, J. Mater. Chem. A, 2015, 3, 1431-1441; (i) H.

Published on 09 September 2019. Downloaded by JAMES COOK UNIVERSITY on 9/9/2019 2:46:05 PM

View Article Online DOI: 10.1039/C9TC03265G

Zhong, Y. Gong, F. Zhang, L. Li and R. Wang, *J. Mater. Chem. A*, 2014, **2**, 7502-7508.

- 5 H. Zhao, Z. Jin, H. Su, X. Jing, F. Sun and G. Zhu, *Chem. Commun.*, 2011, **47**, 6389-6391.
- 6 (a) G. Das, B. P. Biswal, S. Kandambeth, V. Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma and R. Banerjee, *Chem. Sci.*, 2015, **6**, 3931-3939; (b) D. Ma, B. Li, Z. Cui, K. Liu, C. Chen, G. Li, J. Hua, B. Ma, Z. Shi and S. Feng, *ACS Appl. Mater. Interfaces*, 2016, **8**, 24097-24103; (c) J. L. Novotney and W. R. Dichtel, *ACS Macro Lett.*, 2013, **2**, 423-426; (d) R. Gomes and A. Bhaumik, *RSC Adv.*, 2016, **6**, 28047-28054; (e) Z. Li, Y. Zhang, H. Xia, Y. Mu and X. Liu, *Chem. Commun.*, 2016, **52**, 6613-6616; (f) S. Dalapati, E. Jin, M. Addicoat, T. Heine and D. Jiang, *J. Am. Chem. Soc.*, 2016, **138**, 5797-5800; (g) P. Das and S. K. Mandal, *J. Mater. Chem. A*, 2018, **6**, 16246-16256.
- 7 (a) P. Peng, L. Shi, F. Huo, S. Zhang, C. Mi, Y. Cheng and Z. Xiang, *ACS Nano*, 2019, **13**, 878-884; (b) G. Zhang, Y. L. Hong, Y. Nishiyama, S. Bai, S. Kitagawa and S. Horike, *J. Am. Chem. Soc.*, 2019, **141**, 1227-1234; (c) X. Song, M. Zhang, M. Yao, C. Hao and J. Qiu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 43896-43903; (d) C. Jiang, M. Tang, S. Zhu, J. Zhang, Y. Wu, Y. Chen, C. Xia, C. Wang and W. Hu, *Angew. Chem. Int. Ed.*, 2018, **57**, 16072-16076; (e) D.-G. Wang, N. Li, Y. Hu, S. Wan, M. Song, G. Yu, Y. Jin, W. Wei, K. Han, G.-C. Kuang and W. Zhang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 42233-42240; (f) X. Liu, L. Wang, P. Yu, C. Tian, F. Sun, J. Ma, W. Li and H. Fu, *Angew. Chem. Int. Ed.* 2018, **57**, 16166-16170.
- 8 (a) C. R. DeBlase, K. Hernández-Burgos, J. M. Rotter, D. J. Fortman, D. D. Abreu, R. A. Timm, I. C. Diógenes, L. T. Kubota, H. D. Abruña and W. R. Dichtel, *Angew. Chem. Int. Ed.*, 2015, 54, 13225-13229; (b) F. Vilela, K. Zhang and M. Antonietti, *Energy Environ. Sci.*, 2012, 5, 7819-7832; (c) L. Hao, B. Luo, X. Li, M. Jin, Y. Fang, Z. Tang, Y. Jia, M. Liang, A. Thomas, J. Yang and L. Zhi, *Energy Environ. Sci.*, 2012, 5, 9747-9751; (d) J. Han, G. Xu, H. Dou and D. R. MacFarlane, *Chem. Eur. J.*, 2015, 21, 2310-2314.
- 9 (a) D. W. Kang, K. S. Lim, K. J. Lee, J. H. Lee, W. R. Lee, J. H. Song, K. H. Yeom, J. Y. Kim and C. S. Hong, *Angew. Chem. Int. Ed.*, 2016, **55**, 16123-16126; (b) B. Li, Y. Zhang, D. Ma, Z. Shi and S. Ma, *Nat. Commun.*, 2014, **5**, 5537.
- (a) D.-M. Chen, N.-N. Zhang, C.-S. Liu and M. Du, *J. Mater. Chem. C*, 2017, **5**, 2311-2317; (b) Y. Zhou, H.-H. Chen and B. Yan, *J. Mater. Chem. A*, 2014, **2**, 13691-13697; (c) B. Wang, Q. Yang, C. Guo, Y. Sun, L.-H. Xie and J.-R. Li, *ACS Appl. Mater. Interfaces*, 2017, **9**, 10286-10295; (d) M. Zheng, H. Tan, Z. Xie, L. Zhang, X. Jing and Z. Sun, *ACS Appl. Mater. Interfaces*, 2013, **5**, 1078-1083; (e) M. Chen, W.-M. Xu, J.-Y. Tian, H. Cui, J.-X. Zhang, C.-S. Liu and M. Du, *J. Mater. Chem. C*, 2017, **5**, 2015-2021.
- 11 (a) Y.-T. Yan, W.-Y. Zhang, F. Zhang, F. Cao, R.-F. Yang, Y.-Y. Wang and L. Hou, *Dalton Trans.*, 2018, **47**, 1682-1692; (b) F.-Y. Yi, S.-C. Wang, M. Gu, J.-Q. Zheng and L. Han, *J. Mater. Chem. C*, 2018, **6**, 2010-2018.
- 12 B. Mennucci and J. Tomasi, J. Chem. Phys., 1997, **106**, 5151-5158.