

Supporting Information

Covalent organic frameworks constructed step by step using a [(C3 + C2) + C2] strategy toward fluorescence detection of Fe³⁺

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Experimental Section:

Materials: Phloroglucinol (98%), Trifluoroacetic acid (TFA, 99%), 1,4-Dioxane (99%), 1, 4-Phthalaldehyde (98%), p-Dimethoxybenzene (99%), Paraformaldehyde (98%), Pyridinium chlorochromate (PCC, 98%), Hydrobromic acid (33 wt% in acetic acid), Lithium Aluminum Tetrachloride (97%) were purchased from Energy Chemical, Sun Chemical Technology (Shanghai). Mesitylene (97%) was purchased from Macklin Company. Hexamethylenetetramine (HMTA, 99%), Hydrazinemonohydrate (85%), Hydrochloric acid (36%~38%), Trichloromethane (99%) were purchased from China National Medicines Corporation Ltd. These reagents were used as received. The other reagents or solvents were of analytical purity, and used without further purification.

Characterizations: The ¹H, and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Avance III HD 500MHz Superconducting FT NMR Spectrometer. Powder X-ray diffraction (XRD) data were collected on a D8 Advance diffractometer in reflection geometry operating with a Cu K α anode ($\lambda = 1.54178 \text{ \AA}$) at 30 kV and 40 mA. The attenuated total reflection Fourier transformed infrared (FT-IR) spectra were collected on a Nicolet iS50 spectrometer. Nitrogen adsorption/desorption isotherms were measured at 77 K with an ASAP 2020 plus HD88 analyzer. The Brunauer-Emmett-Teller (BET) method and density functional theory (DFT) pore model were utilized to calculate the specific surface areas (SSAs) and pore size distributions. The Luminescence excitation and emission spectra were conducted on Hitachi F-7000 Series of Fluorescence Spectrometers utilizing a 150 W xenon lamp as an excitation source.

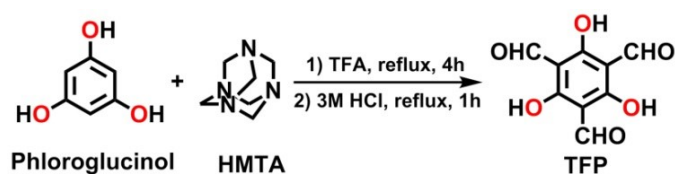
Crystal structure modeling: The crystal models were generated by Materials Studio software employing the Crystal Building module. Unit cell dimensions were initially evaluated using the experimental PXRD peak positions. The lattice parameters were then optimized using Pawley refinement till the R_w values converges.

Elemental analysis: TSCH-COFs were also analyzed using energy dispersive X-ray spectroscopy (EDS) element mapping to confirm the composition (Figure S4). Figure S4 shows the TSCH-COFs contain N and O elements.

Recyclability cycles of TSCH-COFs: The quenched fluorescence of TSCH-COFs could be recovered by EDTA (ethylenediaminetetraacetic acid disodium). The recyclability cycles of TSCH-COFs are obtained by quenching and recovery test. As shown in Figure S8-S10, the quenching efficiency of TSCH-COFs changes little after 5 cycles, indicating the good recyclability of TSCH-COFs. The recovered TSCH-COFs after sensing Fe³⁺ was evaluated by FT-IR spectra (Figure S11) and SEM (Figure S12). After recovery, the TSCH-COFs maintained the same morphology and structure, which confirms its good stability.

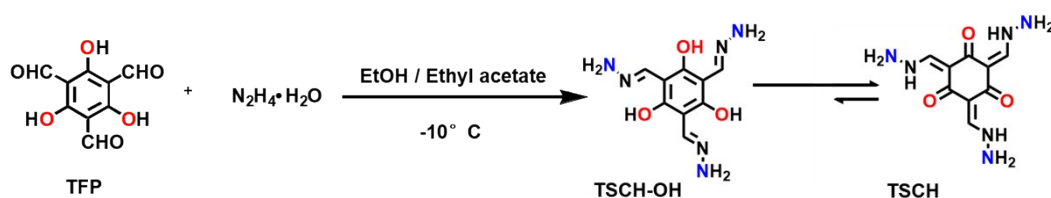
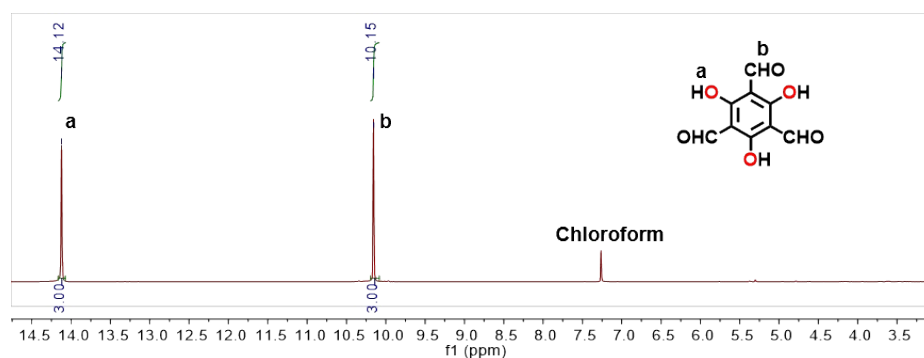
Solid-state sensing: A solid-state sensing experiment was conducted by depositing TSCH-COF suspensions onto filter papers, and drying them at 60°C for 6 hours. The paper strips deposited with COFs shows bright fluorescence, while the fluorescence quenched when the fluorescent paper strips soaked into Fe³⁺ solutions (Figure S13). The results indicate that TSCH-COFs can be used as solid-state sensing for Fe³⁺.

Experimental details:



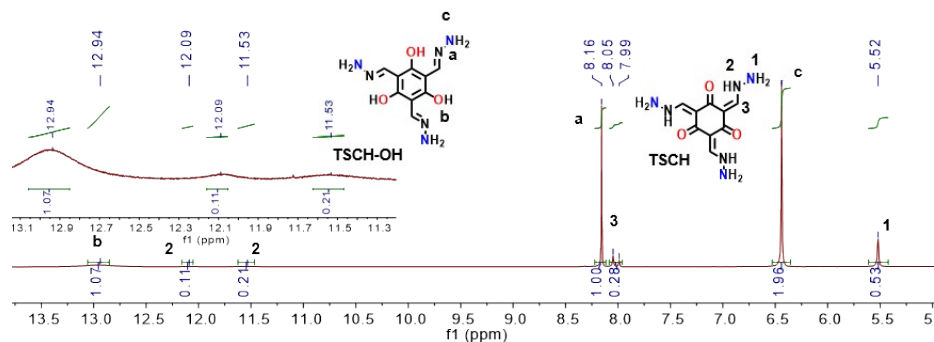
2,4,6-Triformylphloroglucinol (TFP): TFP was synthesized according to our previous report.¹ HMTA (15.098 g, 108 mmol) was added to 90 mL TFA and the mixture was sonicated for 10min until the solid dissolved, and then phloroglucinol (6.014 g, 49 mmol) was added under N₂ atmosphere. The solutions were heated at 100 °C for ca.2.5 h, 150 mL of 3 M HCl was added and the solutions were continued to proceed for 1 h at 100 °C. After cooling to room temperature, the solution was filtered through Celite, extracted with dichloromethane, dried over magnesium sulfate, and filtered. Rotary evaporation of the solutions to obtain a crude product. Pure TFP was obtained through sublimation with a yield is 1.1g, 10%. ¹H NMR (500 MHz, CDCl₃) δ 14.10 (s, 3H, OH), 10.14 (s, 3H, CHO). ¹³C NMR (126 MHz, DMSO-d₆) δ 191.90, 173.77, 103.63.

¹H NMR of TFP:

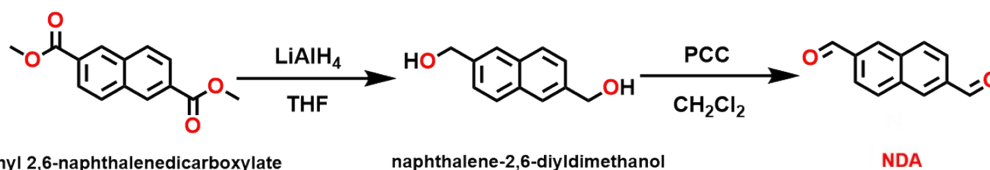
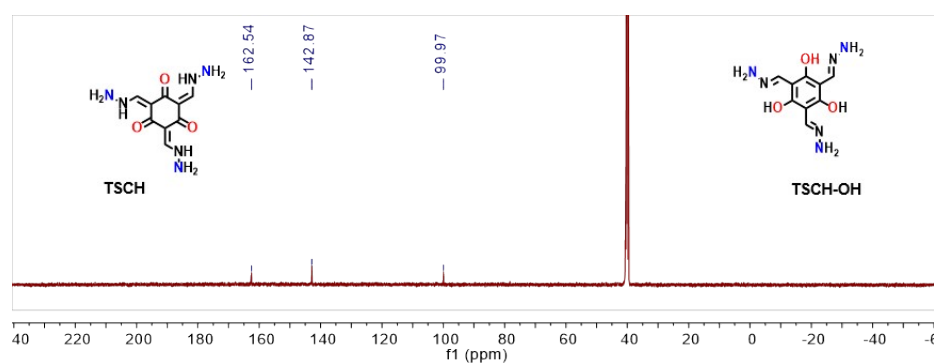


Tris(N-salicylidenehydrazine) (TSCH): Hydrazine hydrate (2.0 mL, 2.0 g, 35 mmol, 73 equiv.) was added to a suspension of TFP (100 mg, 0.476 mmol, 1 equiv.) in ethanol (10 mL) chilled in a dry ice-ethylene glycol bath at -10 °C. After 3 min, ethanol (10 mL) and ethyl acetate (30 mL) were added. The resulting yellow suspension was filtered immediately and washed with ethanol, ethyl acetate, and DCM, giving the product as a yellow powder (98.4 mg, 0.390 mmol, 82%). ¹H NMR (500 MHz, DMSO-d₆) minor tautomer (TSCH-OH): δ = 12.94 (s, 3H; OH), 8.16 (s, 3H; CH), 6.44 (s, 6H; NH₂); major tautomer (TSCH): δ = 12.09 (d, 1H; NH), 11.53 (d, 2H; NH), 8.05 (d, 2H; CH), 7.99 (d, 1H; CH), 5.52 (s, 6H; NH₂); ¹³C NMR (500 MHz, DMSO-d₆) δ 162.54, 142.87, 99.97.²

¹H NMR of TSCH:



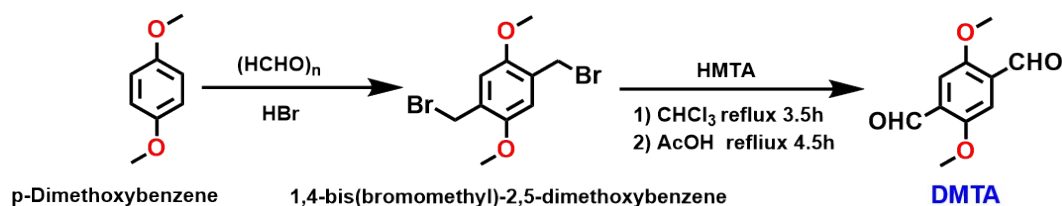
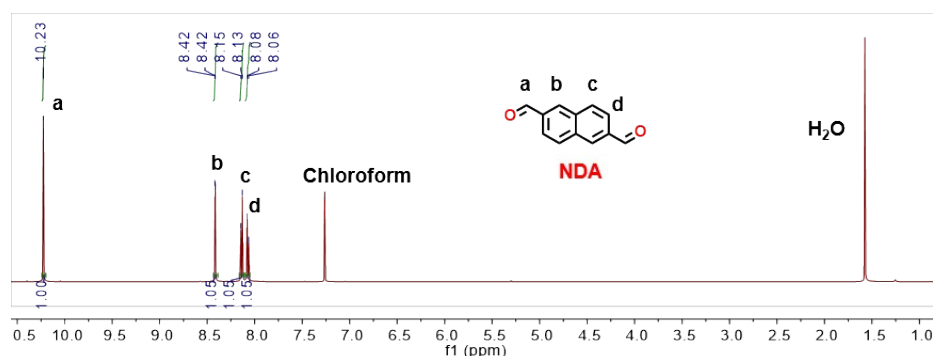
¹³C NMR of TSCH:



Naphthalene-2,6-diylidimethanol: Dimethyl 2,6-naphthalenedicarboxylate (3.66 g, 15 mmol) was dissolved in dry THF (150 mL) in ice-water bath, and LiAlH₄ (2.28 g, 60 mmol) was carefully added to the above solutions under nitrogen. The mixture was stirred at room temperature for 40 min, and then was warmed up to 70°C for 3h. The mixture was carefully treated in sequence with 2.3 mL of water, 2.3 mL of a 15% NaOH aqueous solution, and 6.8 mL of water. Afterwards, the suspension was filtered and the solution was evaporated to yield a white solid (2.6 g, 92%).

Naphthalene-2,6-dicarbaldehyde (NDA): To a stirred suspension of pyridinium chlorochromate (PCC) (8.85 g, 41.1 mmol) in anhydrous CH₂Cl₂ (100 mL) at 50 °C under nitrogen, a suspension of naphthalene-2,6-diylidimethanol (2.50 g, 13.6 mmol) in anhydrous CH₂Cl₂ (50 ml) was added dropwise. The mixture was rigorously stirred at 50 °C for 4 h, and cooled to room temperature. The precipitate was filtered and purified with column chromatography eluting with CH₂Cl₂. After the solvent was evaporated, the pure NDA was obtained as fluffy white needles (0.85 g, 35%). ¹H NMR (500 MHz, Chloroform-*d*) δ 10.23 (s, 2H), 8.42 (s, 2H), 8.14 (d, 2H), 8.07 (d, 2H).³

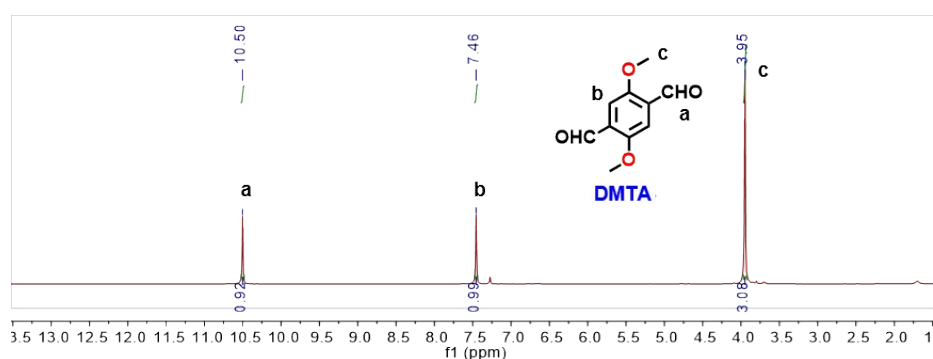
¹H NMR of NDA:



1,4-bis(bromomethyl)-2,5-dimethoxybenzene: A mixture of p-Dimethoxybenzene (8.3 g, 60 mmol), paraformaldehyde (8.1 g, 270 mmol) and acetic acid (150 mL) was heated to 60 °C, then 40% HBr (40 mL) was added to it using a pressure equalizing funnel and the reaction mixture was stirred for 4 h, cooled to room temperature and refrigerated overnight at 0 °C. The solid was filtered and washed with water until the pH=7. After dried in the vacuum oven at 90°C overnight to give white needle crystals (12.98 g, 66%).

2,5-dimethoxyterephthalaldehyde (DMTA): A mixture of hexamethylenetetramine (HMTA) (12.60 g, 90mmol), 1,4-bis(bromomethyl)-2,5-dimethoxybenzene (9.72 g, 30 mmol) and CHCl₃ (200 mL) was heated under reflux for 3.5 h, the solvent was evaporated under reduced pressure and 50% acetic acid (200 mL) was added to the residue, heated under reflux for 4.5 h, then concentrated hydrochloric acid (10 mL) was added to the mixture, cooled to room temperature, extracted with CHCl₃ and dried with anhydrous sodium sulfate. after the solvent was evaporated under reduced pressure and the residue was recrystallized from ethyl alcohol to give bright yellow needle crystals (1.46 g, 34.0%). ¹H NMR (500 MHz, CDCl₃) δ 10.50 (s,2H), 7.46 (s, 2H), 3.95 (s, 6H).⁴

¹H NMR of DMTA:



TSCH-BDA COF: A 20 mL pyrex tube was charged with TSCH (25.2 mg, 0.1 mmol), 1, 4-Phthalaldehyde (BDA) (20.1 mg, 0.15 mmol), 0.4 mL of 6M AcOH, 0.15 mL of 1, 4-dioxane and 2.85 mL of 1, 3, 5-trimethylbenzene (Mes). The mixture was sonicated for five minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120°C for 72 h. After cooling to room temperature, the precipitate was centrifuged and washed constantly with THF until the supernatant was clear. After dried in the vacuum oven at 120°C overnight,

the TSCH-BDA COF was synthesized.

TSCH-DMTA COF: A 20 mL pyrex tube was charged with TSCH (25.2 mg, 0.1 mmol), 2,5-dimethoxyterephthalaldehyde (DMTA) (29.1 mg, 0.15 mmol), 0.4 mL of 6M AcOH, 0.15 mL of 1, 4-dioxane and 2.85 mL of 1, 3, 5-trimethylbenzene (Mes). The mixture was sonicated for five minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120°C for 72 h. After cooling to room temperature, the precipitate was centrifuged and washed constantly with THF until the supernatant was clear. After dried in the vacuum oven at 120°C overnight, the TSCH-DMTA COF was synthesized.

TSCH-NDA COF: A 20 mL pyrex tube was charged with TSCH (25.2 mg, 0.1 mmol), naphthalene-2,6-dicarbaldehyde (NDA) (27.6mg, 0.15 mmol), 0.4 mL of 6M AcOH, 0.2 mL of 1, 4-dioxane and 2.8 mL of 1, 3, 5-trimethylbenzene (Mes). The mixture was sonicated for five minutes, degassed through three freeze-pump-thaw cycles, sealed under vacuum and heated at 120°C for 72 h. After cooling to room temperature, the precipitate was centrifuged and washed constantly with THF until the supernatant was clear. After dried in the vacuum oven at 120°C overnight, the TSCH-NDA COF was synthesized.

Figure S1 -S13:

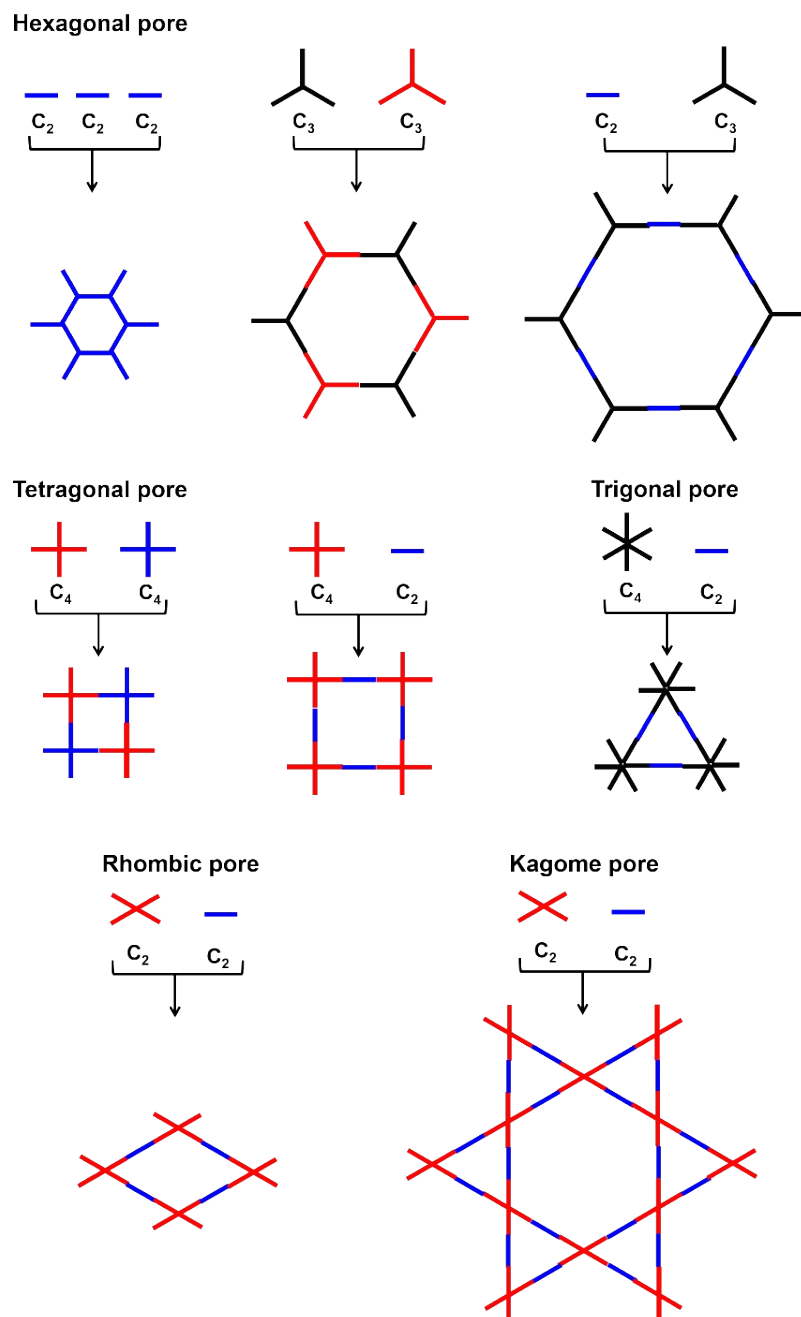


Figure S1. The topology design diagrams of COFs.

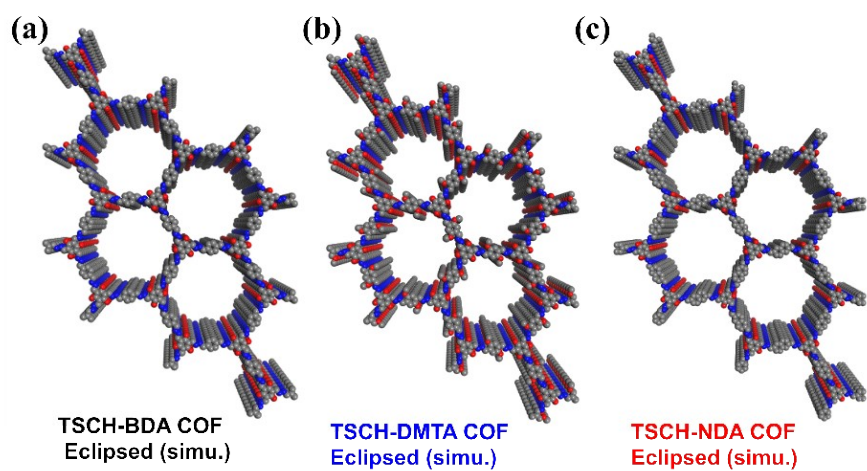


Figure S2. Schematic for the simulated eclipsed AA stacking structures of TSCH- COFs.

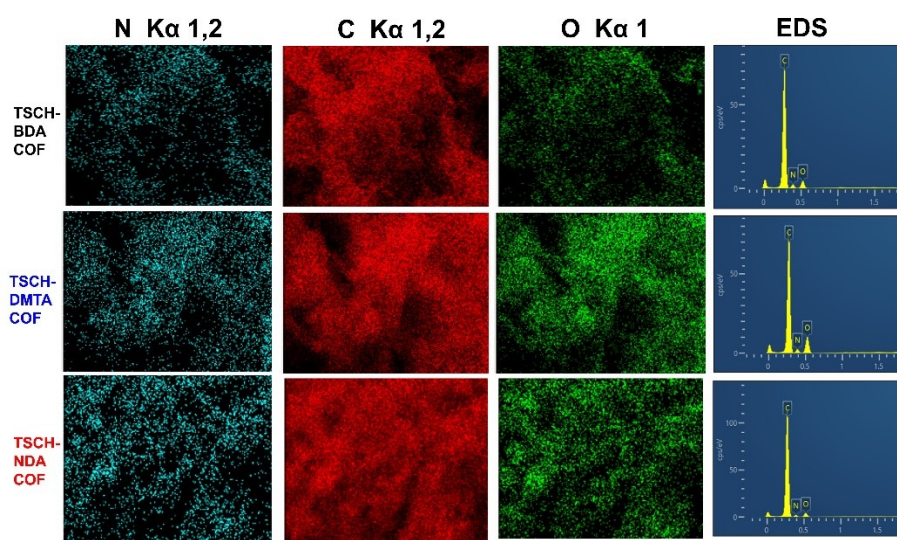


Figure S3 EDS elemental mapping of TSCH- COFs.

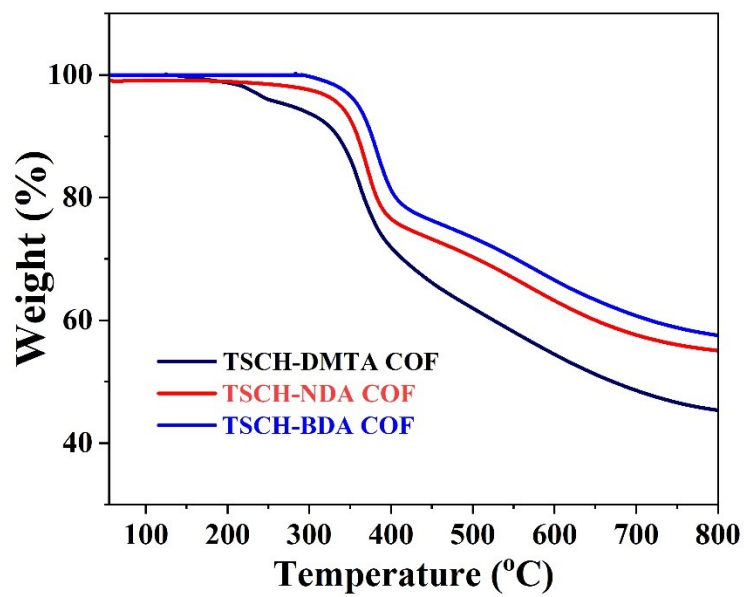


Figure S4 TGA curve of TSCH-COFs.

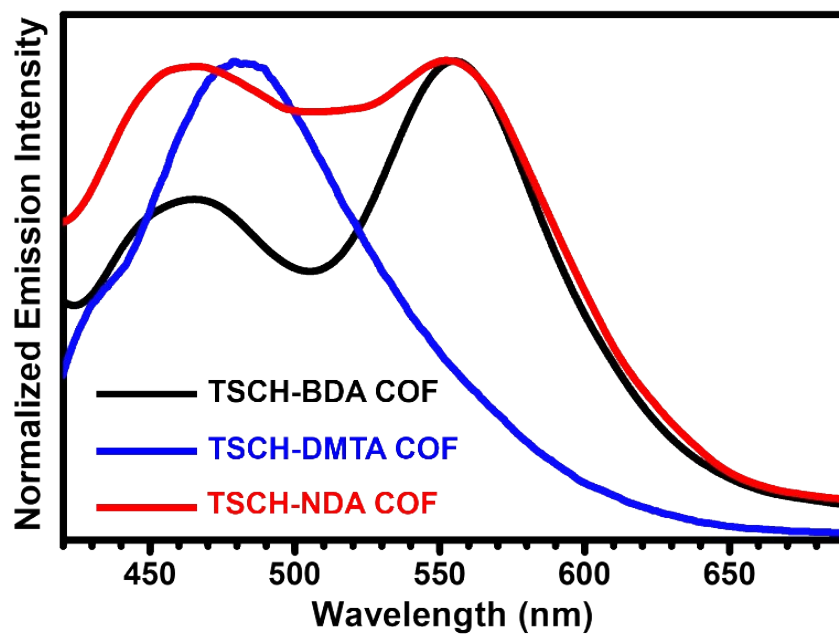


Figure S5 Emission spectra of TSCH-COFs in EtOH : H₂O = 1:1.

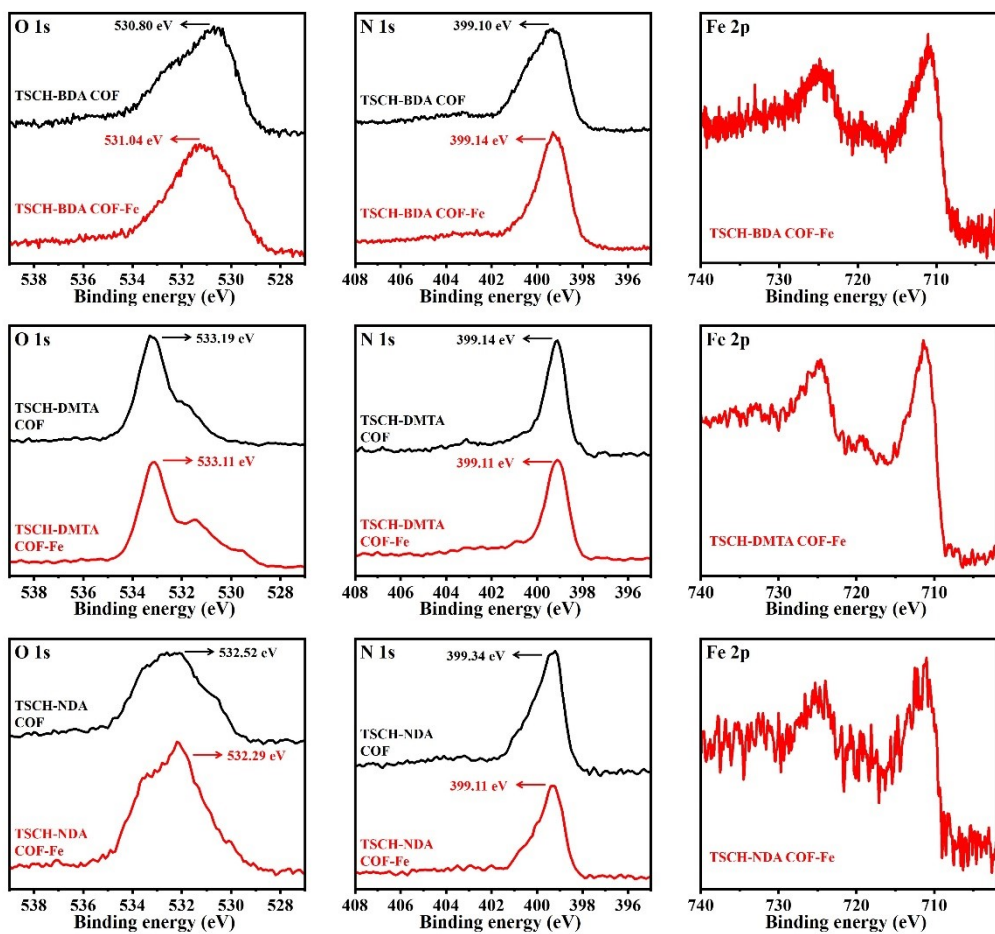


Figure S6. XPS spectra of the O1s, N1s and Fe 2p region of TSCH-COFs before and after treated with Hg^{2+} .

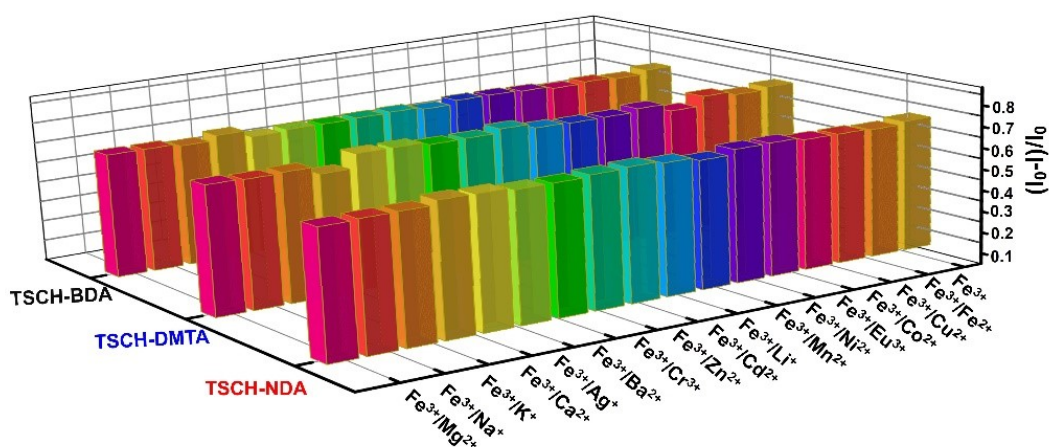


Figure S7. Detection properties of TSCH-COFs for different metal ions.

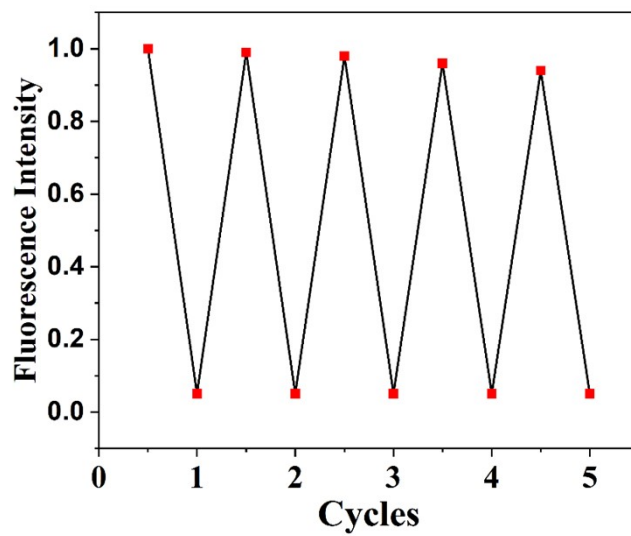


Figure S8. Quenching and recovery tests of TSCH-BDA COF for Fe^{3+} .

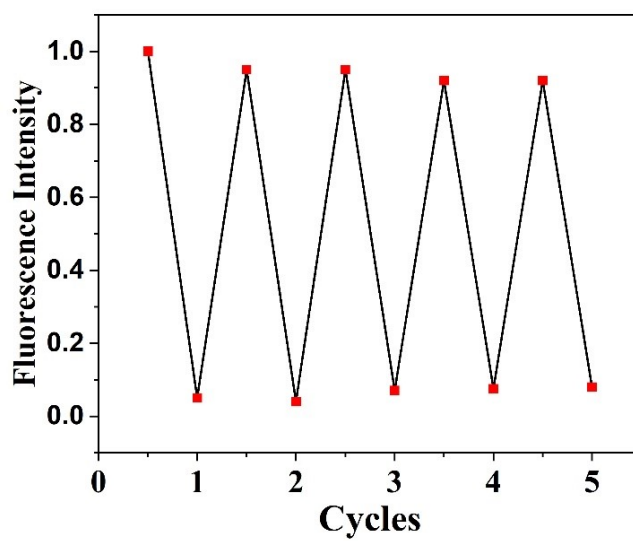


Figure S9. Quenching and recovery tests of TSCH-DMTA COF for Fe^{3+} .

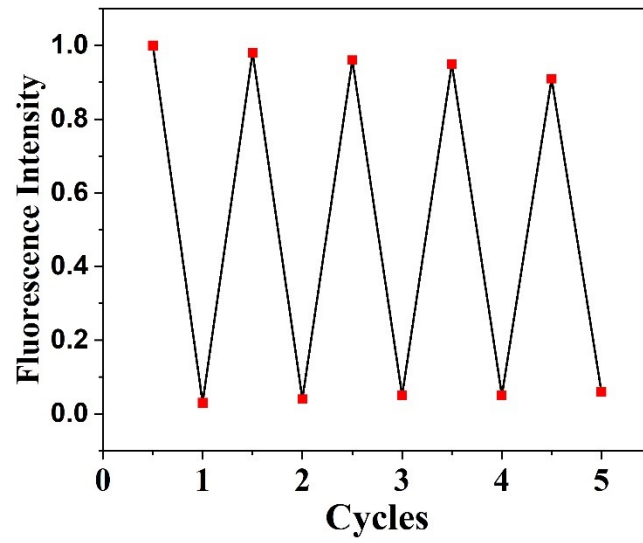


Figure S10. Quenching and recovery tests of TSCH-NDA COF for Fe^{3+} .

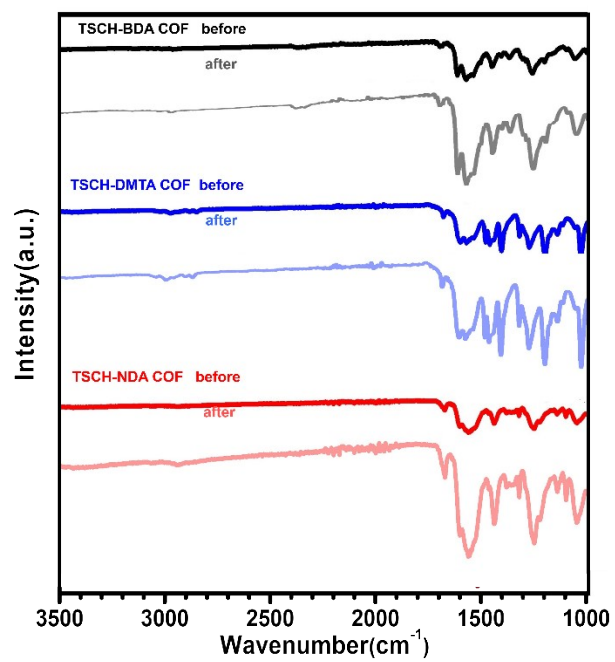


Figure S11. FT-IR spectra of TSCH COFs before and after treated with Fe^{3+} .

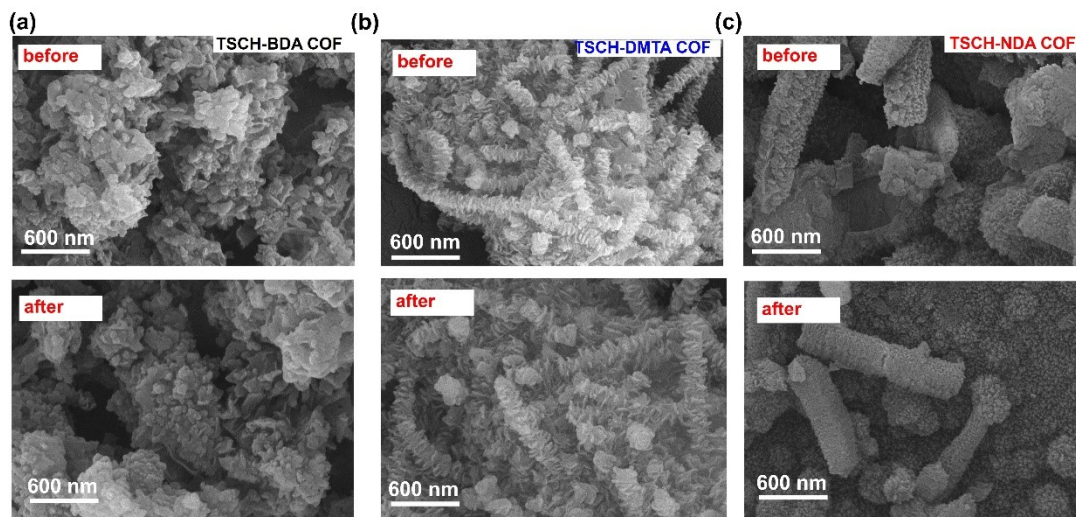


Figure S12. SEM images of TSCH COFs before and after treated with Fe³⁺.

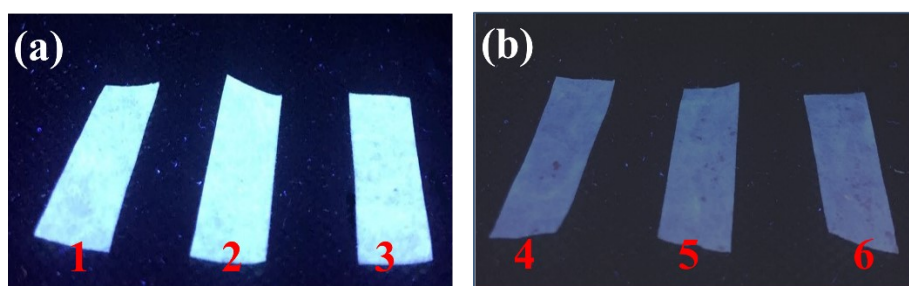


Figure S13. Photos of TSCH-COFs deposited on the filter paper before (a) and after (b) treated with Fe³⁺ taken under a UV lamp with $\lambda_{\text{ex}} = 365 \text{ nm}$ (1 is TSCH-BDA COF sensor paper, 2 is TSCH-DMTA COF sensor paper, 3 is TSCH-NDA COF sensor paper, 4 is TSCH-BDA COF sensor paper treated with Fe³⁺, 5 is TSCH-DMTA COF sensor paper treated with Fe³⁺ and 6 is TSCH-NDA COF sensor paper treated with Fe³⁺).

Table S1 – S4.**Table S1.** Comparison of COFs used for Fe³⁺ ions recognition.

COFs	LOD (M)	Ref.
DPA-CTF	5.8×10 ⁻⁶ M	5
TT-COF	8.4×10 ⁻⁵ M	6
Bth-Dma COFs	1.7×10 ⁻⁷ M	7
PI-COF 201	1.3×10 ⁻⁷ M	8
COF-TT	3.69 × 10 ⁻⁴ M	9
HM-COF	1.7×10 ⁻⁷ M	10
CZ-DHZ-COF	3.89×10 ⁻⁷ M	11
TSCH-BDA COF	9.6×10 ⁻⁸ M	This work
TSCH-DMTA COF	1.6×10 ⁻⁷ M	This work
TSCH-NDA COF	2.1×10 ⁻⁷ M	This work

Table S2. Fractional atomic coordinates for TSCH-BDA COF: space group P 6/m; a=b=29.367 Å, c=3.512 Å;
alpha=beta=90°, gamma=120°

Atom	x(Å)	y(Å)	z(Å)
C1	1.29261	1.67899	0
C2	1.28049	1.62605	0
C3	1.41492	1.64418	0
N4	1.40448	1.59481	0
O5	1.30885	1.56563	0
C6	1.46737	1.89343	0
N7	1.41724	1.85859	0
C8	1.48378	1.94668	0
C9	1.53704	1.98411	0
C10	1.44693	1.9634	0
H11	1.45552	1.67513	0
H12	1.36366	1.56689	0
H13	1.49641	1.88056	0
H14	1.56571	1.97113	0
H15	1.40572	1.9337	0

Table S3. Fractional atomic coordinates for TSCH-DMTA COF without hydrogen atoms: space group P 6/m;**a=b=29.687 Å, c=3.430 Å; alpha=beta=90°, gamma=120°.**

Atom	x(Å)	y(Å)	z(Å)
C1	-0.71792	-0.37186	0
C2	-0.6794	-0.38459	0
O3	-0.56415	-0.25628	0
C4	-0.58962	-0.3588	0
N5	-0.60235	-0.41005	0
N6	-0.56382	-0.42279	0
O7	-0.47404	-0.39699	0
C8	-0.48677	-0.44825	0
C9	-0.53803	-0.48678	0
C10	-0.57656	-0.47404	0
C11	-0.55076	-0.53803	0
C12	-0.42278	-0.35847	0

Table S4. Fractional atomic coordinates for TSCH-NDA COF: space group P 6/m; **a=b=33.463 Å, c=3.525 Å;**

alpha=beta=90°, gamma=120°.

Atom	x(Å)	y(Å)	z(Å)
C1	1.65158	1.28495	0
C2	1.70002	1.31825	0
C3	1.59953	1.36151	0
N4	1.61151	1.4064	0
O5	1.6959	1.42531	0
C6	1.59694	1.46529	0
N7	1.58055	1.42002	0
C8	1.5676	1.4844	0
C9	1.58681	1.53293	0
C10	1.55856	1.55241	0
C11	1.50995	1.52462	0
C12	1.51913	1.45625	0
H13	1.56268	1.33573	0
H14	1.64802	1.42965	0
H15	1.63485	1.48894	0
H16	1.62459	1.5551	0
H17	1.57383	1.59014	0
H18	1.50416	1.41858	0

Supplementary References:

1. J. Ning, Y. Gao, X. Cao, H. Wei, B. Wang and L. Hao, *J. Ener. Chem.*, 2022, **65**, 490-496.
2. S. H. M. Mehr, H. Oshima, V. Carta, B. O. Patrick, N. G. White and M. J. MacLachlan, *Org. Biomol. Chem.*, 2017, **15**, 8418-8424.
3. O. Papaianina, V. A. Akhmetov, A. A. Goryunkov, F. Hampel, F. W. Heinemann and K. Y. Amsharov, *Angew. Chem.*, 2017, **56**, 4834-4838.
4. H. Singh, M. Devi, N. Jena, M. M. Iqbal, Y. Nailwal, A. De Sarkar and S. K. Pal, *ACS Appl. Mater. Inter.*, 2020, **12**, 13248-13255.
5. H. Hong, N. Wu, M. Han, Z. Guo, H. Zhan, S. Du and B. Chen, *Mater. Chem. Front.*, 2021, **5**, 6568-6574.
6. T. Zhang, A. Salah, S. Chang, Z. Zhang and G. Wang, *Tetrahedron*, 2021, **96**, 132405.
7. G. Chen, H. H. Lan, S. L. Cai, B. Sun, X. L. Li, Z. H. He, S. R. Zheng, J. Fan, Y. Liu and W. G. Zhang, *ACS Appl. Mater. Inter.*, 2019, **11**, 12830-12837.
8. T. Wang, R. Xue, H. Chen, P. Shi, X. Lei, Y. Wei, H. Guo and W. Yang, *New J. Chem.*, 2017, **41**, 14272-14278.
9. M. Li, Z. Cui, S. Pang, L. Meng, D. Ma, Y. Li, Z. Shi and S. Feng, *J. Mater. Chem. C*, 2019, **7**, 11919-11925.
10. R. Xue, H. Gou, Y.-P. Zheng, Y.-S. Liu, H.-H. Rao and G.-H. Zhao, *Optik*, 2021, **242**, 167184.
11. W. Gong, C. Liu, H. Shi, M. Yin, W. Li, Q. Song, Y. Dong and C. Zhang, *J. Mater. Chem. C*, 2022, **10**, 3553-3559.