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Supporting Information for

Post-imparting Brønsted Acidity into an Amino-functionalized MOF as Bifunctional Luminescent Turn-ON Sensors for the Detection of Aluminum Ions and Lysine

Yanhong Liu,[a] Mengjie Huangfu,[a] Pengyan Wu,*[a] Min Jiang,[a] Xiaoli Zhao,[a] Lili Liang,[a] Liheng Xie,[a] Jianguo Bai[a] and Jian Wang*[a]

[a] School of Chemistry and Materials Science & Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu, 221116, China. E-mail: wpyan@jsnu.edu.cn; wjian@jsnu.edu.cn

Table S1 Crystallographic data and structural refinement summary for Cd−TCHO.

	Cd−TCHO
Empirical formula	$C_{60}H_{37}N_7O_{16}Cd_3$
Formula wt	1469.32
Crystal System	Triclinic
Space Group	*P-1*
a (Å)	13.5289(6)
b (Å)	14.2783(7)
c (Å)	19.2066(10)
α (°)	73.046(5)
β (°)	73.172(5)
γ (°)	61.890(3)
V (Å^3)	3079.0(3)
Z	2
R_{int}	0.0554
μ(mm^{-1})	1.099
ρ_{calcd}/ g cm^{-3}	1.585
F(000)	1476
Goodness of fit	1.065
Temperature (K)	123(2)
Reflections collected	10402
Independent reflections	9604
R_1 (I > 2σ(I))	0.0492
wR_2 (all data)	0.1416

Crystallography:

Intensities were collected on a Bruker SMART APEX CCD diffractometer with graphite monochromated Mo-*K*α (λ = 0.71073 Å) using the SMART and SAINT programs. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods with SHELXTL *version* 5.1. Non-hydrogen atoms of the ligand backbones were refined anisotropically. Hydrogen atoms within the ligand backbones were fixed geometrically at calculated positions and allowed to ride on the parent non-hydrogen atoms. Hydrogen atoms of the carboxylate moieties were found from the difference Fourier maps and refined with the isotropic parameters fixed as 1.5 times of those oxygen atoms they attached and with the O–H distance fixed at 0.85 Å.

Table S2 Selective bond distance (Å) and angle (°) in Cd−TCHO.

Cd(1)–O(10)	2.204(5)	Cd(1)–O(92)	2.210(5)
Cd(1)–O(13B)	2.211(3)	Cd(1)–O(11A)	2.272(4)
Cd(1)–O(1)	2.301(3)	Cd(1)–O(5A)	2.579(3)
Cd(2)–O(3B)	2.226(3)	Cd(2)–O(6A)	2.232(3)
Cd(2)–O(5A)	2.355(3)	Cd(2)–O(4)	2.308(3)
Cd(2)–O(1)	2.363(3)	Cd(2)–O(9)	2.456(3)
Cd(3)–O(7)	2.235(3)	Cd(2)–O(12A)	2.249(3)
Cd(2)–O(2B)	2.259(3)	Cd(2)–N(2)	2.281(4)
Cd(2)–O(8)	2.386(4)	Cd(2)–O(4B)	2.451(3)
O(10)–Cd(1)–O(92)	82.7(3)	O(10)–Cd(1)–O(13B)	118.45(19)
O(92)–Cd(1)–O(13B)	92.4(2)	O(10)–Cd(1)–O(11A)	104.82(19)

O(92)–Cd(1)–O(11A)	89.2(2)	O(13B)–Cd(1)–O(11A)	136.57(14)
O(10)–Cd(1)–O(1)	90.72(16)	O(92)–Cd(1)–O(1)	173.0(2)
O(13B)–Cd(1)–O(1)	88.40(12)	O(11A)–Cd(1)–O(1)	95.03(14)
O(10)–Cd(1)–O(5A)	157.22(18)	O(92)–Cd(1)–O(5A)	101.4(2)
O(13B)–Cd(1)–O(5A)	83.97(12)	O(11A)–Cd(1)–O(5A)	53.32(12)
O(1)–Cd(1)–O(11A)	85.60(11)	O(4)–Cd(2)–O(9)	91.77(11)
O(3B)–Cd(2)–O(6A)	140.37(13)	O(3B)–Cd(2)–O(4)	84.06(12)
O(6A)–Cd(2)–O(4)	96.05(12)	O(3B)–Cd(2)–O(5A)	86.77(13)
O(6A)–Cd(2)–O(5A)	83.41(12)	O(4)–Cd(2)–O(5A)	164.85(12)
O(3B)–Cd(2)–O(1)	87.98(12)	O(6A)–Cd(2)–O(1)	130.06(12)
O(4)–Cd(2)–O(1)	102.15(11)	O(5A)–Cd(2)–O(1)	89.51(12)
O(3B)–Cd(2)–O(9)	140.40(12)	O(6A)–Cd(2)–O(9)	79.22(12)
O(5A)–Cd(2)–O(9)	102.95(12)	O(1)–Cd(2)–O(9)	54.37(12)
O(7)–Cd(3)–O(12A)	86.71(12)	O(7)–Cd(3)–O(2B)	157.10(12)
O(12A)–Cd(3)–O(2B)	109.19(12)	O(7)–Cd(3)–N(2)	100.51(13)
O(12A)–Cd(3)–N(2)	98.22(13)	O(2B)–Cd(3)–N(2)	93.56(13)
O(7)–Cd(3)–O(8)	56.84(12)	O(12A)–Cd(3)–O(8)	140.07(12)
O(2B)–Cd(3)–O(8)	102.42(12)	N(2)–Cd(3)–O(8)	103.62(14)
O(7)–Cd(3)–O(4)	111.87(12)	O(12A)–Cd(3)–O(4B)	84.22(12)
O(2B–Cd(3)–O(4B)	55.85(11)	N(2)–Cd(3)–O(4B)	147.62(12)
O(8)–Cd(3)–O(4B)	94.20(12)		

Symmetry code A: 1+*x*, *y*, *z*.; B: x, 1+y, z.

Figure S1 Coordinated environment of three independent Cd^{2+} ions in Cd−TCHO, Cd = purple, O = red, N = blue, C = gray and H = pink.

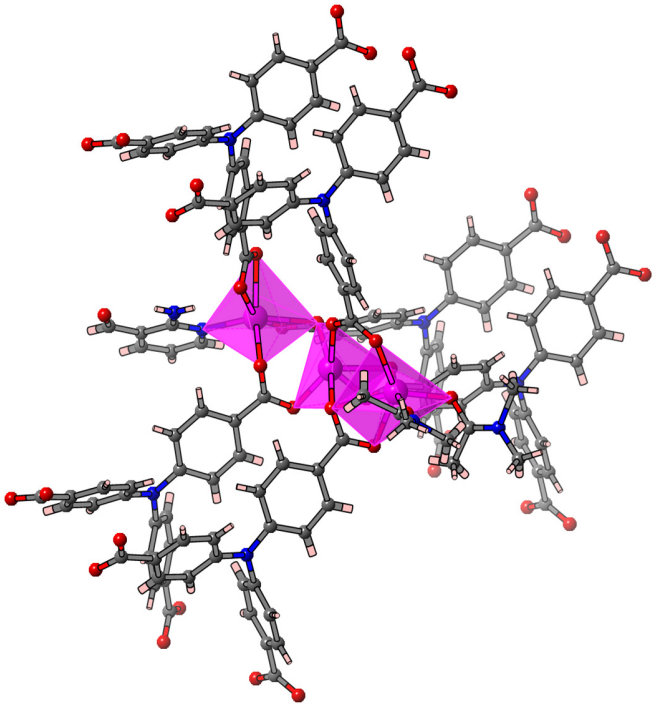


Figure S2 The asymmetric unit of Cd−TCHO, Cd = purple, O = red, N = blue, C = gray, and H = pink.

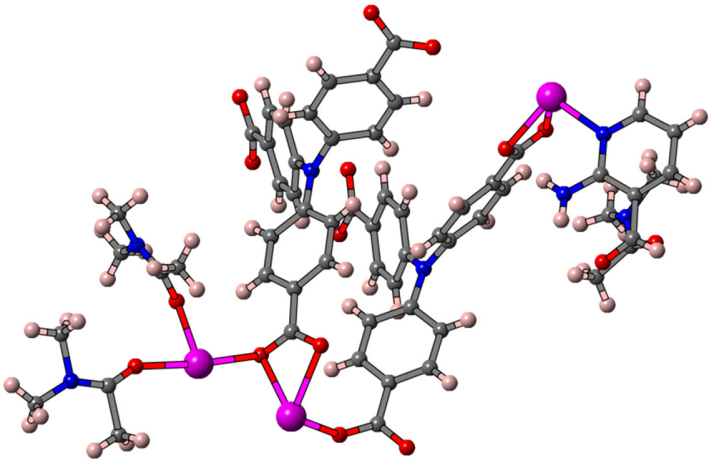


Figure S3 TGA traces of Cd−TCHO ranging from room temperature to 500 °C.

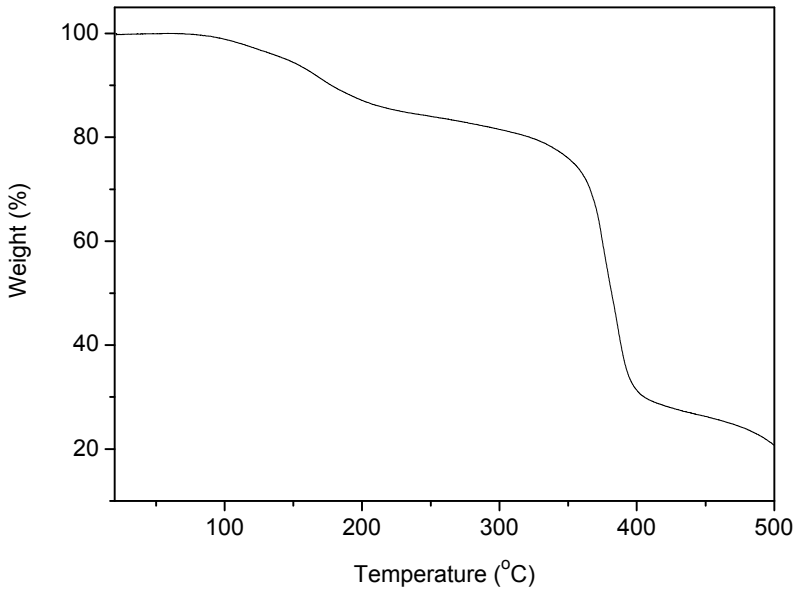


Figure S4 N_2 sorption isotherms at 77 K of Cd−TCHO and Cd−TCOOH.

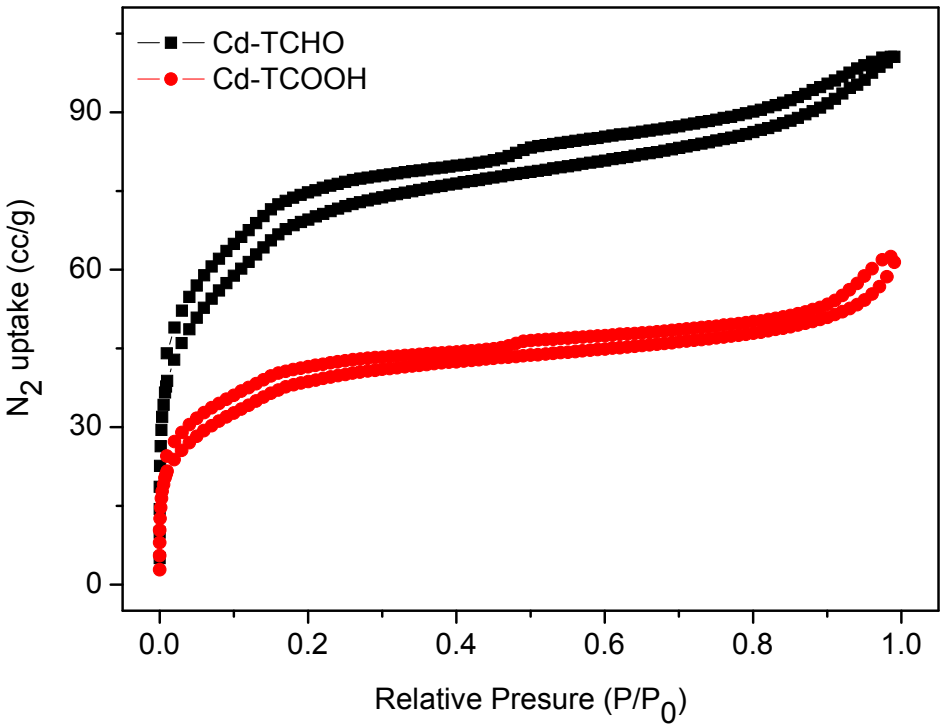


Figure S5 Powder X-ray diffraction (XRD) profiles for as-synthesized Cd−TCHO and Cd−TCOOH, Cd−TCHO and Cd−TCOOH samples soaked in aqueous solutions with pH values of 6.0 and 10.5.

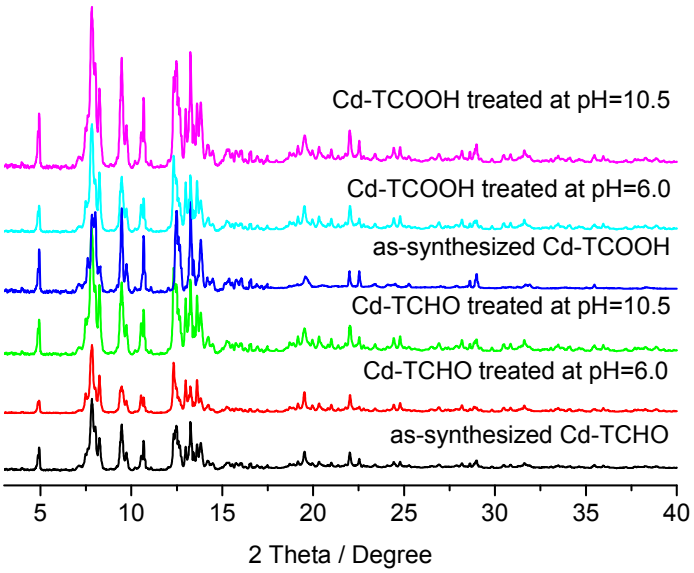
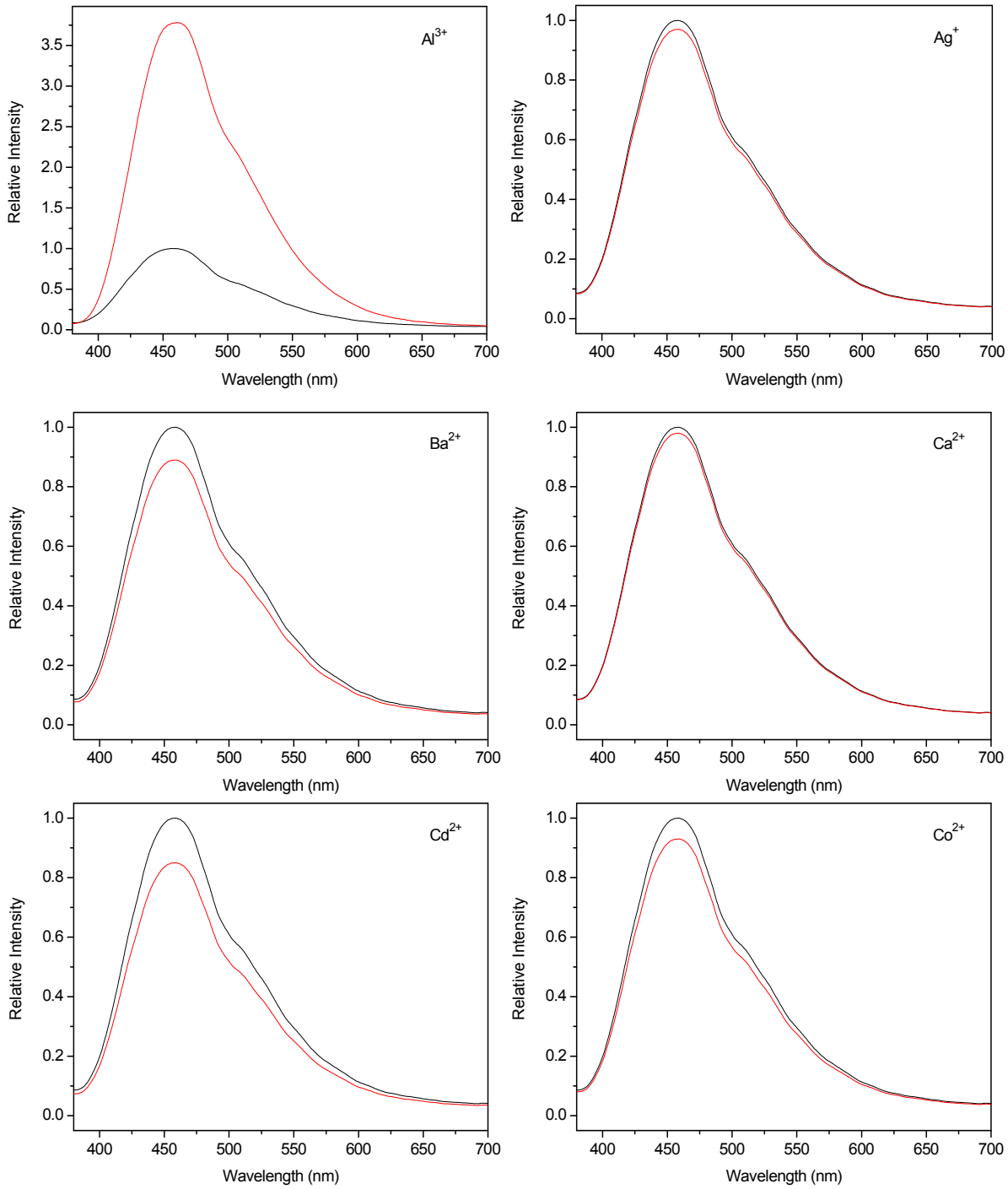
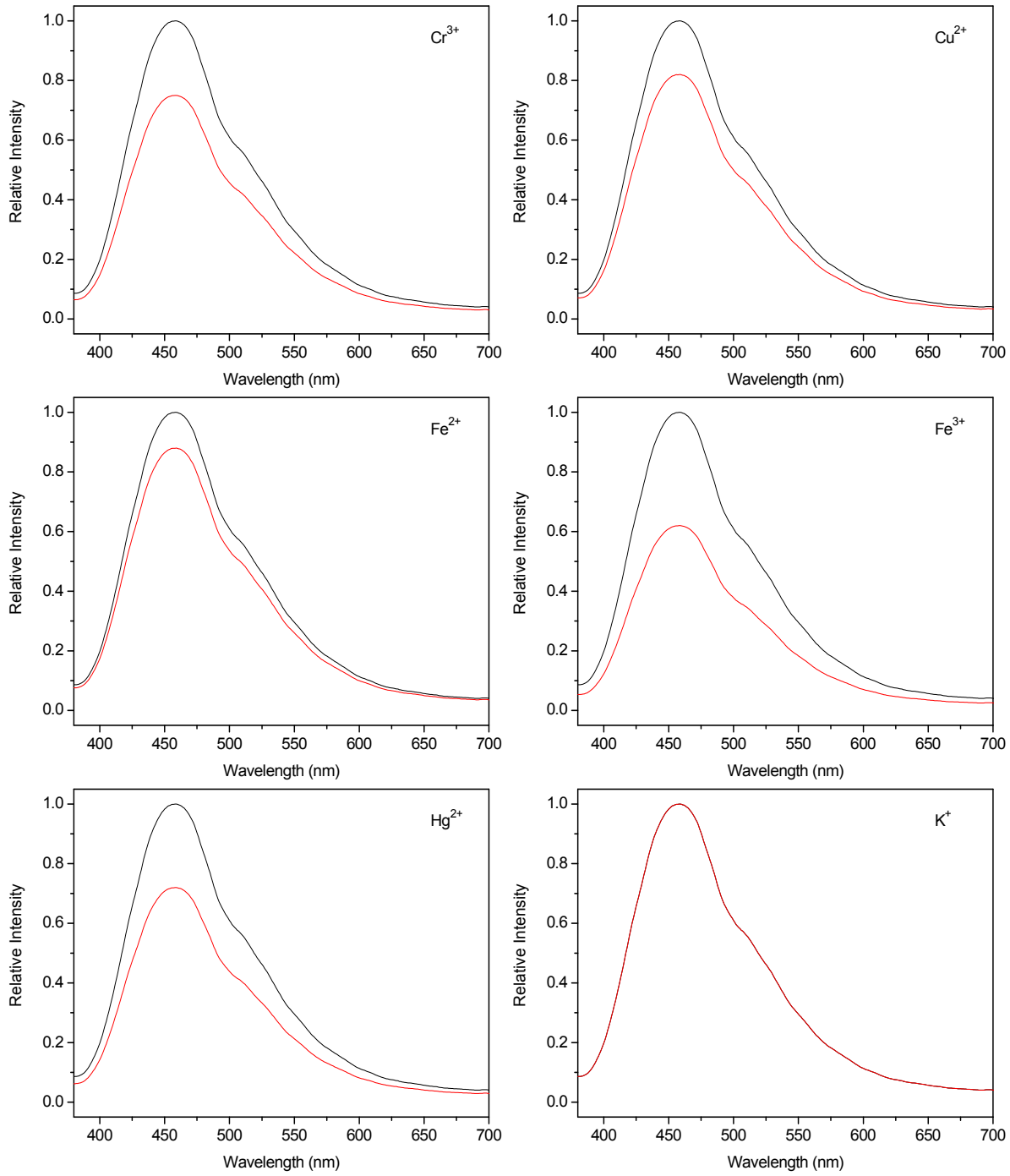
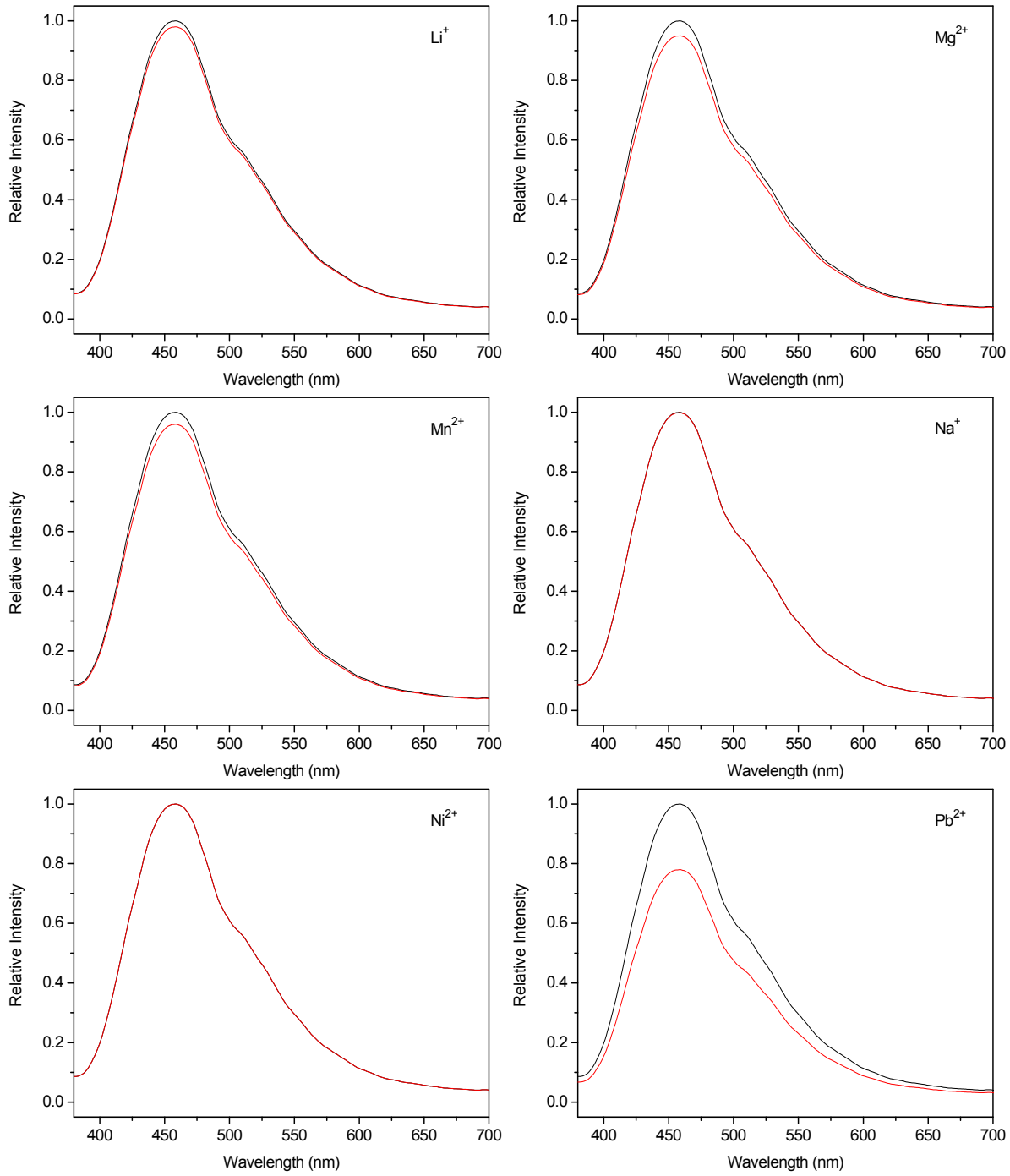


Figure S6 Families of various fluorescence spectra of Cd−TCOOH in HEPES buffer solution upon the addition of 26 μM of different selected metal ions.




Cr3+
Cu2+
Fe2+
Fe3+
Hg2+
K+
Relative Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650
700


Li+
Mg2+
Mn2+
Na+
Ni2+
Pb2+
Relative Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650
700

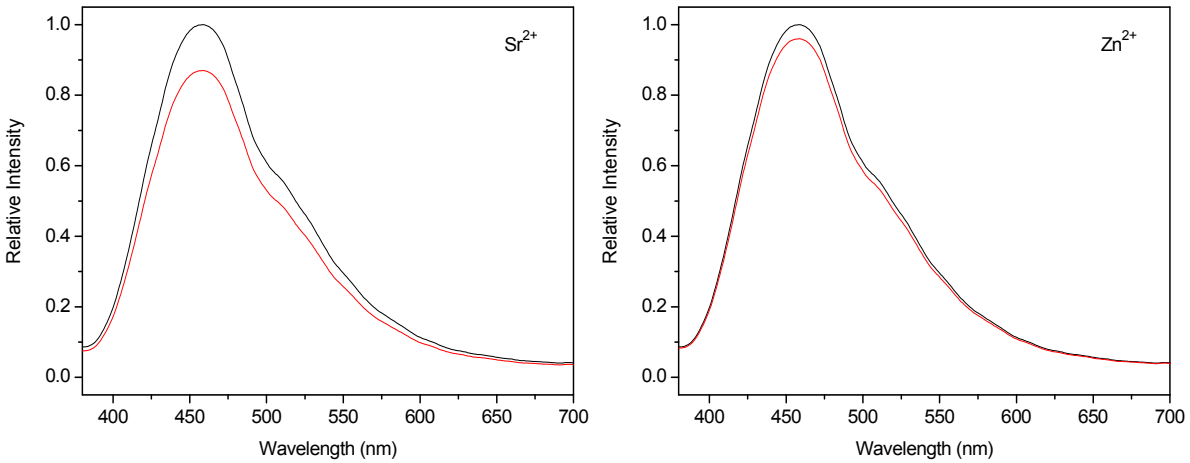


Figure S7 The fluorescence response of Cd−TCHO towards different metal ions (26 μM) at r.t. in HEPES buffer (pH=7.4).

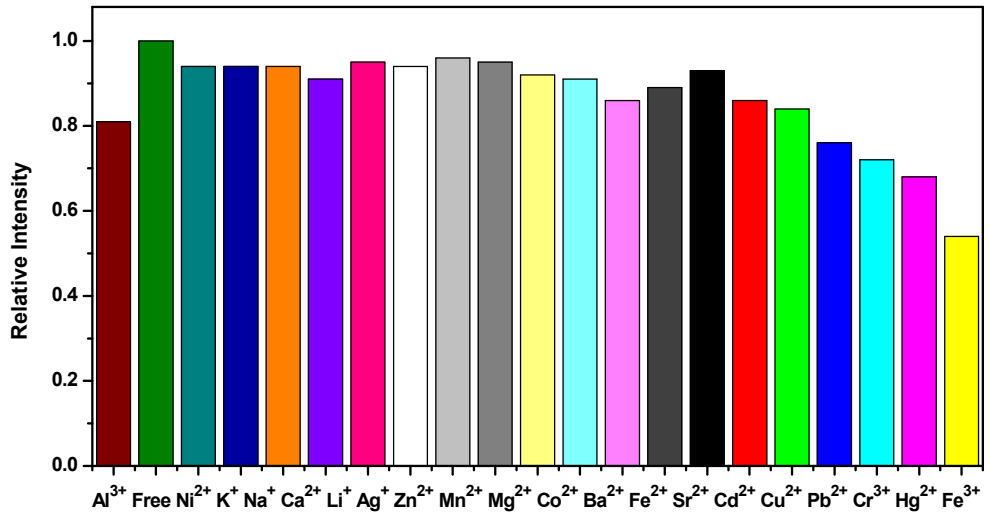


Table S3 Sensing performance comparison of reported fluorescent MOF sensors for Al^{3+} ion

Entry	MOF	Detection limits (μM)	ref
1	[Eu(BTB)(phen)]	0.05	S1
2	$[Ba_3La_{0.5}(\mu_3\text{-}L)_{2.5}(H_2O)_3(DMF)]$	1.11	S2
3	$[Cd(PAM)(4\text{-}bpdb)_{1.5}]$	0.56	S3
4	$[Co_2(dmimpym)(nda)_2]_n$	1.4	S4
5	$[Tb_3(TCA)_2(DMA)_{0.5}(OH)_3(H_2O)_{0.5}]$	0.7	S5
6	[Zn(DMA)(TBA)]	1.97	S6
7	$[Co(OBA)(DATZ)_{0.5}(H_2O)]$	2.13	S7
8	NUM-2	3.7	S8
9	UiO-66-NH_2-SA	6.98	S9
10	$[Eu_{2.5}(BTB)_3(OAc)_{0.5}(H_2O)_3]$	100	S10
11	$[Eu(H_2O)_2(BTMIPA)]$	1000	S11
12	Mg−TPP−DHBDC	0.028	S12
13	$[Eu(L)(OAc)(DMA)]_n$	0.1	S13
14	Cd-MOF-2	0.61	S14
15	Cd−TCOOH	0.02	This work

Figure S8 Luminescence intensity (450 nm) of Cd−TCOOH in HEPES buffer solution during three recycles sensing of Al^{3+}.

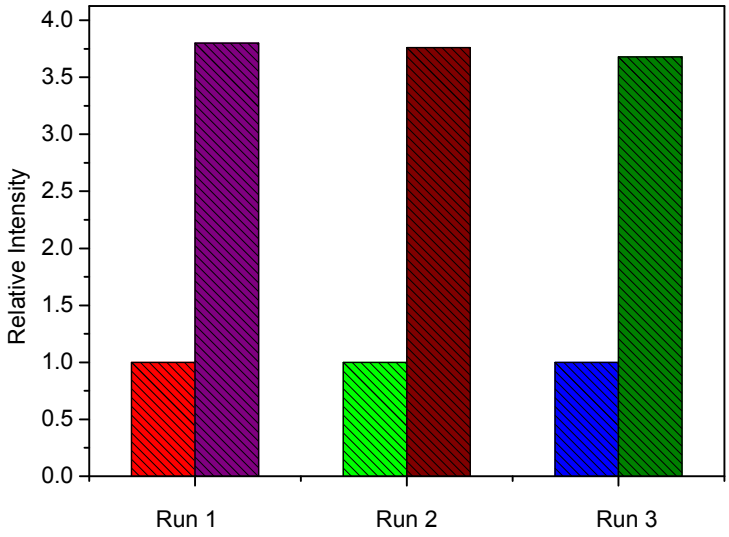


Figure S9 The PXRD patterns of Cd−TCOOH after three recycles sensing of Al^{3+}.

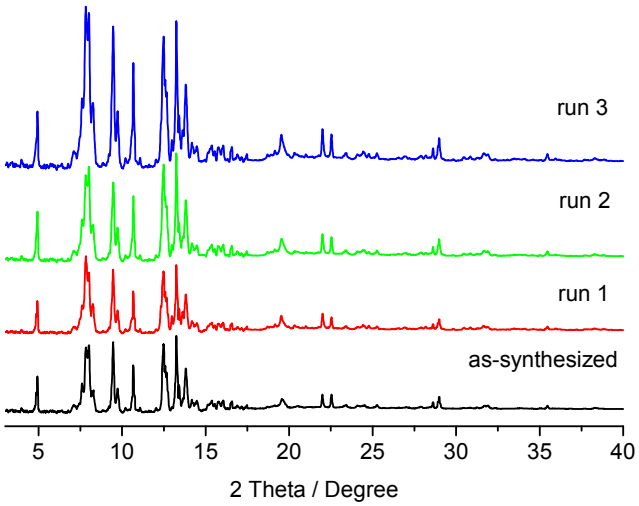
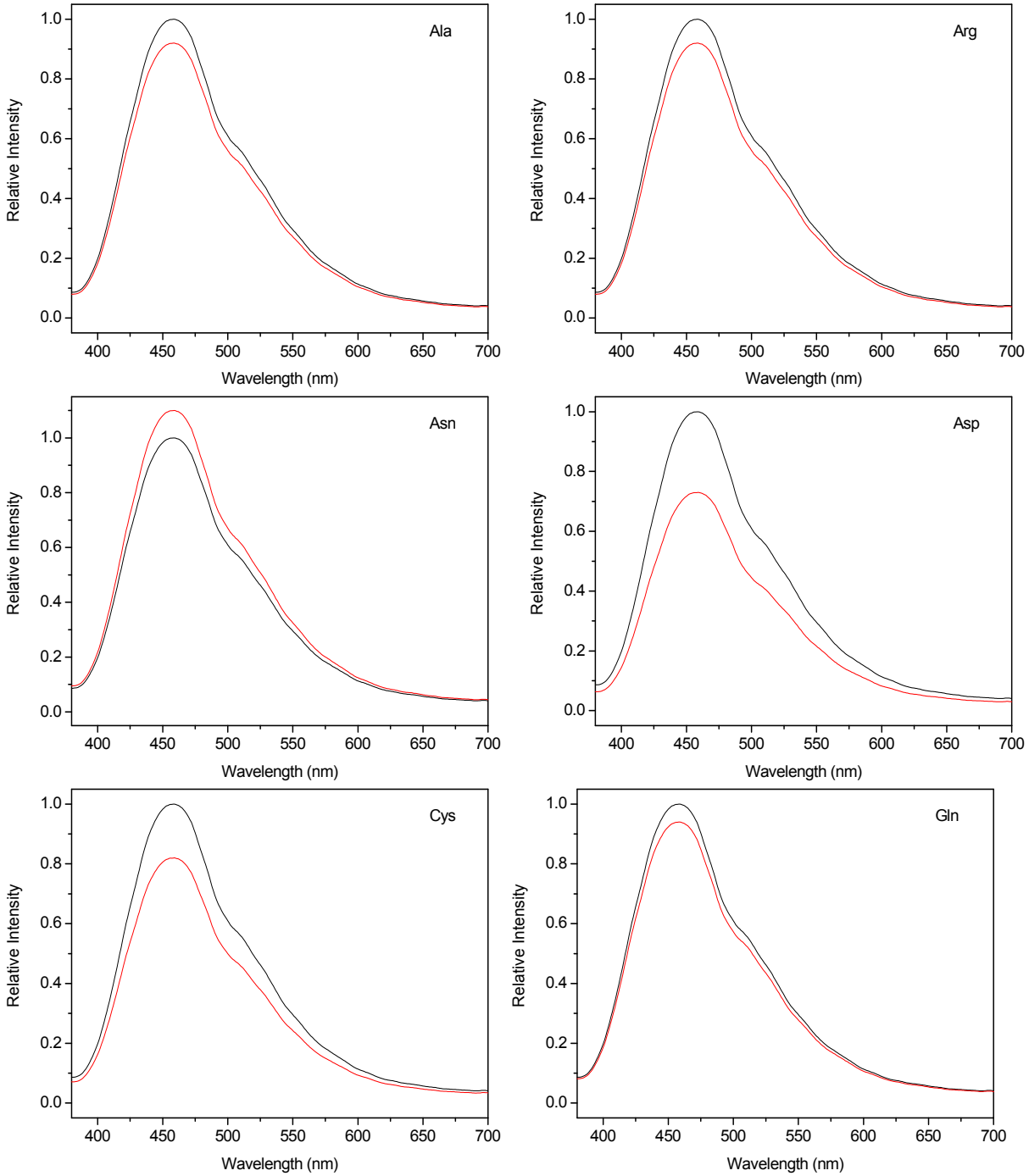
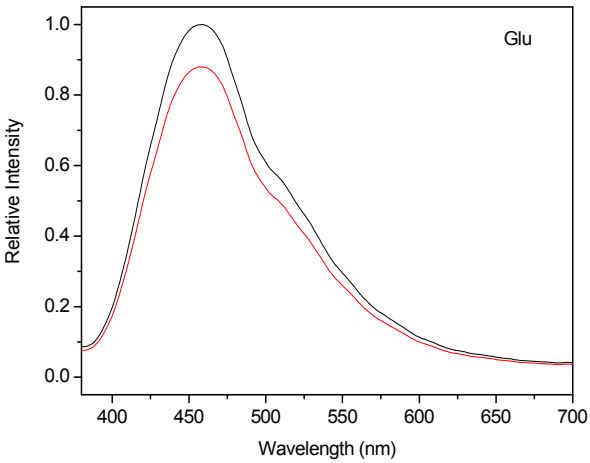
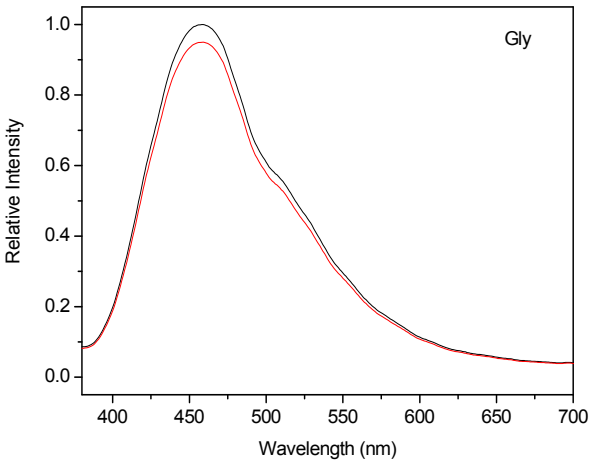
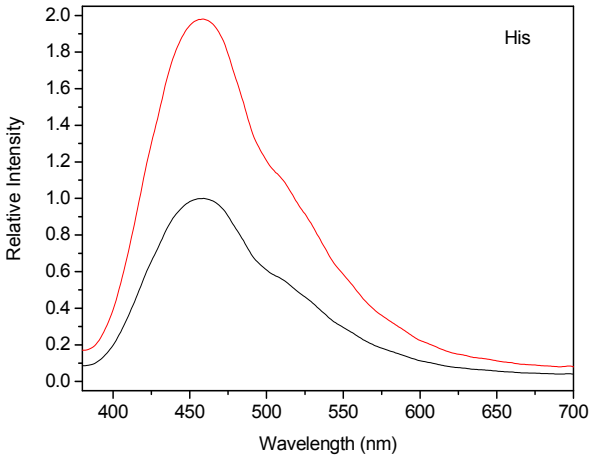


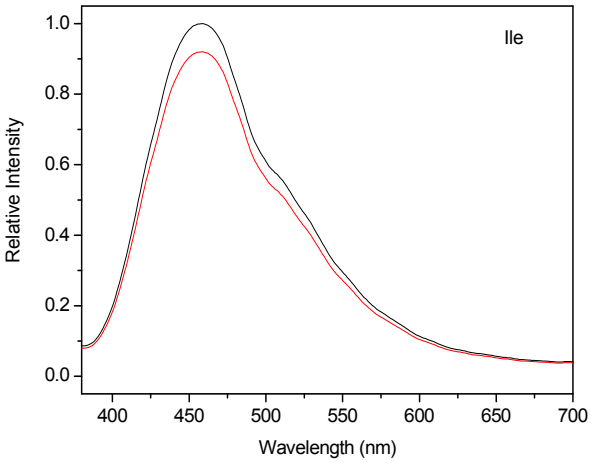
Figure S10 Families of various fluorescence spectra of Cd−TCOOH in HEPES buffer solution upon the addition of 1.2 mM of different selected amino acids.

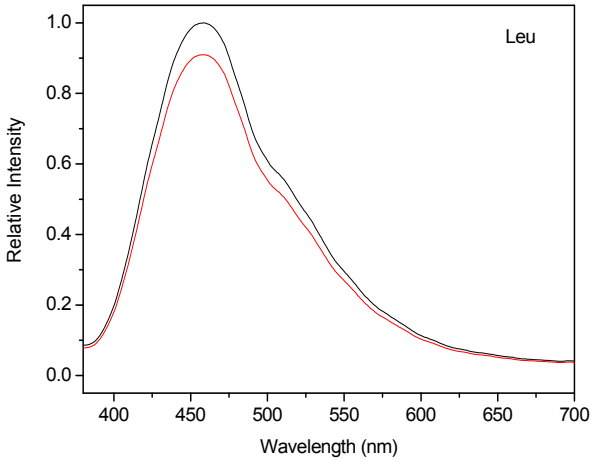


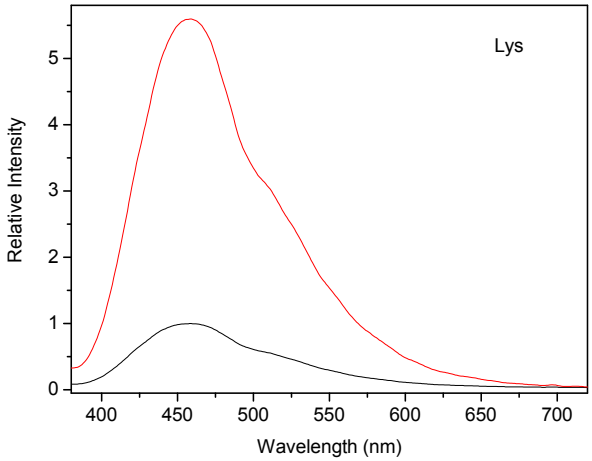

Glu
Relative Intensity
Wavelength (nm)

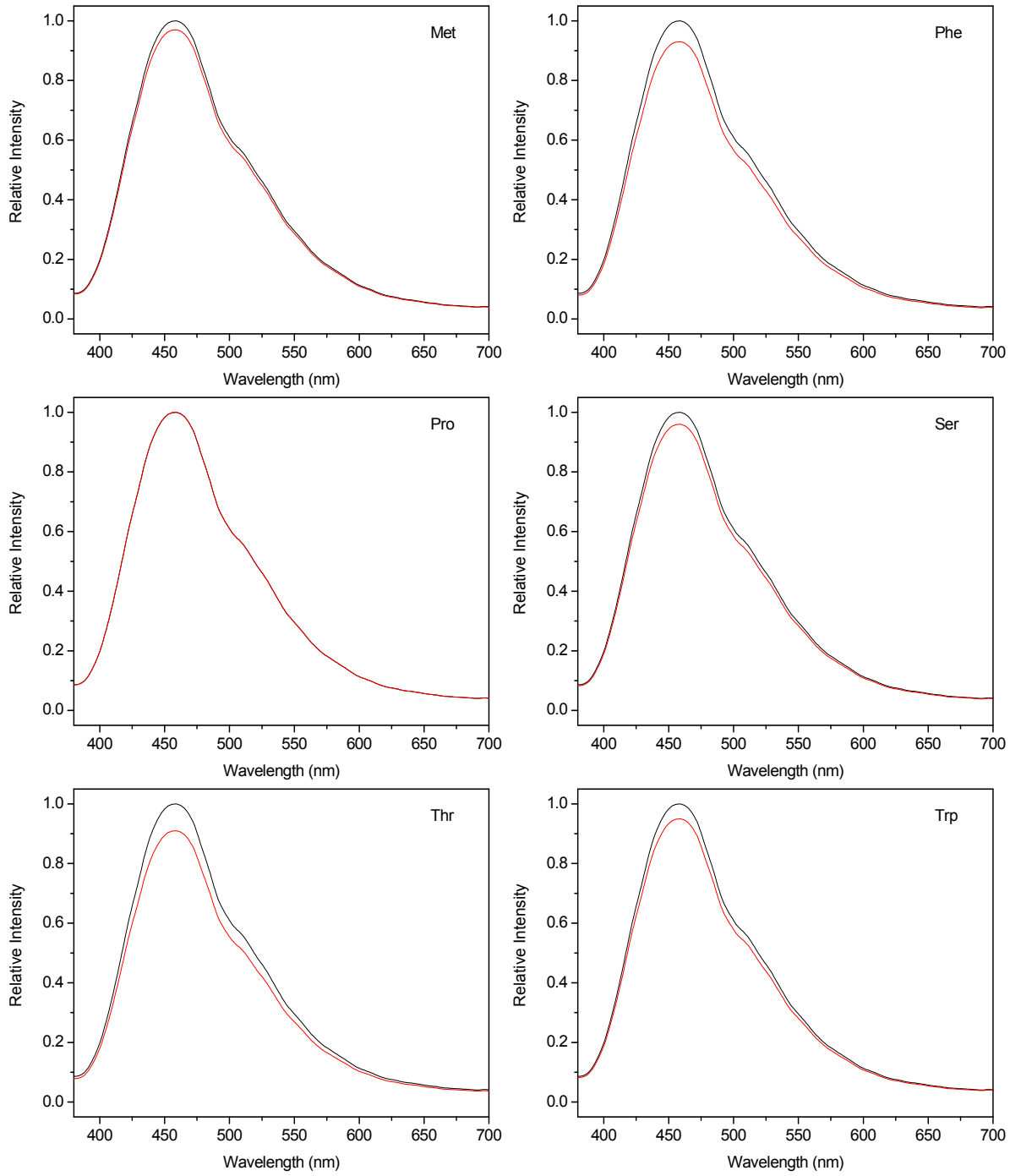

Gly
Relative Intensity
Wavelength (nm)


His
Relative Intensity
Wavelength (nm)


Ile
Relative Intensity
Wavelength (nm)


Leu
Relative Intensity
Wavelength (nm)


Lys
Relative Intensity
Wavelength (nm)


Met
Phe
Pro
Ser
Thr
Trp
Relative Intensity
Wavelength (nm)
0.0
0.2
0.4
0.6
0.8
1.0
400
450
500
550
600
650
700

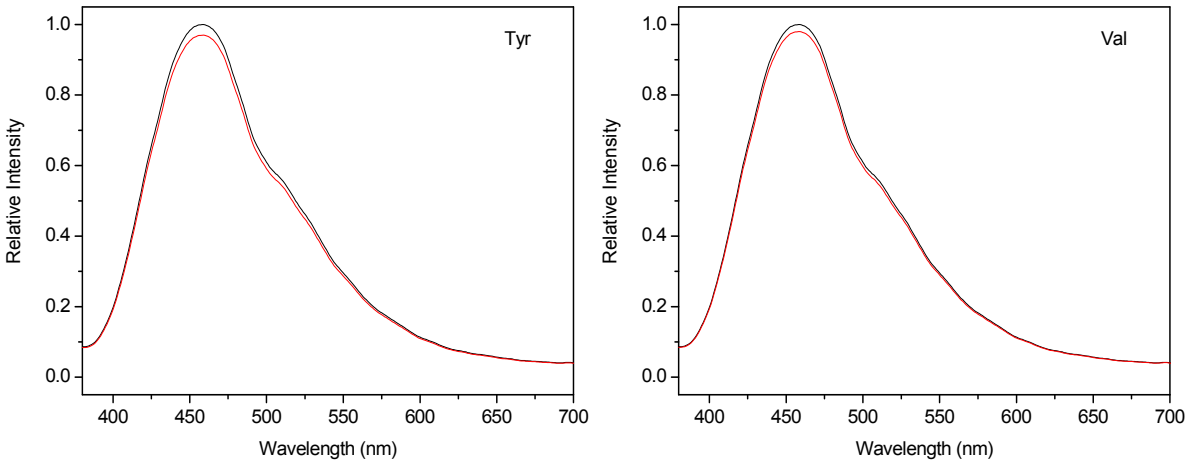

Tyr
Relative Intensity
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
400
450
500
550
600
650
700
Val
Relative Intensity
Wavelength (nm)

Figure S11 The fluorescence response of compound Cd−TCOOH in water at different pH values, λ_{ex} = 350 nm.

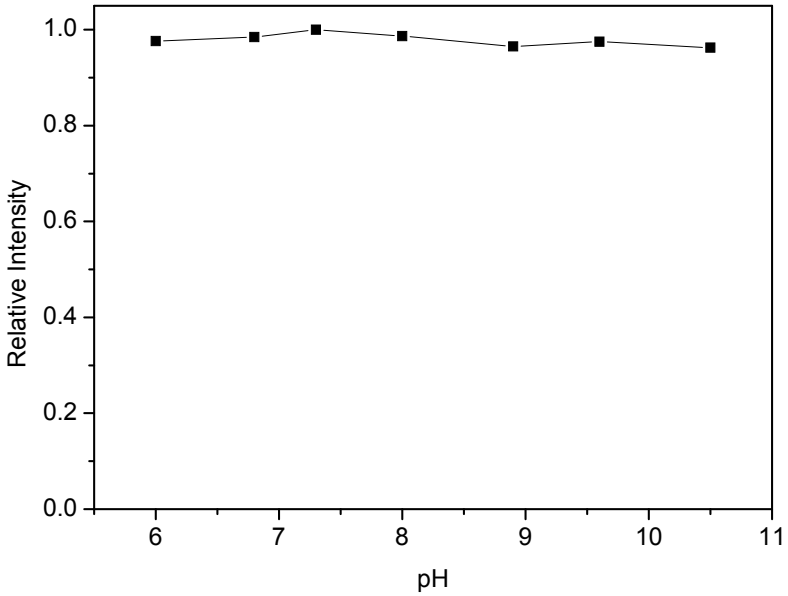


Figure S12 The fluorescence response of Cd−TCHO towards various amino acids (1.2 mM) at r.t. in HEPES buffer (pH=7.4).

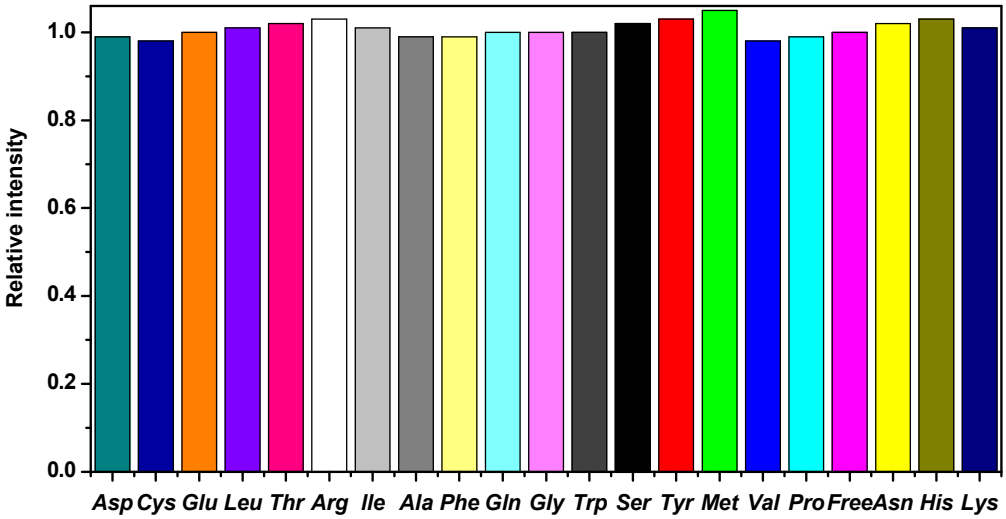


Figure S13 The ^{1}H NMR spectra (400 MHz, DMSO-d_6) of H_3tca (4,4′,4″-tricarboxytriphenylamine).

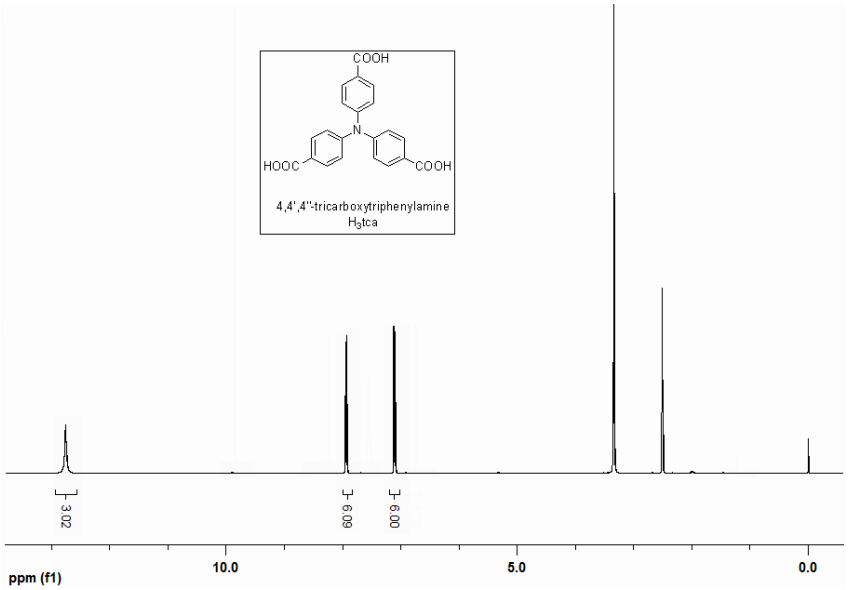
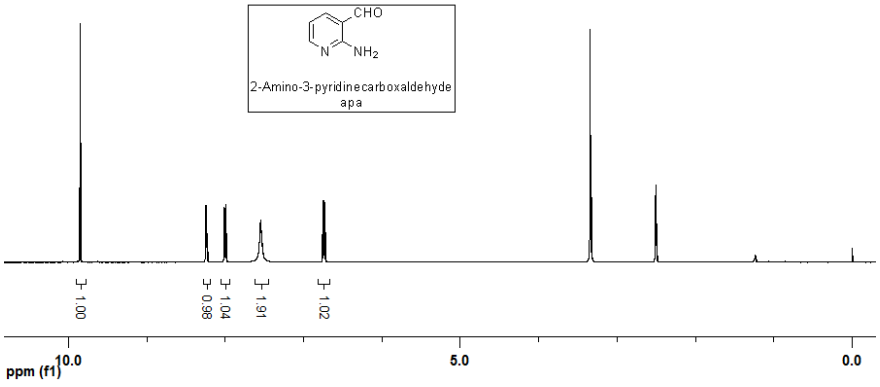


Figure S14 The ^{1}H NMR spectra (400 MHz, DMSO-d_6) of apa (2-Amino-3-pyridinecarboxaldehyde).



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