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A water-stable Zn_4O-based MOF decorated with carbazolyl chromophores for multi-responsive fluorescence sensing of Fe^{3+}, $Cr_2O_7^{2-}$ and nitro-compounds

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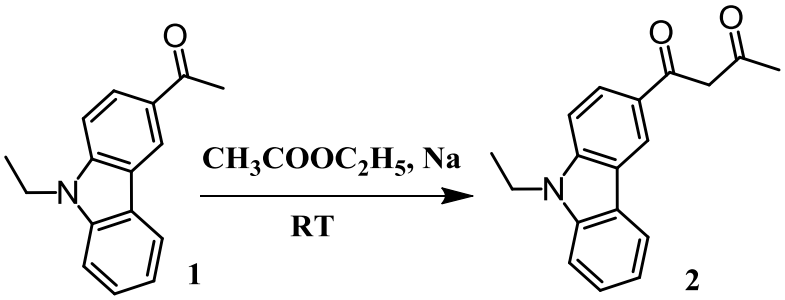
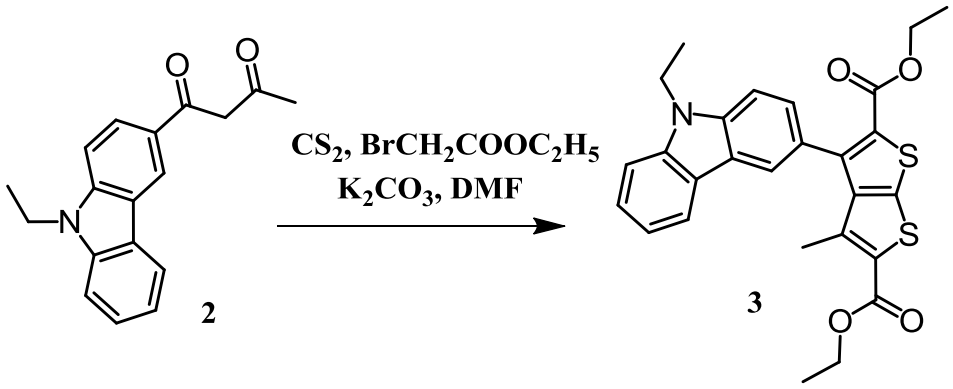
I. Experimental section

Synthesis of H_2ECMTDC

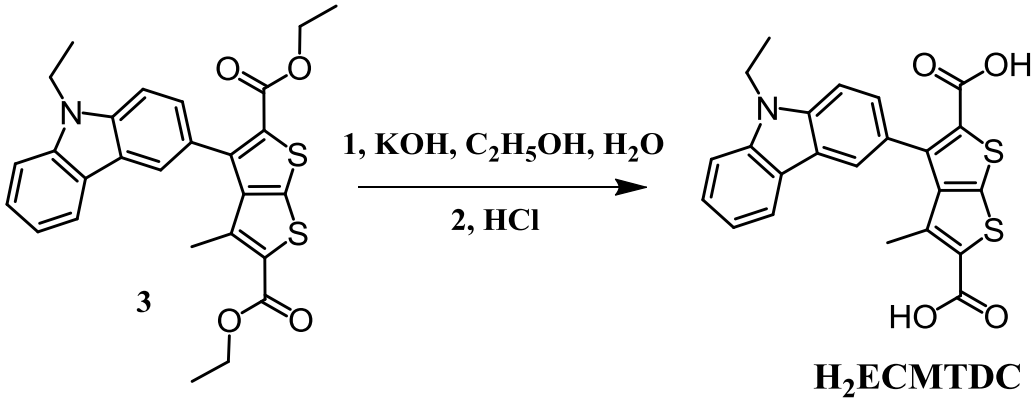


1-(9-ethyl-9*H*-carbazol-3-yl) butane-1,3-dione (2). Compound 2 was synthesized according to a similar route from the reference.[S1] Compound 1 (2.37 g, 10 mmol) and anhydrous ethyl acetate (20 mL) were added to the three-neck flask (100mL) with the ice bath under N_2 protection, sodium (0.56 g, 25 mmol) was cut into small pieces and added in batches, then stirring reaction at room temperature for 4 h. After the reaction, 5 mL of ethanol was added to make the remaining sodium reaction completely. The reaction was then quenched with 20 mL water and adjusted for pH to neutral by 1M of HCl. The reaction mixture was extracted with diethyl ether, and the organic layer was washed twice with brine and dried with anhydrous Na_2SO_4, then ethyl acetate was removed out by rotary evaporation. The obtained crude product was recrystallized with petroleum ether/ethyl acetate (12/1) mixed solvent, yellow product compound **1** in 72% yield. FT-IR: 3047(m), 2976(m), 2927(m), 1720(m), 1591(vs), 1469(vs), 1355(s), 1381(s), 1282(w), 777(s), 744(s). ^{1}H NMR (500 MHz, Chloroform-*d*): δ 16.53 (s, O(18)-H, 1H), 8.69 (dd, *J* = 1.8, 0.6 Hz, Ar(C10)-H, 1H), 8.14 (dt, *J* = 7.8, 1.0 Hz, Ar(C12)-H, 1H), 8.03 (dd, *J* = 8.7, Ar(C13)-H, 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.1, 1.2 Hz, Ar(C4)-H, 1H), 7.45-7.35 (m, Ar(C2, C3)-H, 2H), 7.29 (ddd, *J* = 7.9, 7.1, 1.0 Hz, Ar(C1)-H, 1H), 6.31 (s, C(17)-H, 1H), 4.37 (q, *J* = 7.2 Hz, C(14)-H, 2H), 2.21 (s, C(20)-H, 3H), 1.45 (t, *J* = 7.3 Hz, C(15)-H, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.62 (C16), 185.67 (C18), 142.45 (C6), 140.53 (C8), 126.36 (C11), 125.78 (C7), 125.01 (C13), 123.06 (C5), 120.62 (C1), 120.33 (C12), 119.85 (C3), 108.90 (C4), 108.21 (C2), 95.90 (C17), 37.73 (C14), 25.11 (C20), 13.73 (C15).



3-(9-ethyl-9H-carbazol-3-yl)-4-methylthieno[2,3-b]thiophene-2,5-dicarboxylate (3). Compound 3 was synthesized according to a similar route from the references.[S2, S3] A solution of compound 2 (2.79 g, 10 mmol), anhydrous potassium carbonate (13.82 g, 100 mmol) and DMF (10 mL) was added into a flask with three necks (100 mL) followed by 0.72 mL carbon disulfide (12 mmol) were added dropwise under vigorous stirring. After 30 min, the mixture was cooled to 0 °C and 2.78 mL Ethyl bromoacetate (25 mmol) was added slowly. The mixture was then stirred at room temperature for 8 h. After this reaction was completed, a large amount of ice cold water was poured, and the precipitated white solid was obtained. The crude product was recrystallized from ethyl acetate and ethanol to afford pure compound **3** in 60% yield. FT-IR: 2977(w), 2923(w), 2854(w), 1681(vs), 1622(s), 1467(s), 1292(s), 1083(vs), 991(vs), 810(m). ^{1}H NMR (500 MHz,

Chloroform-*d*) δ 8.09 (t, *J* = 5.6 Hz, Ar(C11, C15)-H, 2H), 7.59-7.42 (m, Ar(C12, C29, C31, C32)-H, 4H), 7.27 (dd, *J* = 9.1, 5.3 Hz, Ar(C30)-H, 1H), 4.45 (q, *J* = 7.1 Hz, C(22)-H, 2H), 4.36 (q, *J* = 7.1 Hz, C(24)-H, 2H), 4.17 (q, *J* = 7.1 Hz, C(33)-H, 2H), 2.16 (s, C(9)-H, 3H), 1.53 (t, *J* = 7.1 Hz, C(23)-H, 3H), 1.39 (t, *J* = 7.0 Hz, C(25)-H, 3H), 1.11 (t, *J* = 7.1 Hz, C(34)-H, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 162.51 (C16), 161.84 (C17), 147.41 (C13), 144.64 (C27), 144.14 (C4), 141.46 (C3), 140.37 (C1), 139.74 (C7), 131.94 (C2), 130.20 (C6), 126.84 (C11), 125.85 (C12), 124.59 (C10), 122.96 (C14, C28), 122.54 (C14, C28), 121.17 (C29), 120.53 (C31), 118.99 (C15), 108.60 (C30), 107.74 (C32), 61.01 (C22, C24), 60.95 (C22, C24), 37.73 (C33), 14.31 (C23, C25, C34), 13.95 (C23, C25, C34), 13.87 (C23, C25, C34).



H_2ECMTDC. Compound 3 (2 g) and KOH (5 g) were refluxed in ethanol/water (4/6) solution at 85 °C for 4 h. After being cooled to room temperature, the solution was acidified with1M HCl to pH 2, and the faint yellow solid was obtained. The mixture was filtered and washed to neutral to afford pure H_2ECMTDC in 95% Yield. FT-IR: 3485(m), 3047(w), 2972(w), 2923(w), 1665(vs), 1500(vs), 1467(vs), 1413(s), 1267(s), 1232(s), 767(m), 744(m). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.04 (s, O(19, 21)-H, 2H), 8.24-8.06 (m, Ar(C12, 15)-H, 2H), 7.64 (t, *J* = 8.2 Hz, Ar(C25, 27)-H, 2H), 7.53-7.34 (m, Ar(C11, 28)-H, 2H), 7.19 (t, *J* = 7.4 Hz, Ar(C26)-H, 1H), 4.49 (q, *J* = 7.1 Hz, C(29)-H, 2H), 1.97 (s, C(9)-H, 3H), 1.39 (t, *J* = 7.1 Hz, C(30)-H, 3H). ^{13}C NMR (126 MHz, DMSO): δ 163.98 (C16), 163.25 (C17), 147.34 (C13), 143.85 (C23), 143.36 (C4), 140.31 (C3), 139.96 (C1), 139.56 (C7), 133.43 (C2), 131.72 (C6), 127.51 (C11), 126.31 (C12), 124.97 (C10), 122.67 (C14), 122.08 (C24), 121.69 (C25), 121.04 (C27), 119.30 (C19), 109.57 (C26), 108.62 (C28), 37.59 (C29), 14.29 (30).

II. Supplementary illustrations and explanations

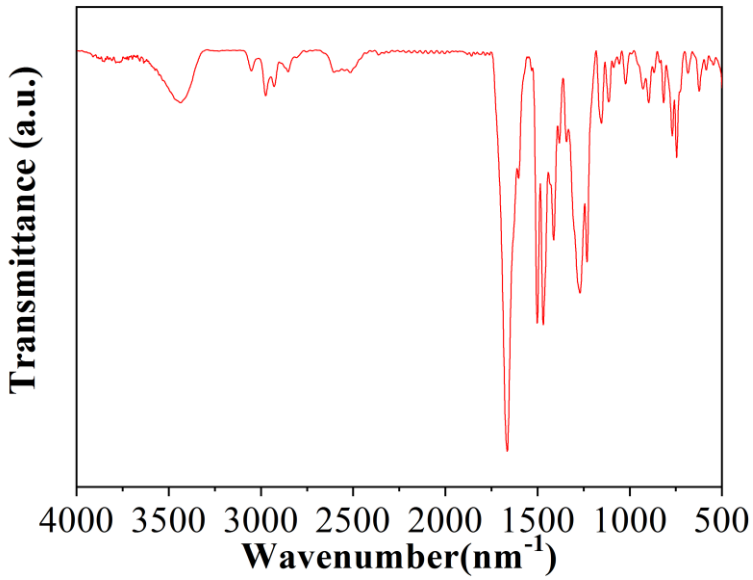


Fig. S1 The FT-IR spectra of H_2ECMTDC

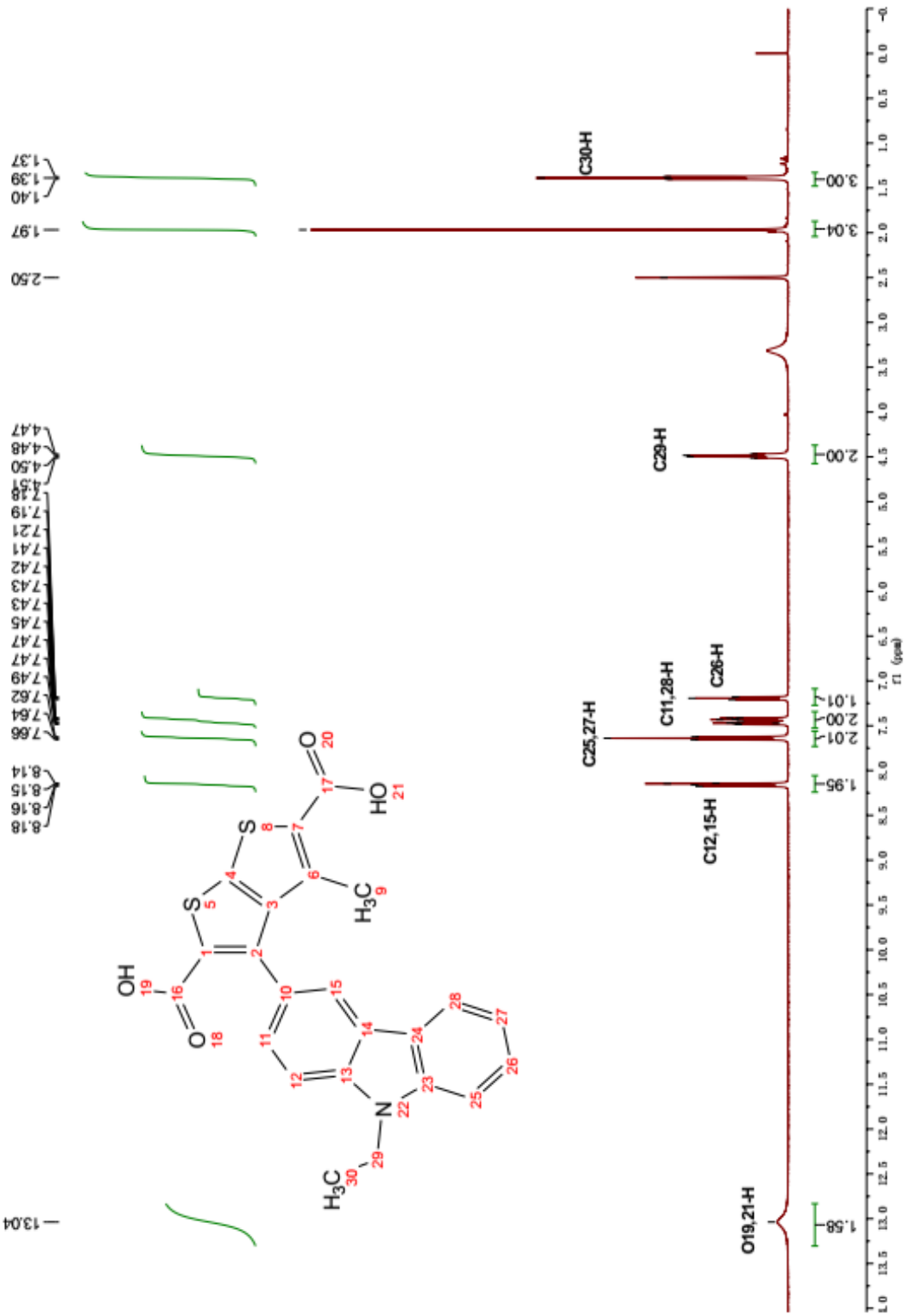


Fig. S2 ^{1}H NMR spectra of H_2ECMTDC

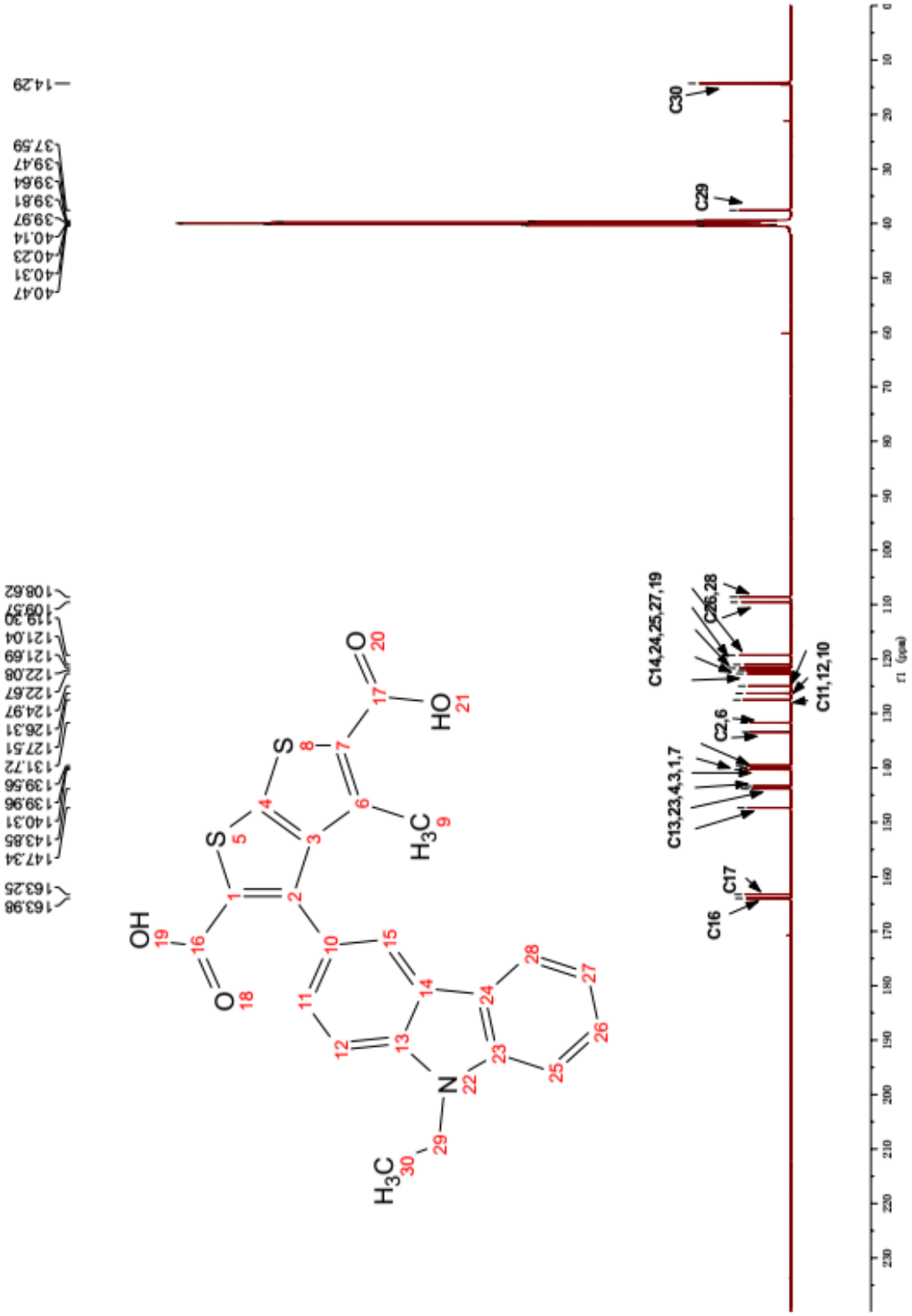


Fig. S3 ^{13}C NMR spectra of H_2ECMTDC

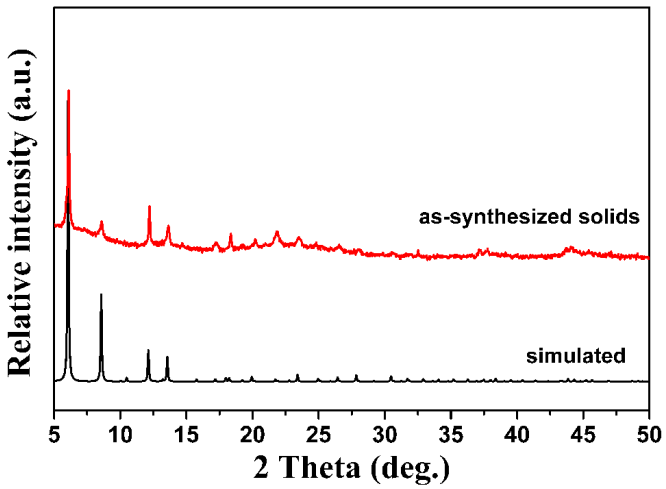


Fig. S4 PXRD patterns of Cz-MOF-1

Table S1 Details for structural analysis of Cz-MOF-1

Compound	Cz-MOF-1
Formula	$C_{99}H_{115}N_{13}O_{23}S_6Zn_4$
Formula weight	2308.87
Crystal system	Cubic
Space group	*Fm*-3*m*
a /Å	29.171(2)
b /Å	29.171(2)
c /Å	29.171(2)
α/°	90
β/°	90
γ/°	90
V/Å^3	24823(5)
Z	8
$D_{calcd.}$[g cm^{-3}]	1.236
μ/mm^{-1}	0.930
F(000)	9600
Observed reflection/unique	31619/1139
R_{int}	0.0933
Goodness-of-fit	1.021
R_1, wR_2 [I >2σ(I)]	0.0949, 0.2608
R_1, wR_2 (all data)	0.1264, 0.3312

Table S2 Selected bond lengths [Å] and angles [deg.] for Cz-MOF-1

Zn(1)-O(1)	1.9378(18)
Zn(1)-O(2)	1.86(3)
O(2)-Zn(1)-O(1)	115.0(19)
Zn(1)-O(1)-Zn(1)#1	109.5
Zn(1)-O(1)-Zn(1)#2	109.471(2)

Symmetry transformations used to generate equivalent atoms:

#1 -1/2-Y,-1+X,3/2-Z; #2 1+Y,-1/2-X,3/2-Z

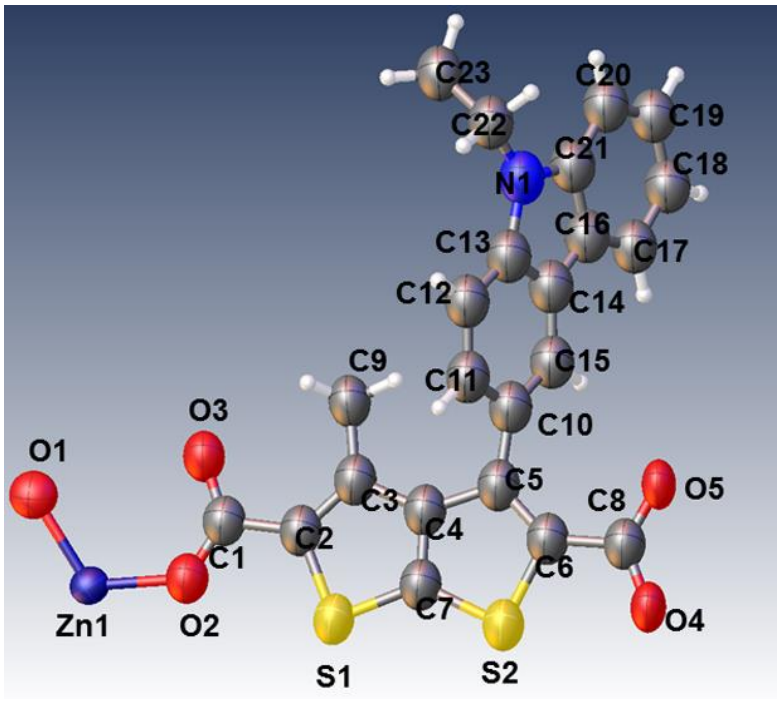


Fig. S5 The ORTEP image of the asymmetric unit.

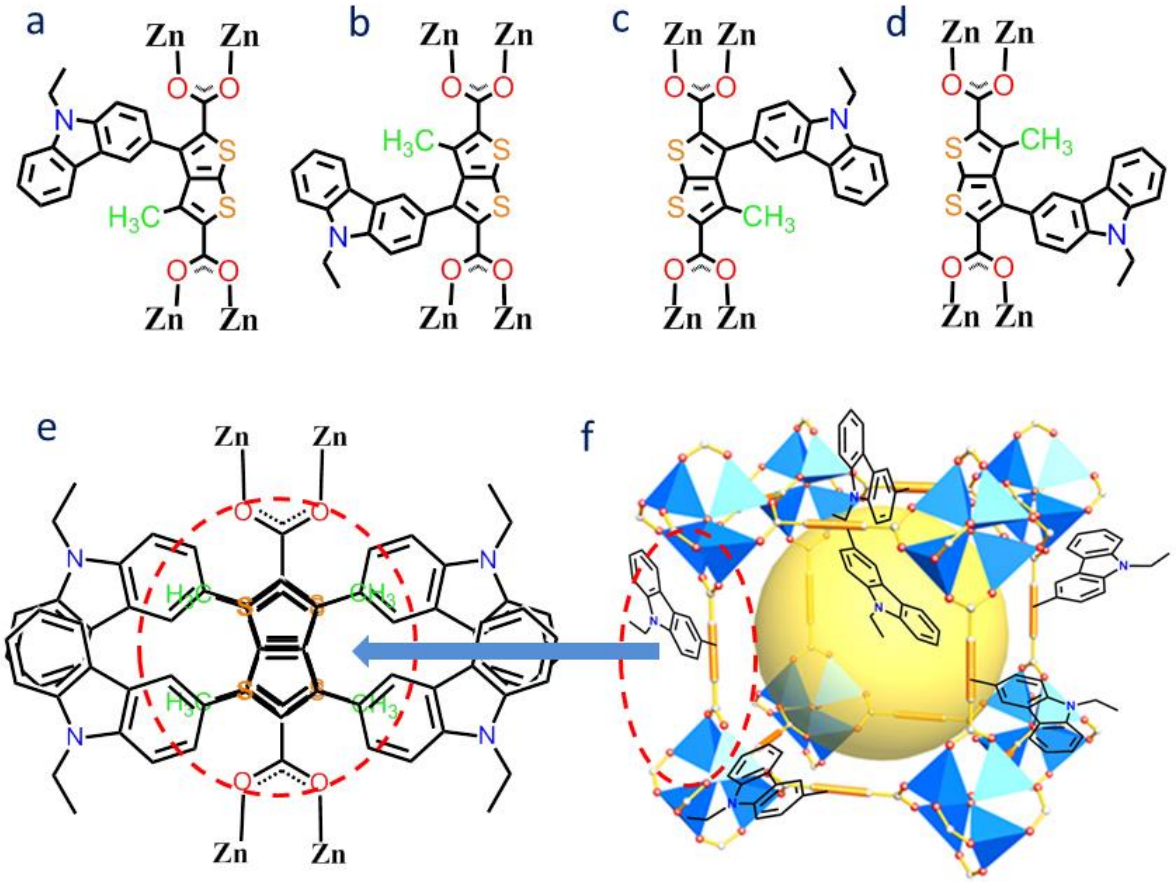


Fig. S6 The disorder of ligands in Cz-MOF-1

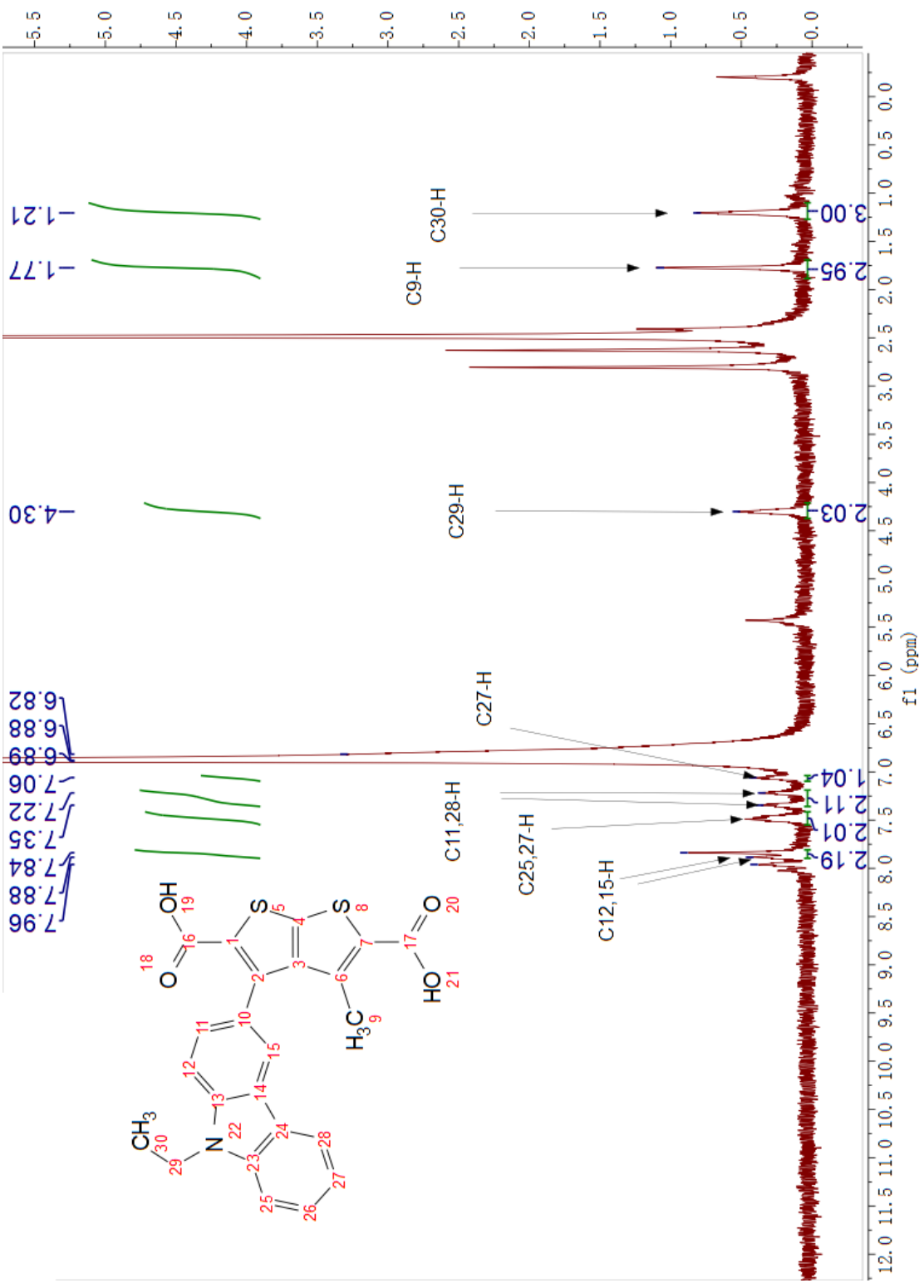


Fig. S7 The ^{1}H NMR signal of Cz-MOF-1 dissolving in d_6-DMSO/DCl/D_2O.

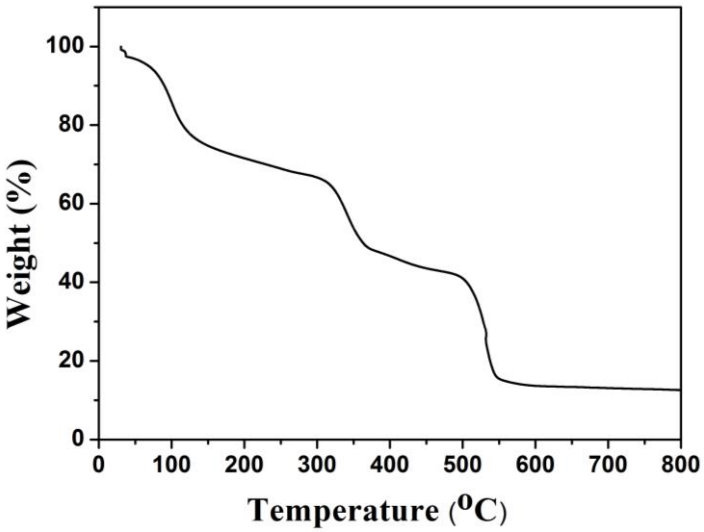


Fig. S8 TGA curve of Cz-MOF-1

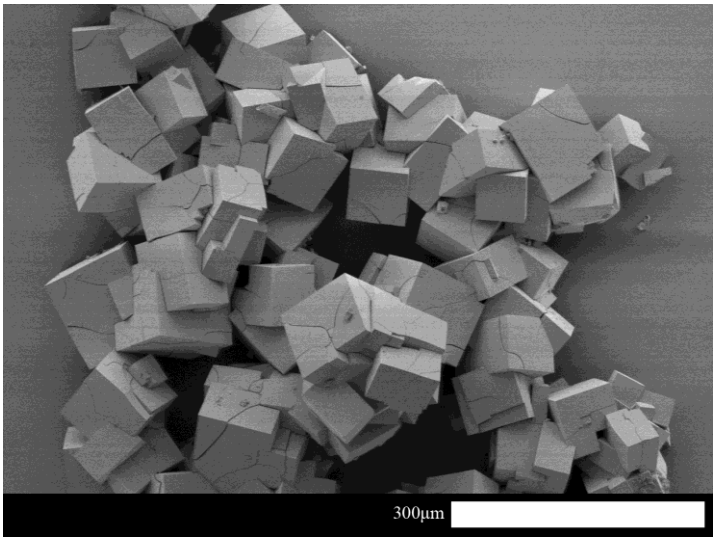


Fig.S9 SEM micrographs of Cz-MOF-1 exposed to water for 24 h.

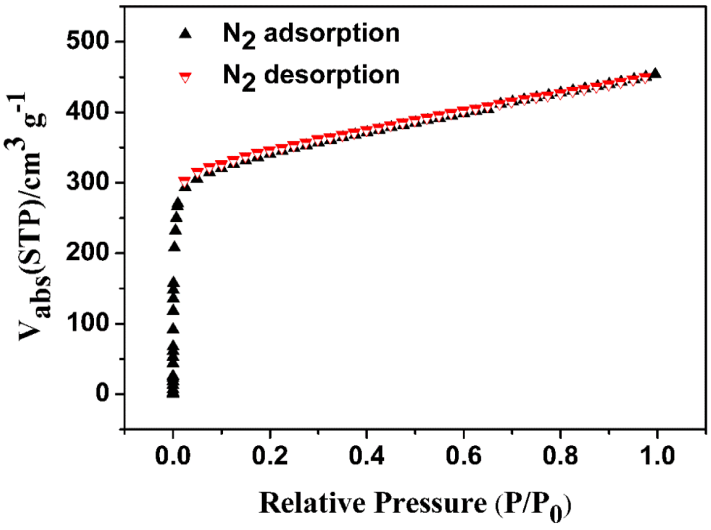


Fig. S10 N_2 sorption isotherms of Cz-MOF-1

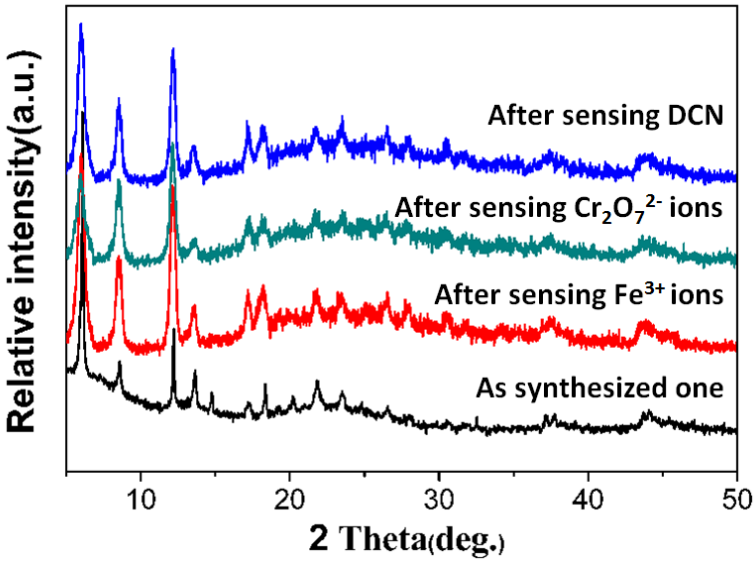


Fig. S11 PXRD patterns of Cz-MOF-1 after sensing Fe^{3+}, $Cr_2O_7^{2-}$ ions and DCN.

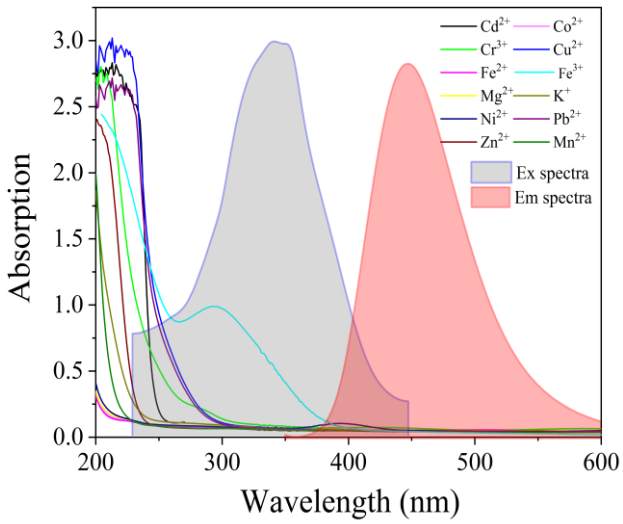


Fig. S12 UV-vis absorption spectra of cationic aqueous and spectra of Cz-MOF-1.

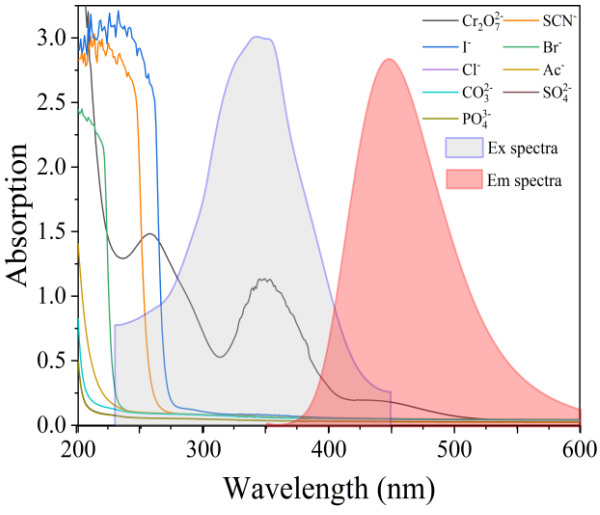


Fig. S13 UV-vis absorption spectra of anionic aqueous and spectra of Cz-MOF-1.

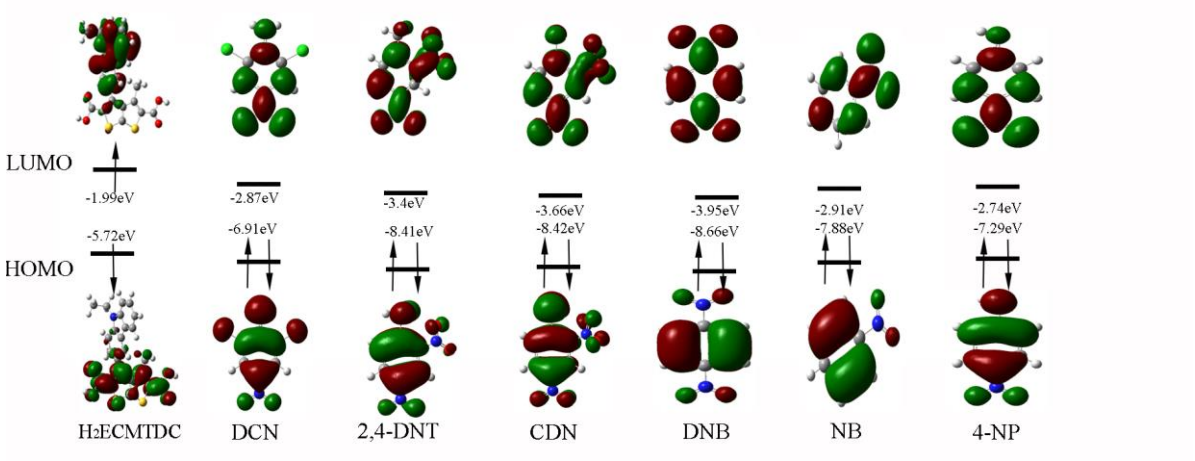


Fig. S14 HOMO and LUMO energy levels of H_2ECMTDC and organic small molecules calculated by density functional theory (DFT) with B3LYP/6-31+G*

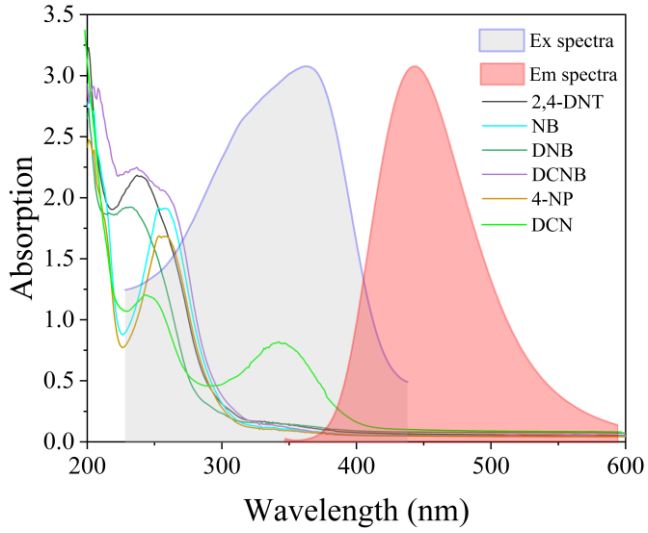


Fig. S15 UV-vis absorption spectra of nitro compounds in ethanol solutions and spectra of Cz-MOF-1.

III. Supplementary References

1. A. S. Sonar, S. G. Dandale and P. R. Solanki, *J. Chem. Pharm. Res.*, 2011, **3**, 752-758.
2. W.-W. He, G.-S. Yang, Y.-J. Tang, S.-L. Li, S.-R. Zhang, Z.-M. Su, and Y.-Q. Lan, *Chem. Eur. J.*, 2015, **21**, 9784-9789.
3. A.Comel and G. Kirsch, *J. Heterocyclic Chem.* 2001, 5, 1167-1171.