

Supporting Information

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

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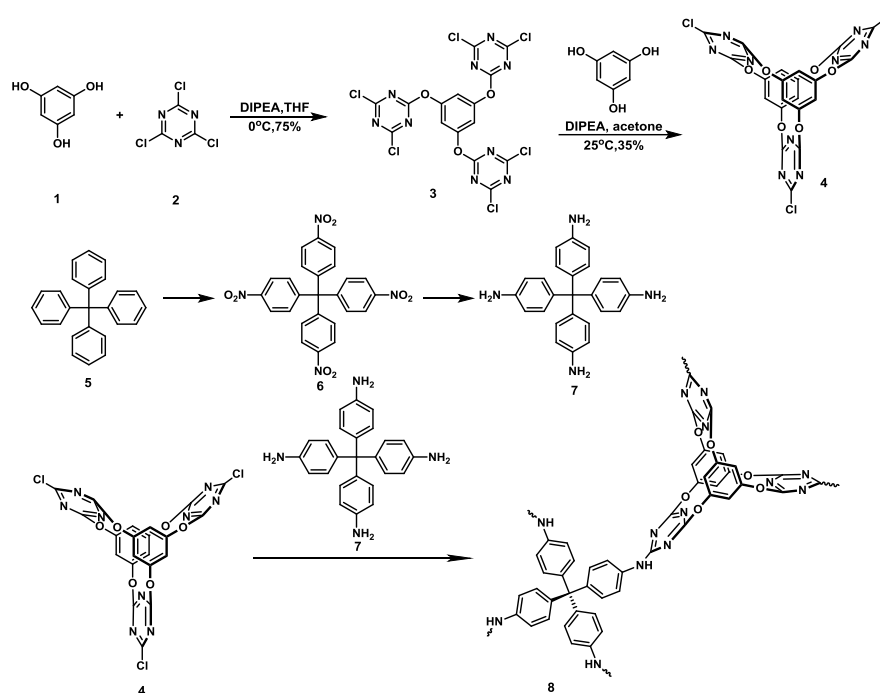
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Section I. Materials and methods

All reagents used in the syntheses were of analytical grade and used without further purification. Extra dry DMAc were purchased from Fisher Scientific. 1, 4-Dioxane and THF were freshly distilled over sodium and benzophenone ketyl. Acetone was dried with anhydrous MgSO₄, and then distilled. All the purification processes were in protection of N₂. Solutions of all cations and anions were made by using high purity metal salt reagents and deionized water.

Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Impact 410 FTIR spectrometer. The ¹³C solid-state NMR spectroscopy was recorded on a Varian Infinity-plus 400 MHz spectrometer. Powder X-ray diffraction (PXRD) was performed with a Rigaku D/MAX2550 diffractometer. Scanning electron microscopy (SEM) was performed on JSM-6700F. Transmission electron microscopy (TEM) was performed on a FEI Tecnai G2 S-Twin with a field emission gun operating at 200 kV. Images were acquired digitally on a Gantan multiple CCD camera. CO₂ gas sorption experiments were carried out on a Micrometrics ASAP 2020 M volumetric gas sorption. Thermogravimetric analysis (TGA) measurements were performed on TGA Q500 instrument. The luminescence spectra were recorded on an Edinburgh Instruments FLS920 spectrofluorometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 X-ray photoelectron spectroscopy, using Mg K α X-ray as the excitation source. The UV-vis absorption spectrum was performed on a HITACHI UV-2450.

Section II. Synthetic Procedures



Preparation of 3: 3 was prepared according to the literature with minor modifications.^[S1] A mixture of phloroglucinol 1 (0.63 g, 5 mmol) and DIPEA (2.42 g, 18.8 mmol) in THF (30 mL) was added dropwisely over a period of 20 min to an ice-cooled and well-stirred solution of cyanuric chloride 2 (4.15 g, 22.5 mmol) in THF (50 mL). The resulting mixture, which contained the precipitates formed from the reaction, was stirred continuously for 3 h at 0 °C. After filtration and concentration, residues were subjected to chromatography on a silica gel (100-200 mesh) column eluting with a mixture of petroleum ether and acetone. Pure 3 was obtained as white solid (yield: 75%). M.p. 240 - 142 °C; ¹H NMR (CDCl₃, 300 MHz): δ=7.17 ppm (s, 3H); ¹³C NMR (CDCl₃, 75 MHz): δ=173.5, 170.4, 151.7, 113.8 ppm; IR (KBr) ν =1613, 1530 cm⁻¹; MS (EI): m/z (%): 573 (4), 571 (8), 569 (10), 567 (5) [M]⁺, 538 (17), 537 (10), 536 (57), 535 (12), 534 (100), 533 (10), 532 (57); elemental analysis calcd (%) for C₁₅H₃N₉O₃Cl₆: C 31.63, H 0.53, N 22.12; found: C 31.74, H 0.84, N 22.22.

cage molecule 4:^[S2] Solution of 1 (0.126 g, 1 mmol) in THF (50 mL) and 3 (0.57 g, 1 mmol) in THF (50 mL) was added dropwisely at the same rate to a solution of DIPEA (0.464 g, 3.6 mmol) in acetone (100 mL) over 4 h at room temperature. After addition, the resulting mixture was stirred at room temperature for 4 days. Solvent was removed and residues were subjected to chromatography on a silica gel (100 - 200 mesh) column eluting with a mixture

of petroleum ether and acetone. Pure cage molecule **4** was obtained as white solid (a yield rate of 35%). M.p. >300 °C; ¹H NMR (CDCl₃, 300 MHz): d=6.69 ppm (s, 6H); ¹³C NMR (CDCl₃, 75 MHz): d=175.1, 172.7, 153.1, 115.1 ppm; IR (KBr) ν =1614, 1550 cm⁻¹; MS (EI): m/z (%): 591 (4), 590 (28), 589 (28), 588 (19), 587 (96), 586 (22), 585 (100) [M]⁺; HRMS: m/z calcd for C₂₁H₆N₉O₆Cl₃: 584.9507; found: 584.0513.

Preparation of 6: **6** was prepared according to the literature with minor modifications.^[S3] To **5** (15 g, 46.8mmol) 75ml of fuming nitric was added in portions at -10 °C with vigorous stirring. To this mixture 25ml of acetic anhydride and 50ml of glacial acetic acid was slowly added and stirred for about 15 minutes. Finally the reaction mixture was diluted with 100ml of glacial acetic acid. The resulting yellow solid was washed with acetic acid and methanol. The crude product was recrystallized with DMF to obtain yellow crystals of **6** (8.9 g, 38.0% yield). ¹H NMR (300 MHz, *d*₆DMSO) 8.51 (d, 8H, Ar-H, *J* = 9.0 Hz), 7.85 (d, 8H, Ar-H, *J* = 8.9 Hz) δ; ¹³C NMR δ 146.6, 136.9, 132.1, 113.6, 62.2; HRMS calculated for C₂₅H₁₆N₄O₈ 500.0968, found 500.0969.

Preparation of 7: To **6** (1.5 g, 2.99mmol) in 100ml of THF, 2.00 g (excess) of hydrazine monohydrate and ~10g of Raney-nickel were added and refluxed for about 3 hours. The mixture was hot filtered and washed with ethanol. The solvent evaporated and the residue was washed with ethanol and dried to obtain 0.7 g of **7** in 61.3% yield. ¹H NMR (300 MHz, *d*₆-DMSO) δ 6.65 (d, 8H, Ar-H, *J* = 8.7 Hz), 6.35 (d, 8H, ArH, *J* = 8.7 Hz), 4.80 (s, 8H, Ar-NH₂); ¹³C NMR δ 149.9, 145.0, 130.4, 122.7, 64.2; HRMS calculated for C₂₅H₂₄N₄ 380.2001, found 380.2004.

Section III. Characterization Details

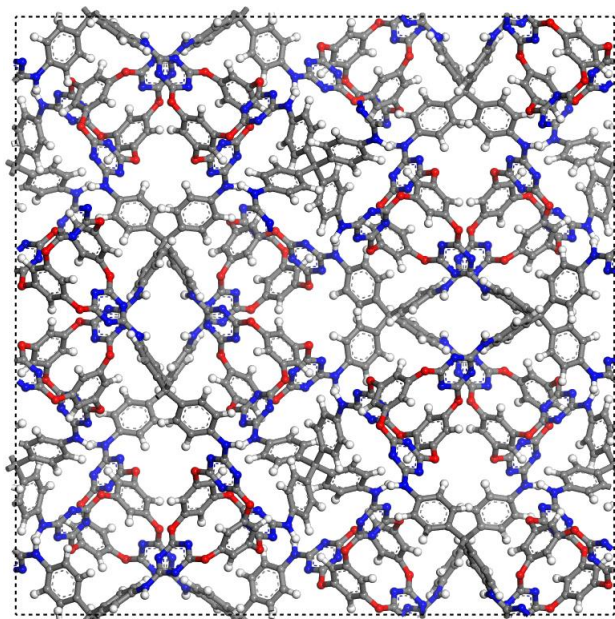


Fig. S1 Simulated structure of COF-TT (structure is based on field-force calculation and crystal lattice parameters; C gray, O red, N blue, H white).

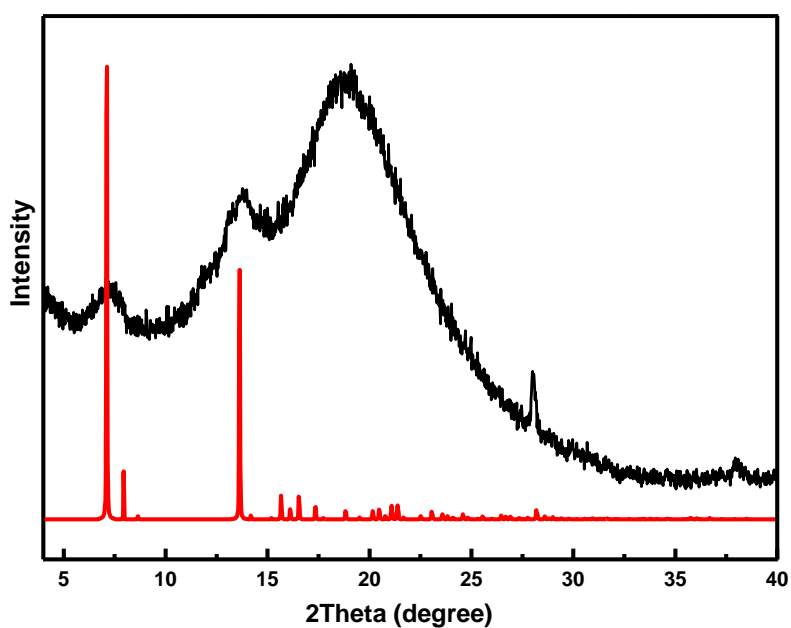


Fig. S2 Experimental PXRD patterns (black) and calculated PXRD patterns (purple) from the simulated structure of COF-TT.

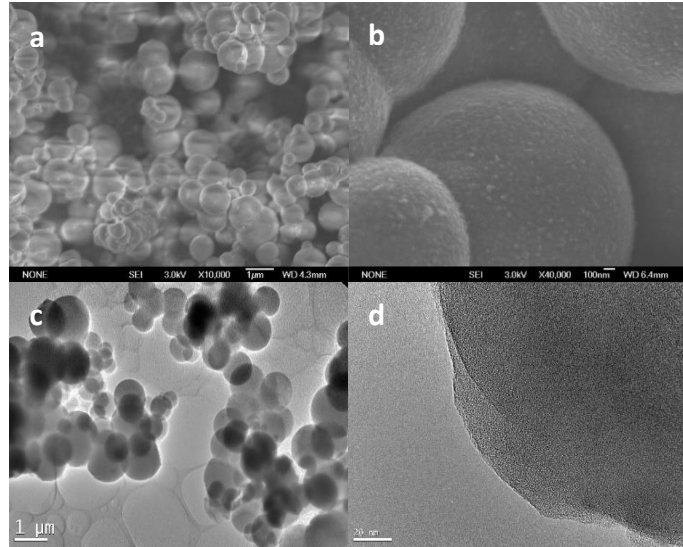


Fig. S3 (a, b) SEM images of COF-TT; (c, d) TEM images of COF-TT.

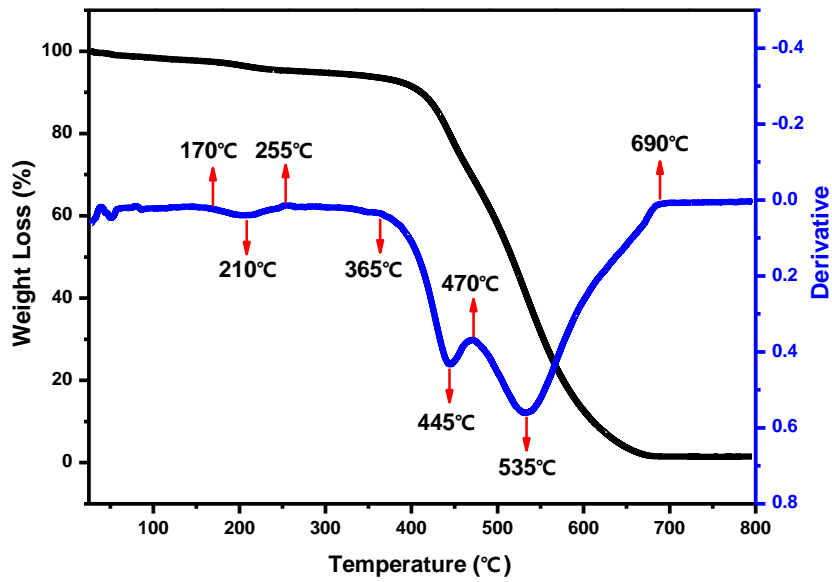


Fig. S4 TGA trace for an activated sample of COF-TT under air atmosphere.

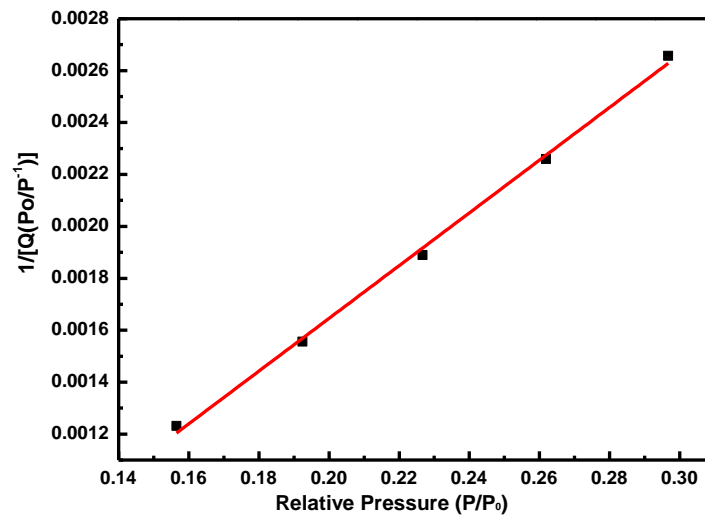


Fig S5. The BET plots for COF-TT.

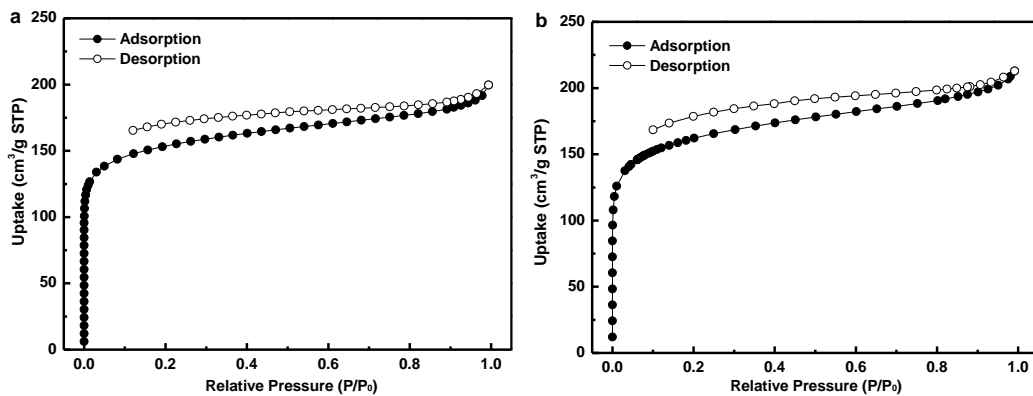


Fig. S6. N₂ sorption isotherms at 77 K (a) and CO₂ sorption isotherms at 195 K (b) of COF-TT.

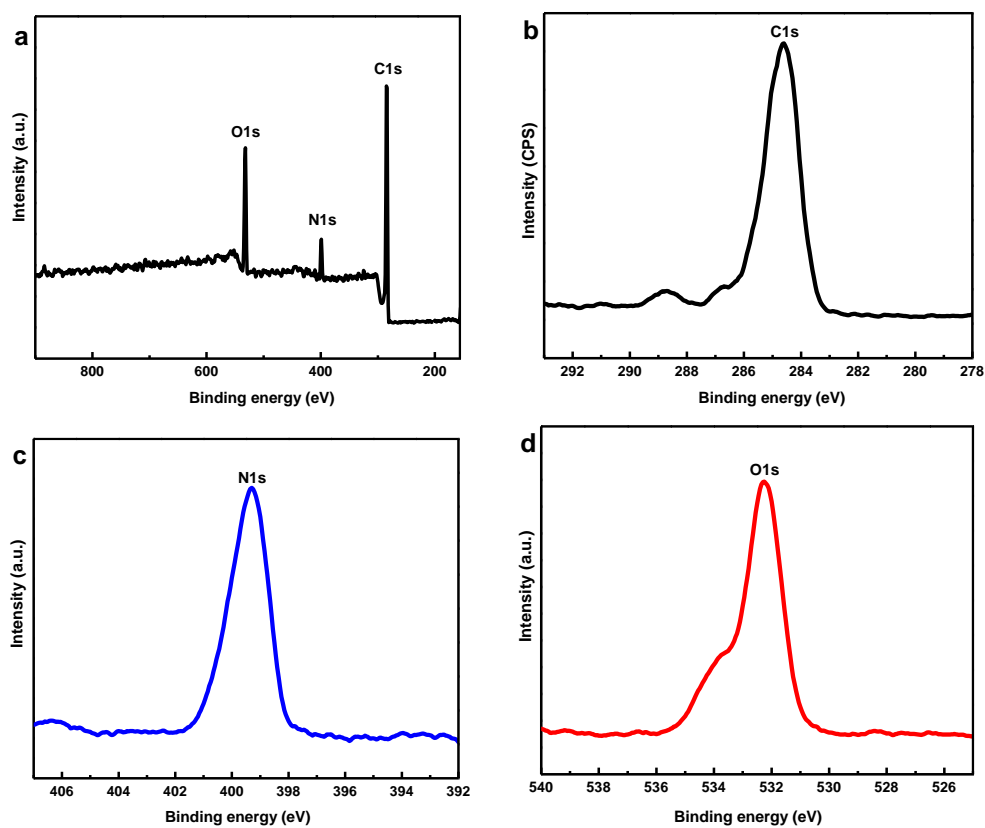


Fig. S7 (a) XPS broad spectral survey and high-resolution XPS spectra of COF-TT: (b) C 1s, (c) N 1s, and (d) O 1s.

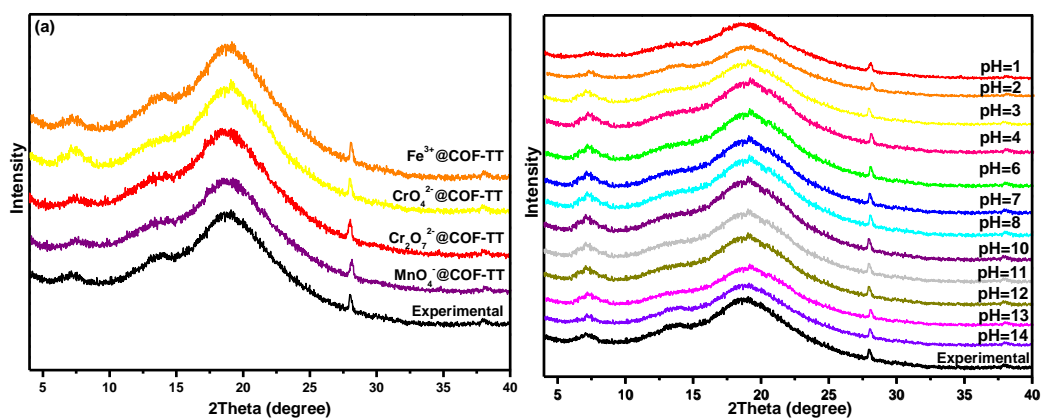


Fig. S8 (a) PXRD patterns for COF-TT after soaking in different quenching agents; (b) The PXRD patterns of COF-TT samples after immersed into different pH aqueous solutions for 12 h.

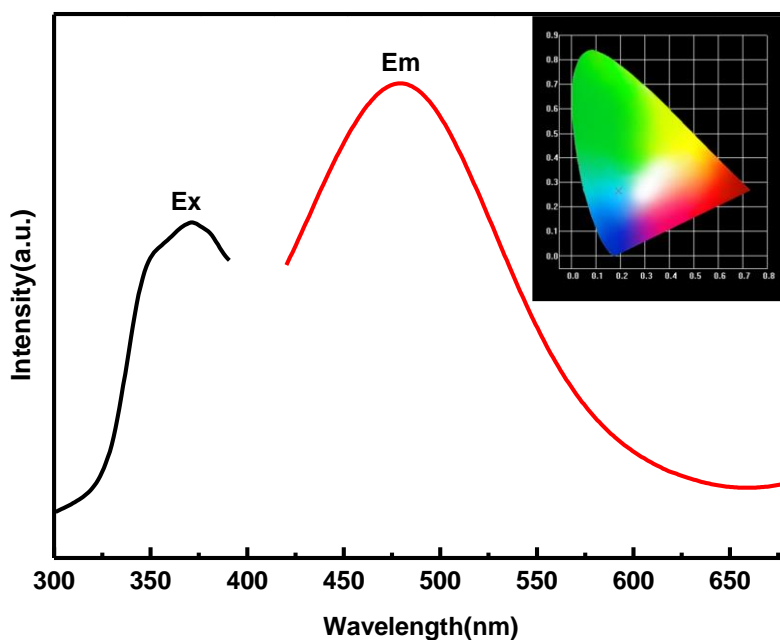


Fig. S9 Excitation (black) and emission (red) spectra for COF-TT. Inset: Corresponding CIE chromaticity diagram for COF-TT.

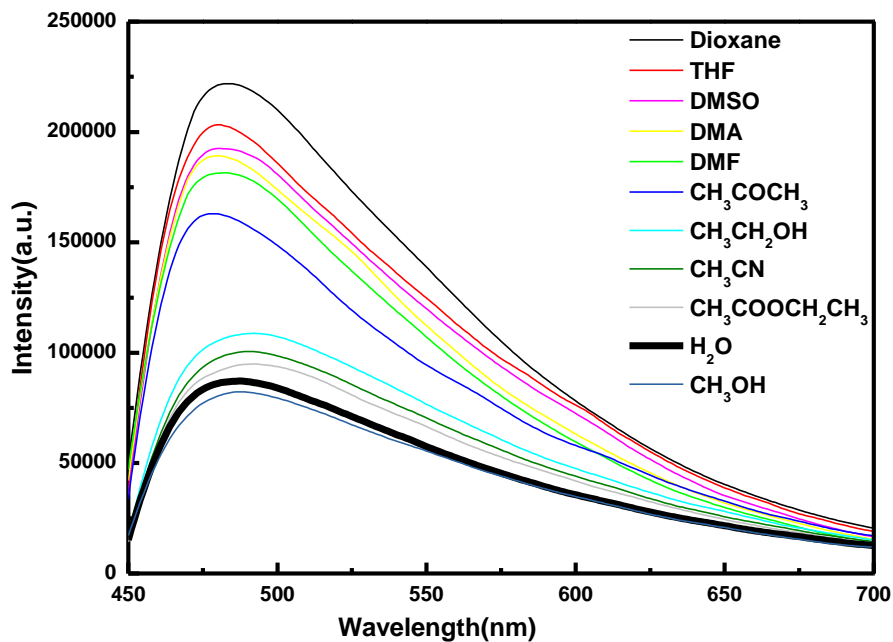


Fig. S10 Emission spectra of COF-TT in different solvents (Ex at 370).

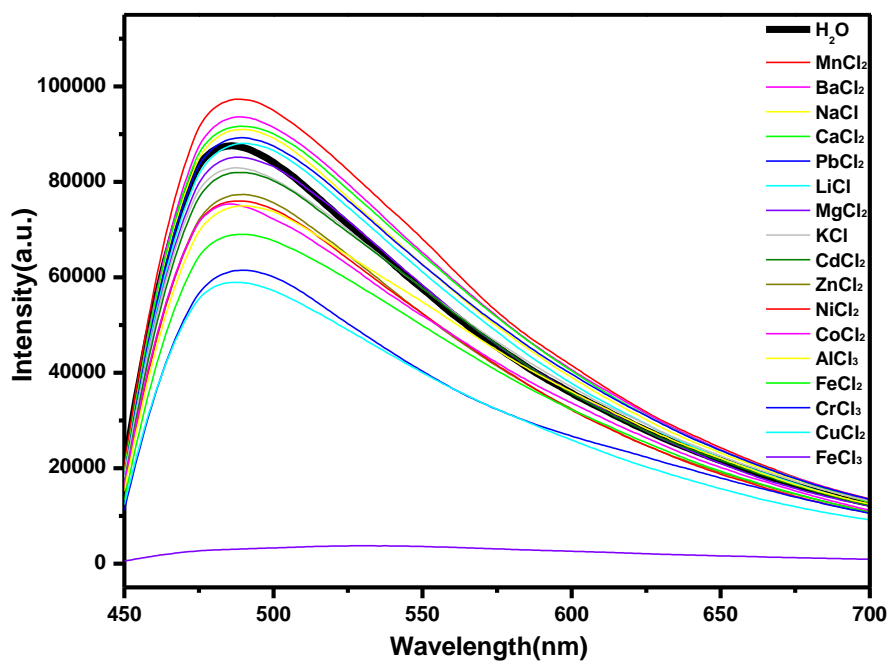


Fig. S11 Luminescent spectra of COF-TT in acidic aqueous solutions with diverse metal ions.

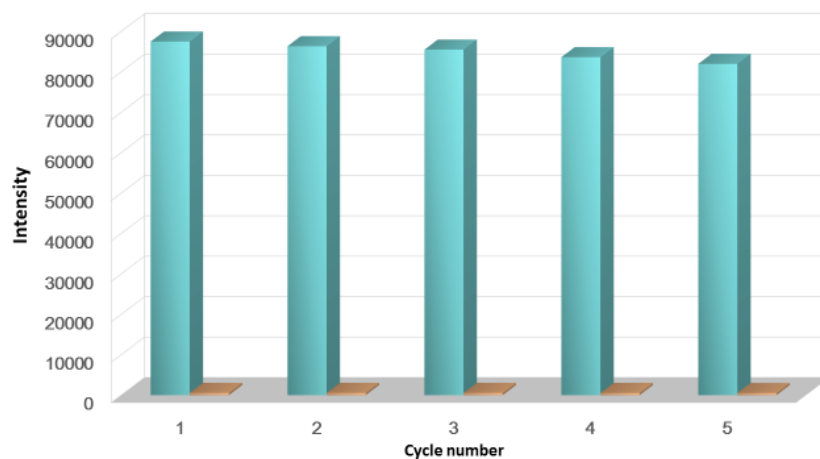


Fig. S12 Cycling tests of COF-TT in Fe³⁺ ions.

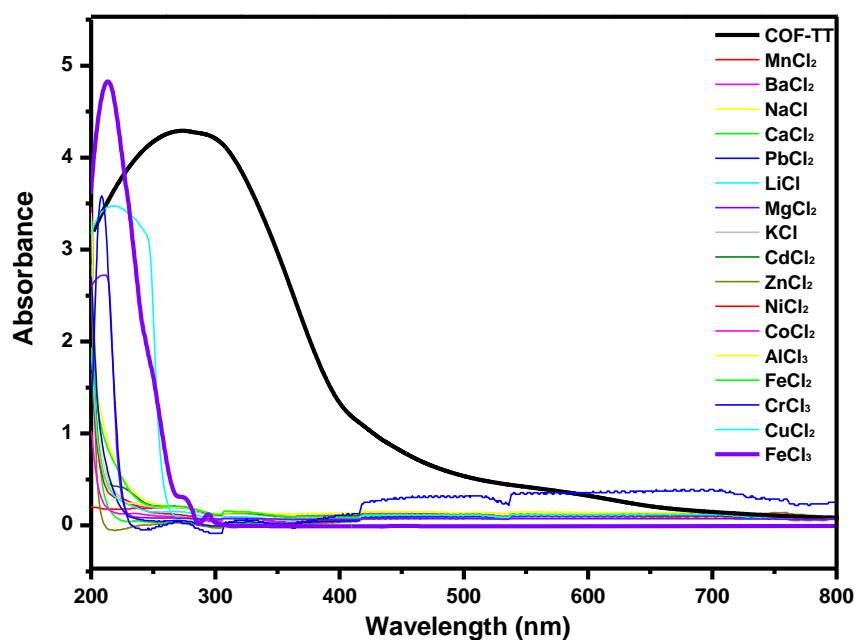


Fig. S13 UV-vis absorption spectra for COF-TT in various cations.

Table S1 Relative energy in kcal/mol for different cationic complexes in water and in gas phase.

Structure	In water (kcal/mol)	In gas phase(kcal/mol)
Figure 8a	-10.1	-24.0
Figure 8b	-21.8	-36.2
Figure 8c	-2.0	14.7

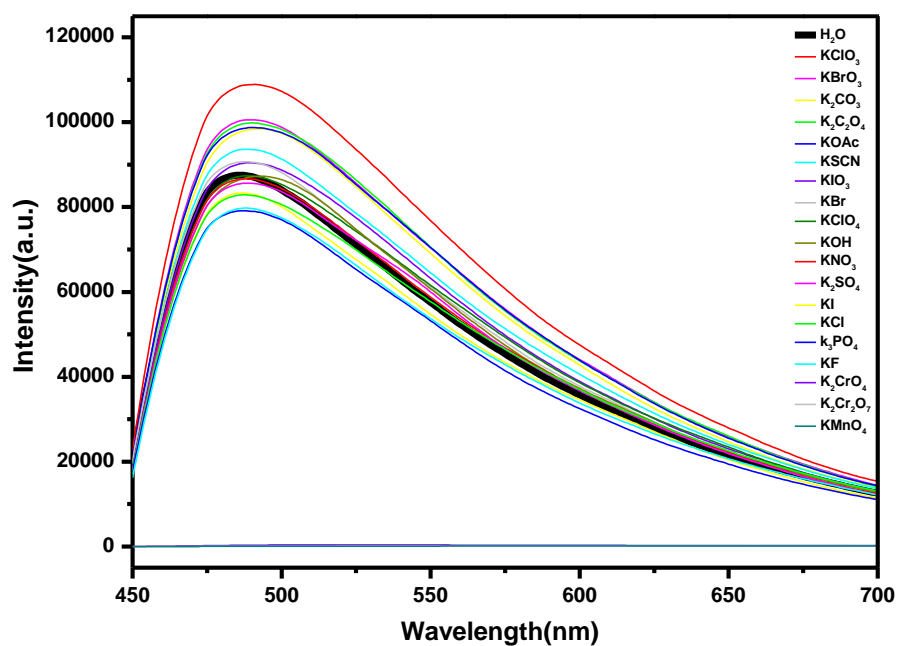


Fig. S14 UV-vis absorption spectra for COF-TT in diverse anions.

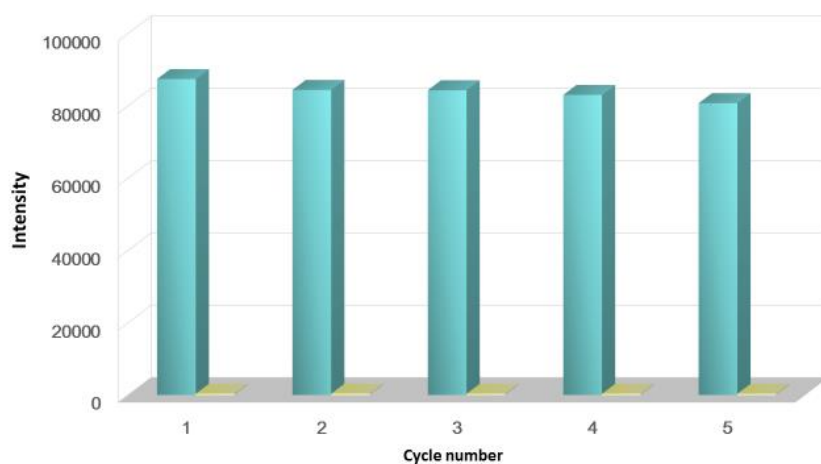


Fig. S15 Cycling tests of COF-TT in CrO_4^{2-} ions.

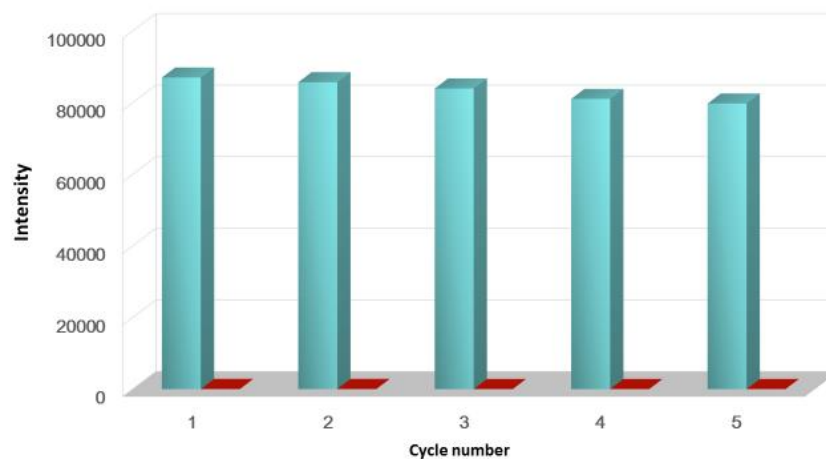


Fig. S16 Cycling tests of COF-TT in $\text{Cr}_2\text{O}_7^{2-}$ ions.

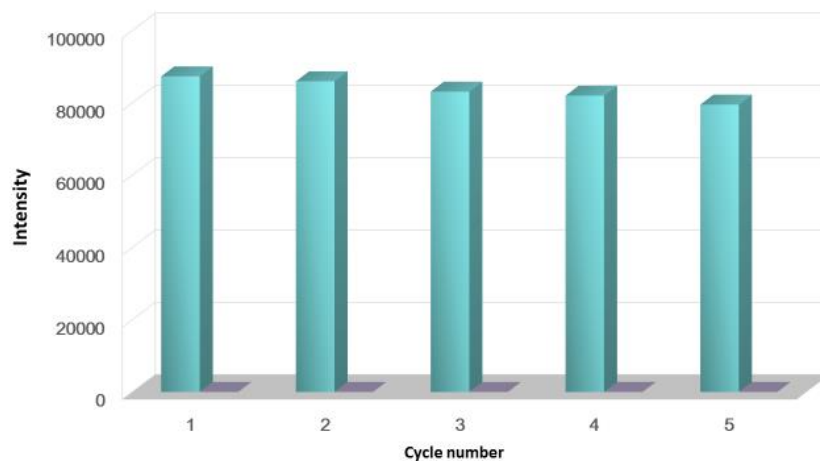


Fig. S17 Cycling tests of COF-TT in MnO_4^- ions.

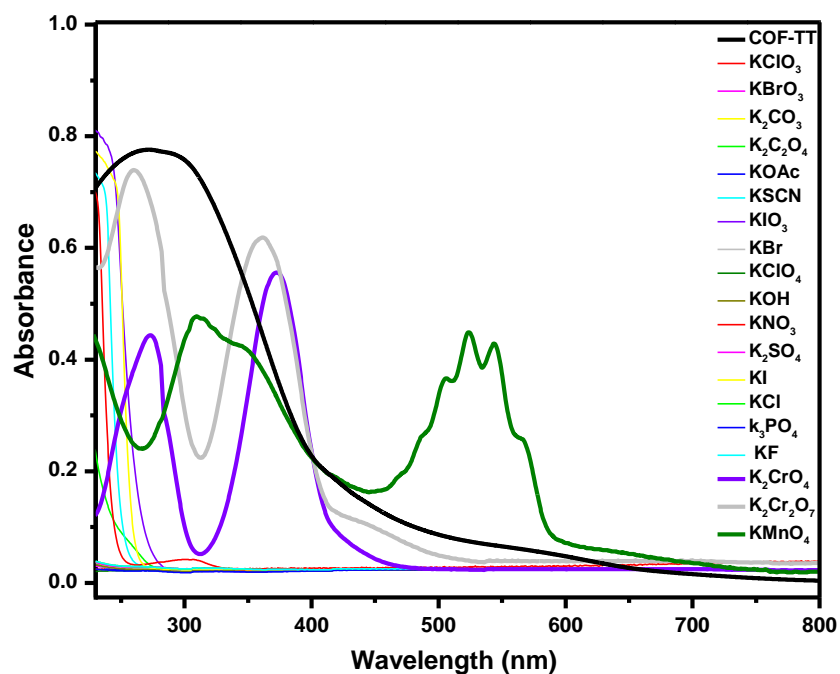


Fig. S18 The UV-vis absorption spectra for COF-TT in diverse anions.

Table S2 Standard deviations for ten replicated luminescence measurements of blank solutions.

Test	fluorescence intensity (nm)
1	87472
2	87471
3	87470
4	87470
5	87470

6	87470
7	87472
8	87469
9	87468
10	87467
average	87470
standard deviation (σ)	1.60

Section VI. Copies of ^1H and ^{13}C NMR for new compounds

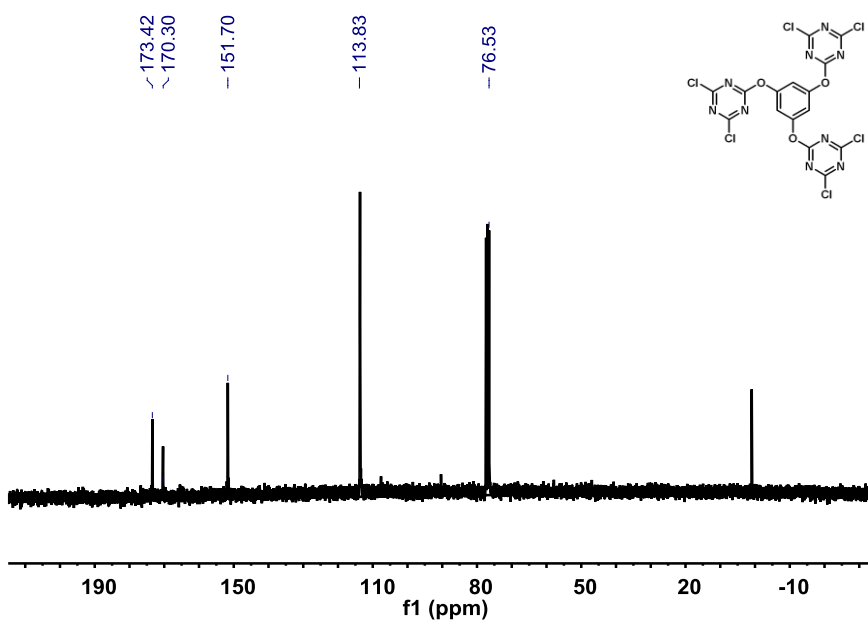
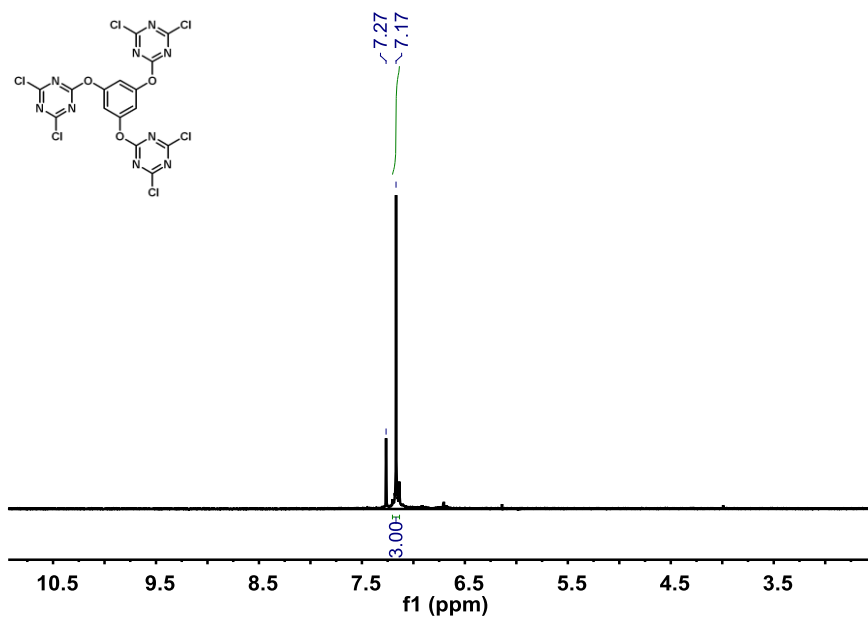


Fig. S19 ^1H and ^{13}C NMR of **3** in CDCl_3 .

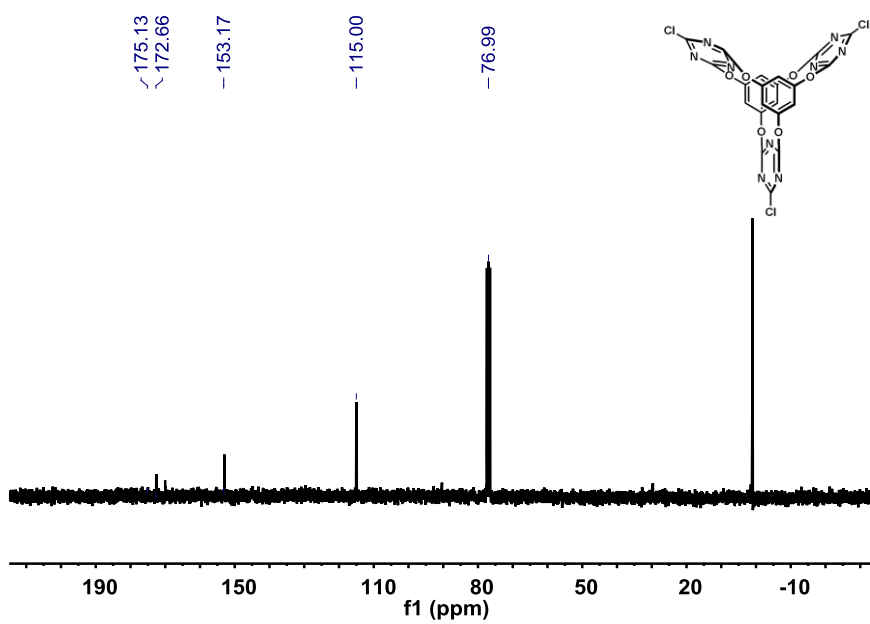
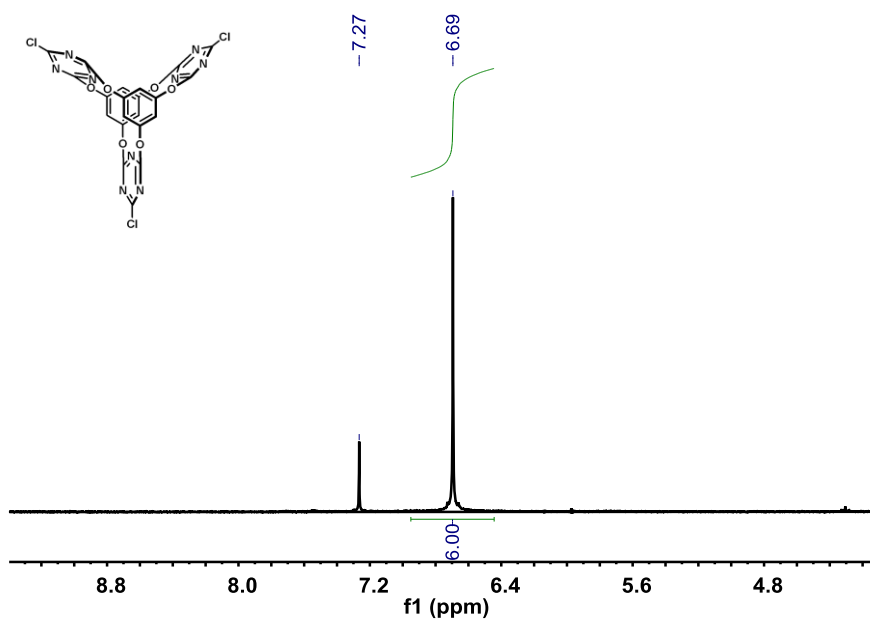


Fig. S20 ^1H and ^{13}C NMR of **4** in CDCl_3 .

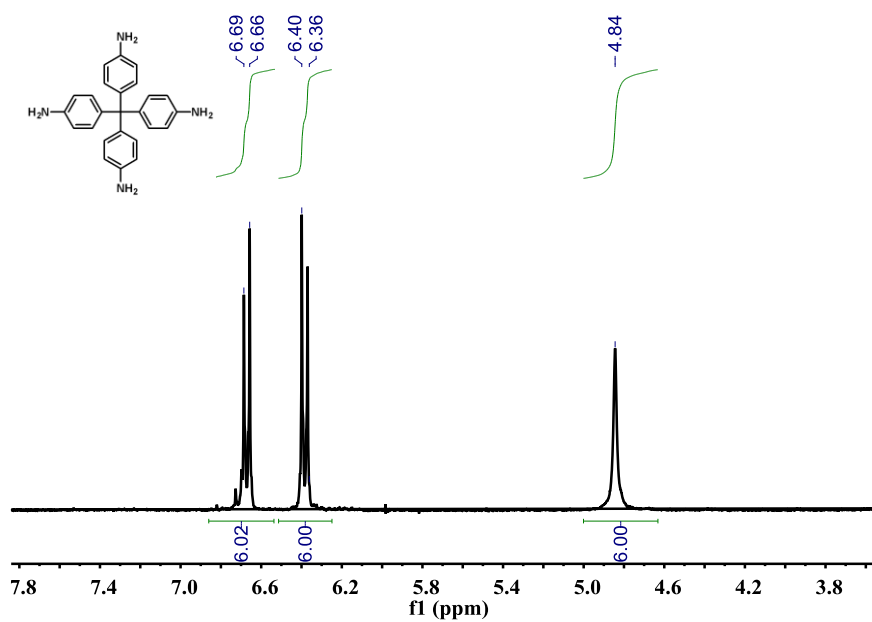
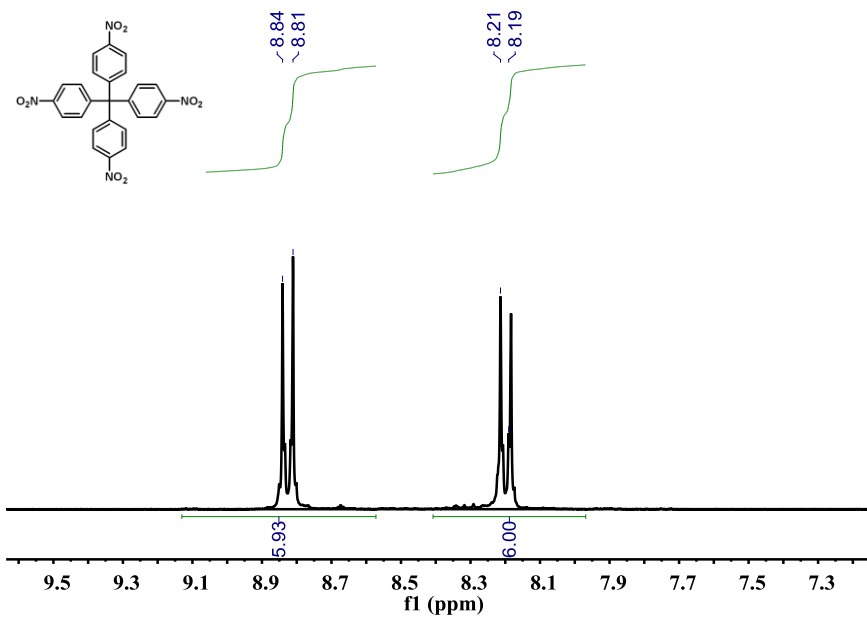


Fig. S21 ^1H of 6 and ^1H of 7 NMR in DMSO.

References

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3. Ganesan, P. Y., X.; Loos, L.; Savenije, T. J.; Abellon, R. D.; Zuilhof, H.; Sudholter, E. J. R., *J. Am. Chem. Soc.* **2005**, *127*, 14530.