Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Construction of a Cd_8Tb_4 nanoring for luminescence response to 2,6-dipicolinic acid as an anthrax biomarker

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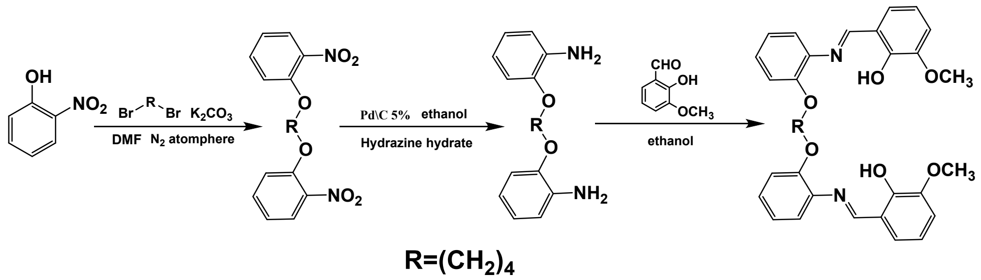
Contents

1. General information

All chemicals were purchased from commercial sources and directly used without further purified. Elemental analysis was performed on a EURO EA3000. NMR spectra were obtained on an AVANCE III AV500 at 298 K. IR spectra were measured on a FTIR-650 spectrometer. The thermogravimetric spectra were obtained on a TA Instruments Q600. Melting points were obtained on an XT-4 electrothermal micromelting point apparatus. Powder XRD spectra were recorded on a D8 Advance. Dynamic light scattering (DLS) measurement was carried out on a Malvern Zetasizer Nano ZS. Scanning electron microscopy (SEM) image and energy dispersive X-ray (EDX) spectroscopy were obtained from a Nova NanoSEM 200 microscope.

Photophysical Studies. UV-vis absorbance spectra were determined on an UV-3600 spectrophotometer. Excitation and visible emission spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. Emission lifetimes were obtained by the attached storage digital oscilloscope. Systematic errors have been deducted through the standard instrument corrections.

2. Synthesis of the ligand H_2L



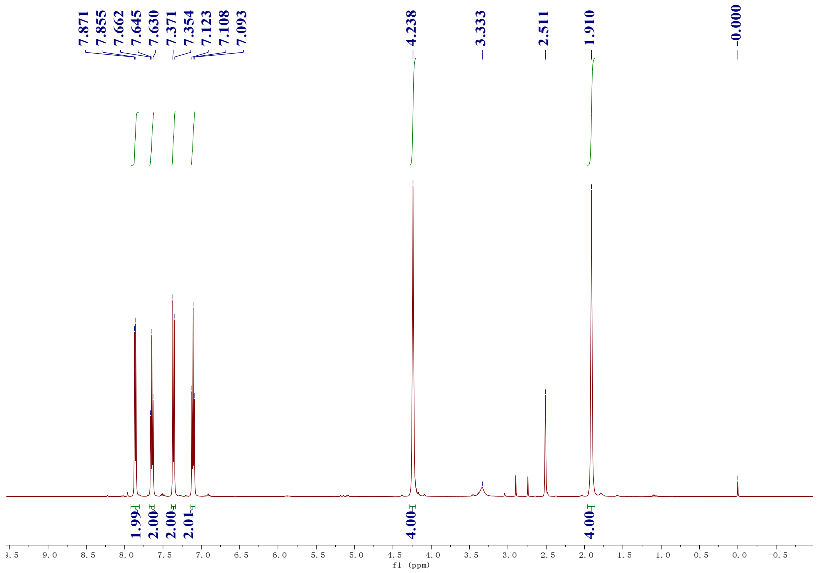
Scheme S1. Synthetic Approach to H_2L

Synthesis of 1,4-bis(2-nitrophenoxy)butane: 4-nitrophenol (6.00 g, 43.11 mmol) and dry K_2CO_3 (2.97 g, 21.55 mmol) were added into a 100 mL round-bottomed flask with 25 mL dry dimethylformamide (DMF). Then a solution of 1,4-dibromobutane (4.17 g, 20.67 mmol) in 5 mL dry DMF was added drop-wise. The mixture was heated to 115°C for overnight, then cooled on crushed ice. The yellow solid product was collected by filtration and washed successively with water, ethanol and diethyl ether, and then dried under vacuum for two hours. Yield: 4.35 g (80%). EA: C, 57.62; H, 4.70; N, 8.61 % (found). Calc. for $C_{16}H_{16}O_6N_2$: C, 57.83; H, 4.85; N, 8.43 %. m. p. = 155°C. ^{1}H NMR (δ_H, ppm, 500MHz, DMSO-*d*$_6$): 7.863 (d, *J* = 8.00 Hz, 2H), 7.65 (t, *J* = 8.50 Hz, 2H), 7.36 (d, *J* = 8.50 Hz, 2H), 7.11 (t, *J* = 7.50 Hz, 2H), 4.24 (s, 4H), 1.910 (s, 4H); ^{13}C NMR (125 MHz, DMSO-d$_6$, δ_C): 151.24, 139.55, 134.32, 124.80, 120.36, 115.03, 68.71, 24.98. ESI-MS (positive, DMF): calc., m/z = 332; found, m/z = 332.10.

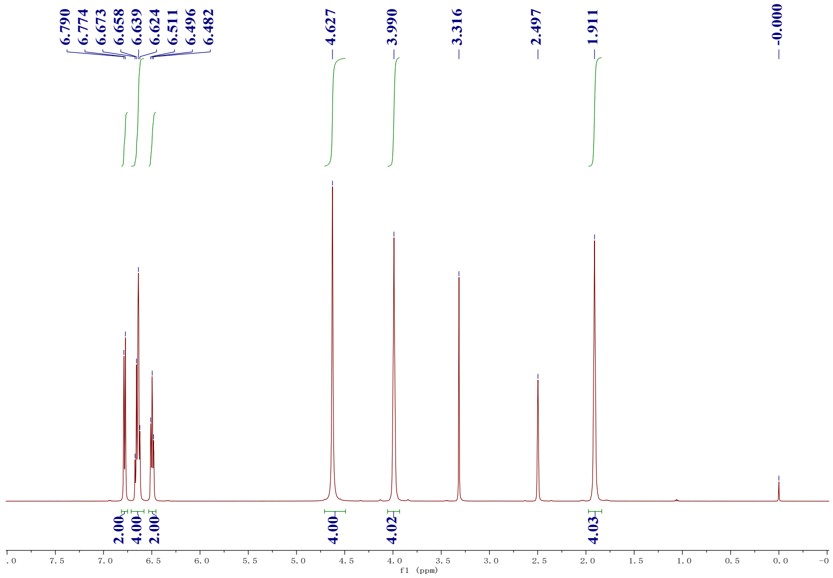
Synthesis of 2,2'- (butane-1,4-diylbis(oxy))dianiline: A mixture of 1,4-bis(2-nitrophenoxy)butane (2 g, 6.02 mmol), Pd-C (0.5 g, 10%), and hydrazine monohydrate (3 mL, 80%) in ethanol (30 mL) was heated to 80°C under nitrogen atmosphere for 8 h. The solution was filtered to remove Pd-C, and cooled to room temperature to give a precipitate, which then was isolated by filtration and recrystallized from ethanol. The solid product was dried under vacuum for two hours. Yield: 1.20 g (72%). EA: C, 70.35; H, 7.67; N, 10.11 % (found). Calc. for $C_{16}H_{20}O_2N_2$: C, 70.56; H, 7.40; N, 10.29 %. m. p. = 162°C. ^{1}H NMR (δ_H, ppm, 500 MHz, DMSO-d$_6$): 6.78 (d, *J* = 8.00 Hz, 2H), 6.65 (q, *J* = 7.50 Hz, 4H), 6.50 (t, *J* = 7.50 Hz, 2H), 4.63 (s, 4H, N-H), 3.99 (s, 4H), 1.91 (s, 4H). ^{13}C NMR (125 MHz, DMSO-d$_6$, δ_C): 145.60, 137.75, 120.83, 116.20, 113.92, 111.77, 67.49, 25.70. ESI-MS (positive, DMF): calc., m/z = 272; found, m/z = 272.15.

Synthesis of H_2L: 2-Hydroxy-3-methoxybenzaldehyde (20.0 mmol, 3.0430 g) was dissolved in 15 mL EtOH, and a solution of 2,2'-(butane-1,4-diylbis(oxy))dianiline (10.0 mmol, 2.7215 g) in 20 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 6 h. It was allowed to cool and was then filtered. The solid was washed with EtOH (3 × 5 mL) and then dried under vacuum to give red product. Yield (based on 2,2'-(butane-1,4-diylbis(oxy))dianiline): 4.6415 g (91%). EA: C, 71.37; H, 5.82; N, 5.26 % (found). Calc. for $C_{32}H_{32}O_6N_2$: C, 71.10; H, 5.97; N, 5.18 %. m. p. = 189°C. ^{1}H NMR (δ_H, ppm, 500 MHz, $CDCl_3$): 14.20 (s, 2H), 8.67 (s, 2H), 7.18 (d, *J* = 7.50 Hz, 2H), 6.93-6.99 (m, 8H), 6.83 (t, *J*=7.00 Hz, 2H), 4.13 (s, 4H), 3.92 (s, 6H), 2.06 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$, δ_C): 161.82, 152.34, 148.73, 127.93, 124.58, 123.68, 120.80, 119.67, 119.57, 118.02, 114.58, 113.14, 68.43, 56.36, 26.20. IR (KBr, cm^{-1}): 1616 (w), 1588 (w), 1450 (s), 1360 (w), 1244 (s), 1114 (s), 1040 (s), 967 (s), 861(s), 725(s). ESI-MS (positive, CH_2Cl_2): calc., m/z = 539.55; found, m/z = 540.23.

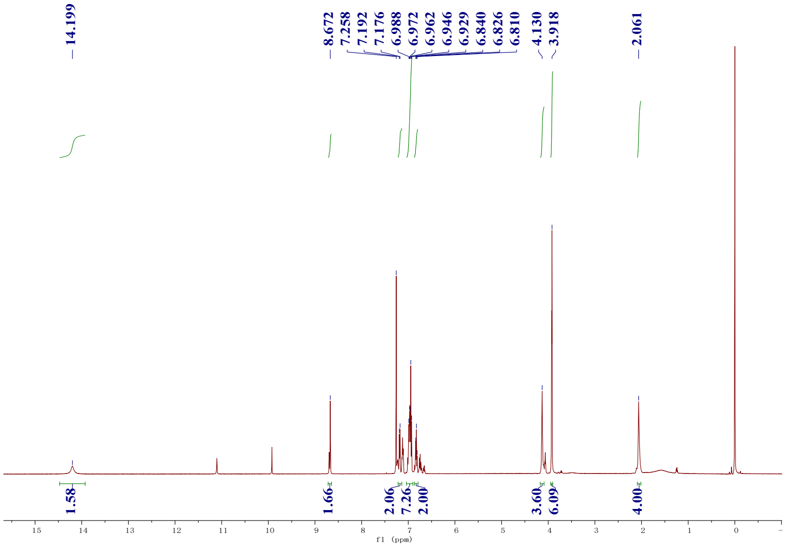
3. ^{1}H NMR spectra of the intermediates and ligand H_2L



(a)



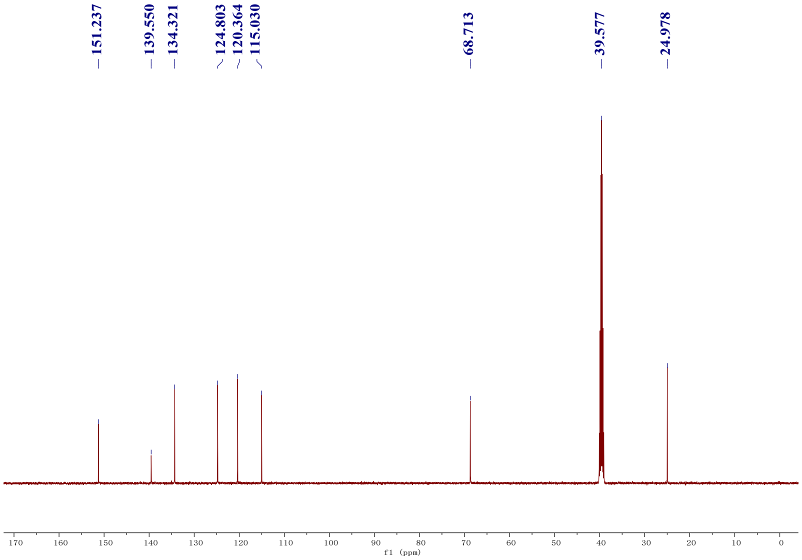
(b)



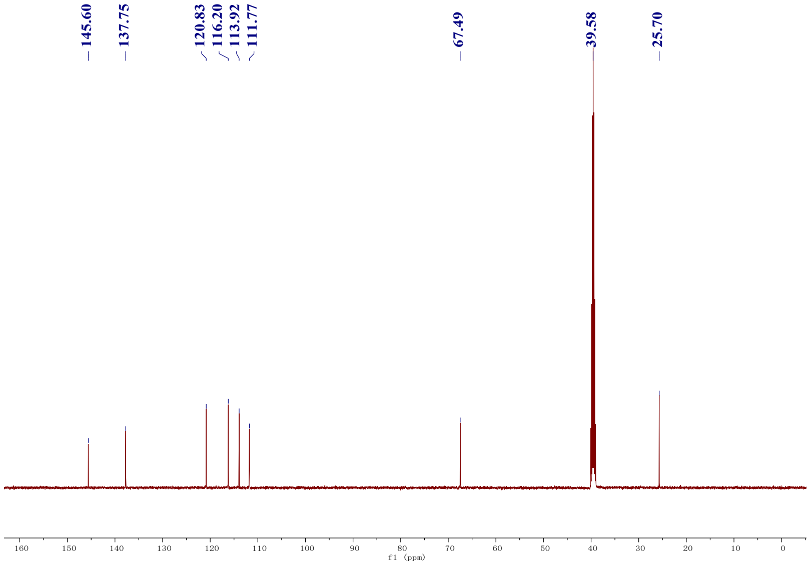
(c)

Figure S1. (a) The ^{1}H NMR spectrum of 1,4-bis(2-nitrophenoxy)butane in DMSO-d_6; (b) The ^{1}H NMR spectrum of 2,2'-(butane-1,4-diylbis(oxy))dianiline in DMSO-d_6; (c) The ^{1}H NMR spectrum of H_2L in $CDCl_3$.

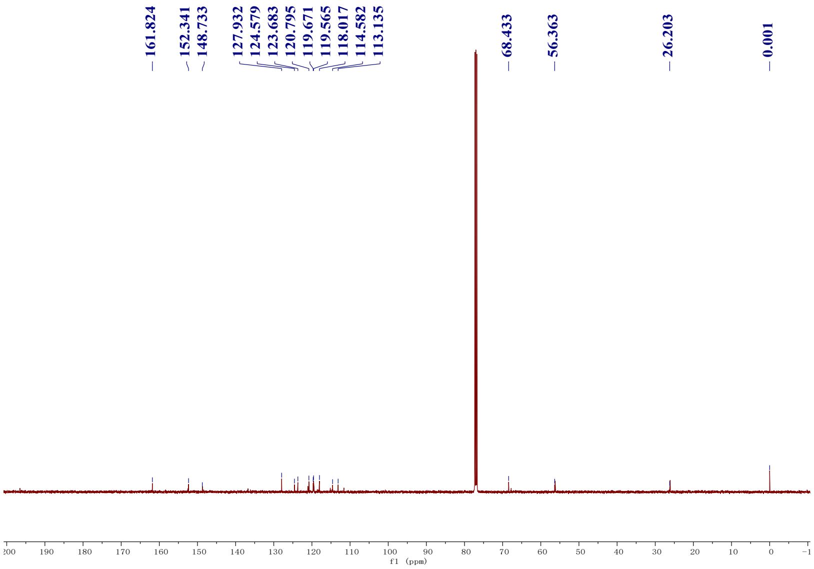
4. ^{13}C NMR spectra of the intermediates and ligand H_2L



(a)



(b)



(c)

Figure S2. (a) The ^{13}C NMR spectrum of 1,4-bis(2-nitrophenoxy)butane in DMSO-d_6; (b) The ^{13}C NMR spectrum of 2,2'-(butane-1,4-diylbis(oxy))dianiline in DMSO-d_6; (c) The ^{13}C NMR spectrum of H_2L in $CDCl_3$.

5. IR spectra of ligand H_2L and 1

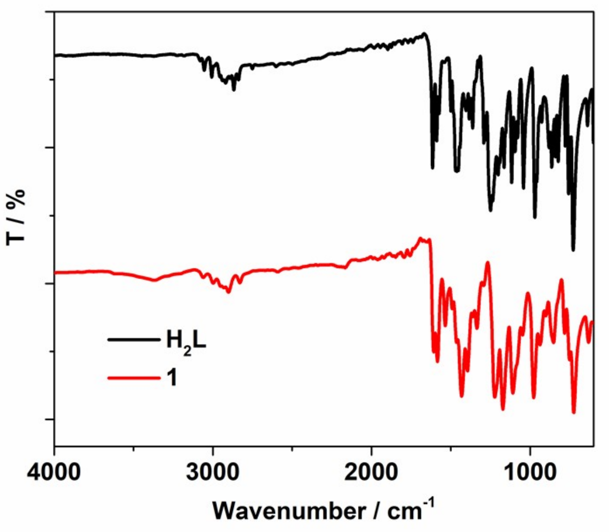


Figure S3. IR spectra of the free ligand H_2L and **1**.

6. The coordination modes of metal ions in 1

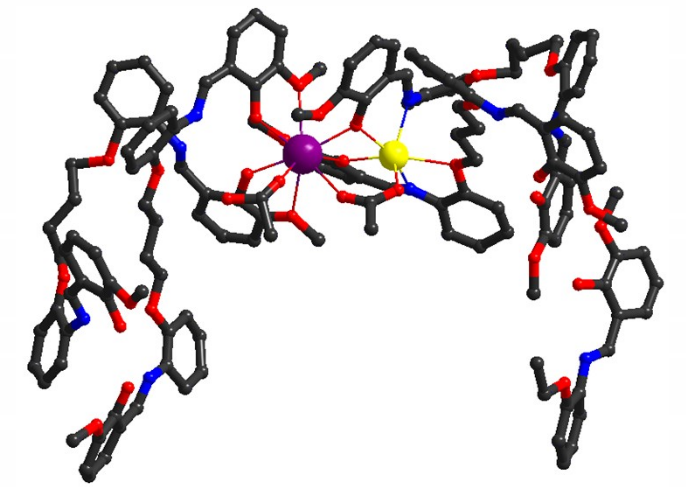


Figure S4. The coordination modes of Cd(II) and Tb(III) ions with four Schiff base ligands and two OAc^- anions in **1**.

7. The thermogravimetric analysis of 1

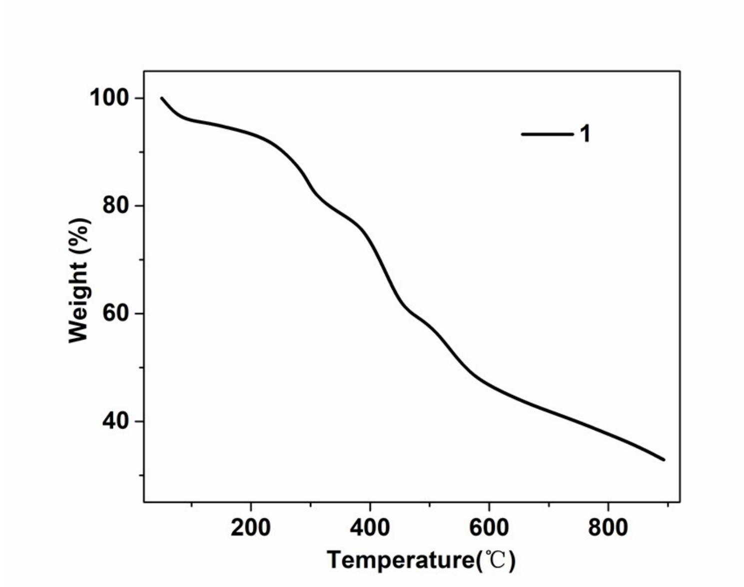


Figure S5. The thermogravimetric analysis of **1**.

8. Powder XRD pattern of 1

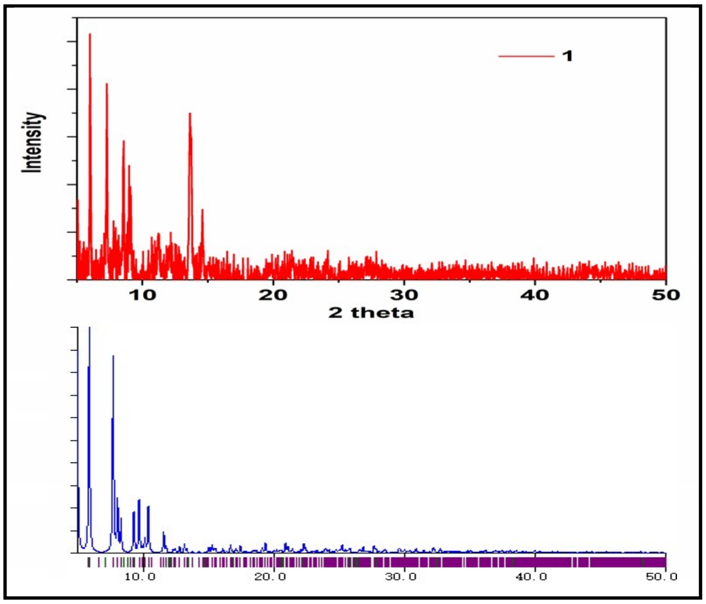


Figure S6. Powder XRD pattern of **1**. (top: experimental XRD; bottom: simulated XRD)

9. UV-vis absorption spectra of the ligand H_2L and 1

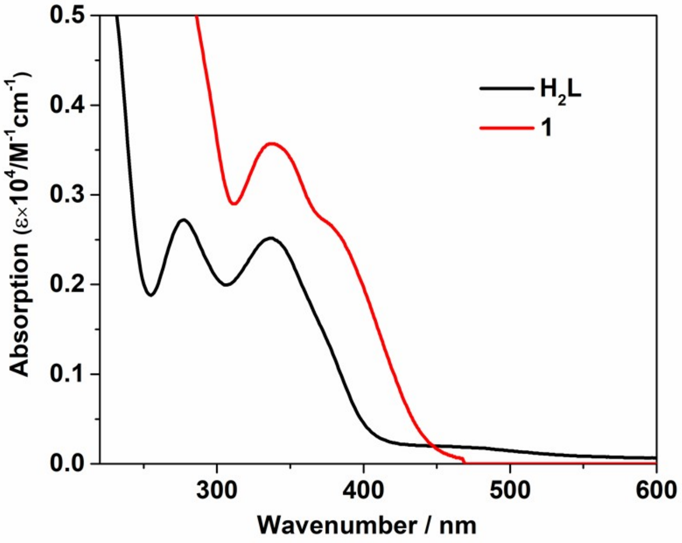
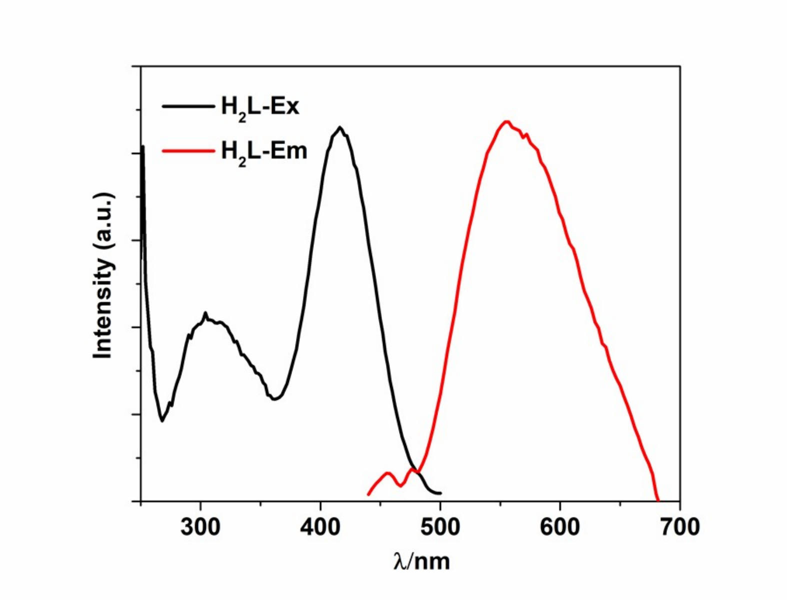


Figure S7. UV-vis absorption spectra of the free ligand H_2L and **1** in CH_3CN.

10. Photophysical properties of H_2L and 1



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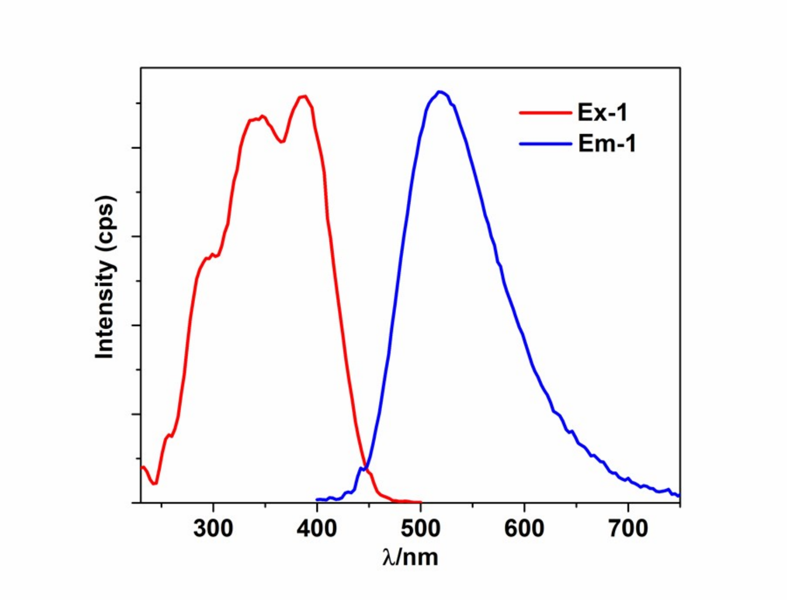


(b)

Figure S8. (a) The excitation (λ_{em} = 552 nm) and emission (λ_{ex} = 418 nm) spectra of the free ligand H_2L in CH_3CN; (b) The excitation (λ_{em} = 520 nm) and emission (λ_{ex} = 386 nm) spectra of **1** in CH_3CN.

11. Photophysical properties of 1 with the addition of DPA

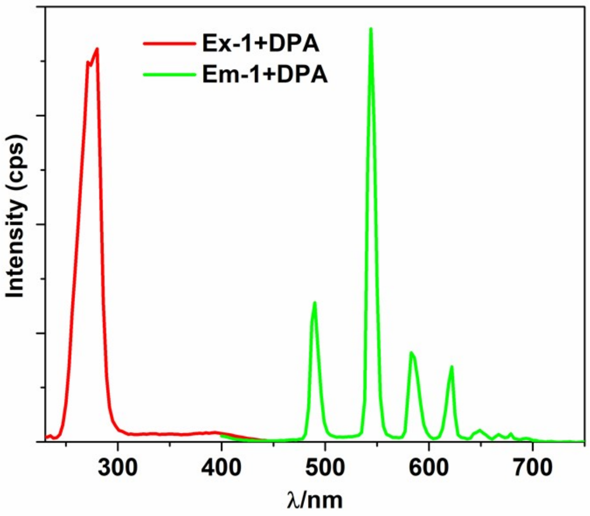
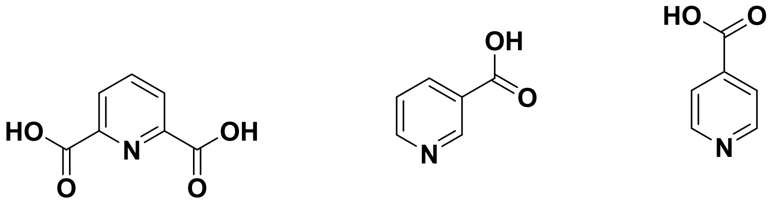
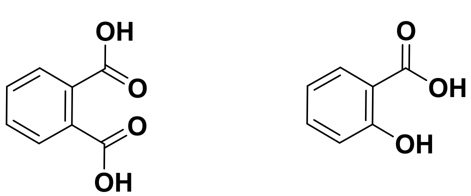


Figure S9. The excitation (λ_{em} = 544 nm) and emission (λ_{ex} = 272 nm) spectra of **1** (10 μM) with the addition of DPA (100 μM) in CH_3CN.

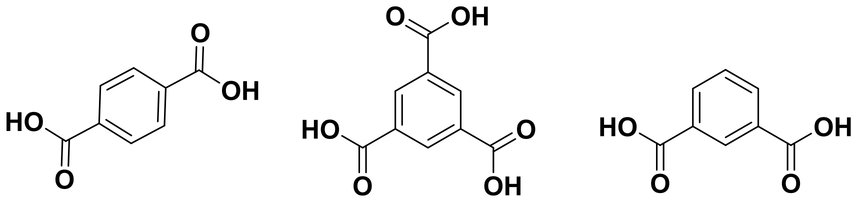
12. Chemical structures of carboxylic acids



Dipicolinic acid **DPA** Nicotinic acid **NA** Isonicotinic acid **INA**



Phthalic acid **PA** Salicylic acid **SA** Benzoic acid **BA**



terephthalic acid **TPA** Trimesic acid **TA** Isophthalic acid **IPA**

Scheme S2. Chemical structures of selected carboxylic acids.

13. The lanthanide emission spectra of 1 with the addition of DPA and carboxylic acids

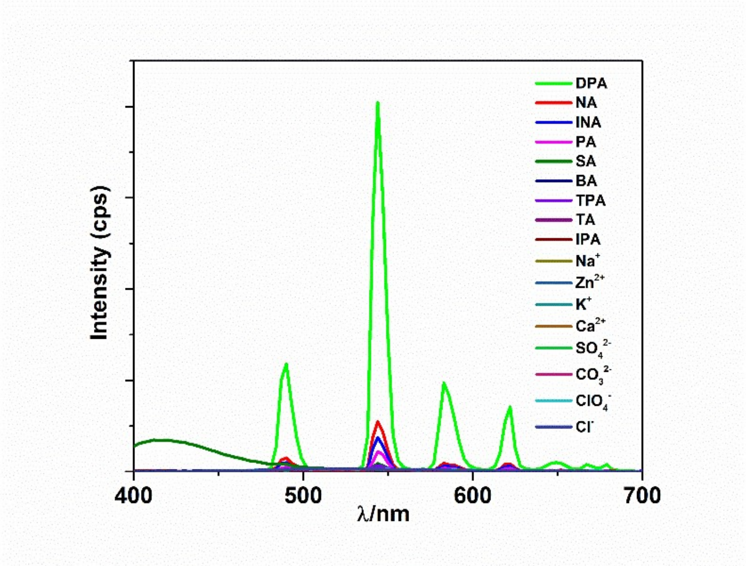


Figure S10. The lanthanide emission spectra of **1** (10 μM) with the addition of DPA (120 μM) and carboxylic acids (120 μM) in CH_3CN (λ_{ex} = 272 nm).

14. UV-vis titration of 1 to the addition of DPA

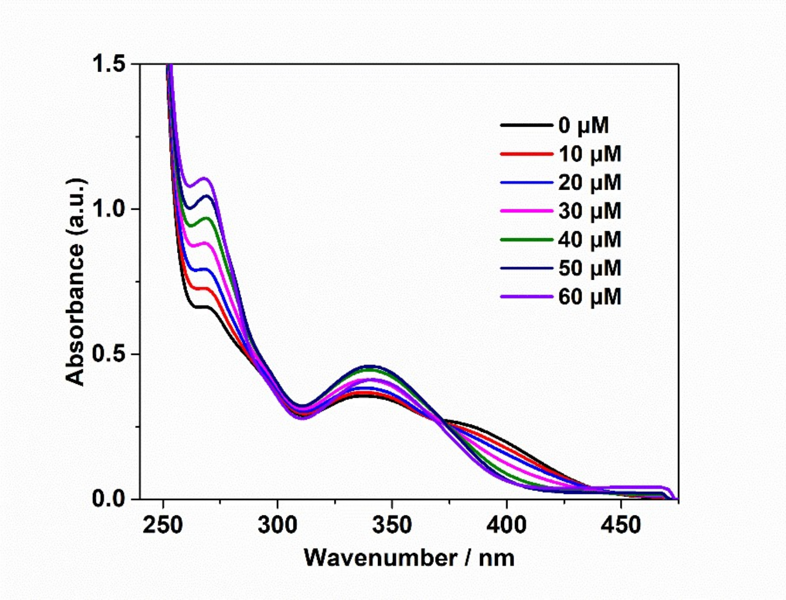


Figure S11. UV-vis titration of **1** (10 μM) with the addition of DPA in CH_3CN.

15. UV-Vis absorption spectra of carboxylic acids

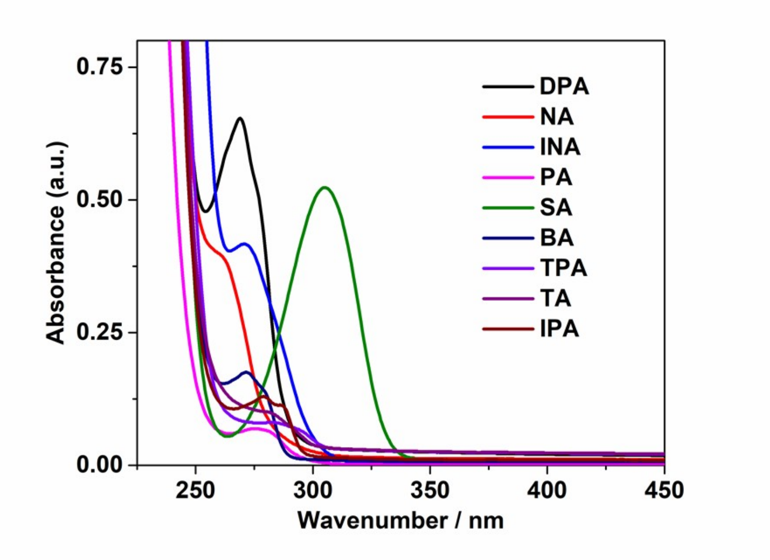


Figure S12. UV-vis absorption spectra of the carboxylic acids in CH_3CN ($c = 10\ \mu M$).

16. The luminescence lifetimes of 1 with the addition of DPA

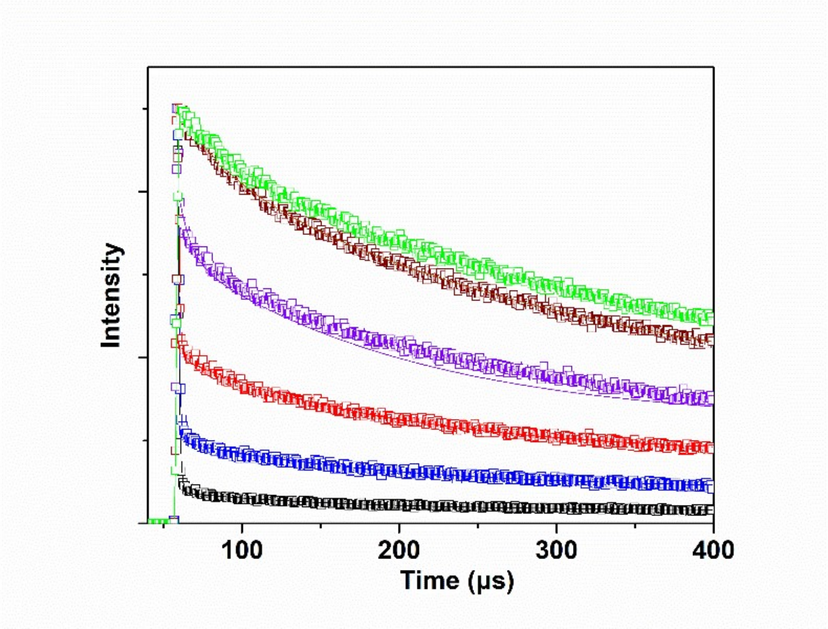


Figure S13. The luminescence lifetimes of **1** after the addition of DPA with different concentrations: black (20 μM, 81.09 μs), blue (40 μM, 140.59 μs), red (60 μM, 156.60 μs), purple (80 μM, 260.25 μs), brown (100 μM, 302.25 μs) and green (120 μM, 312.72 μs) lines.

17. The emission spectra of 1 with the addition of DPA

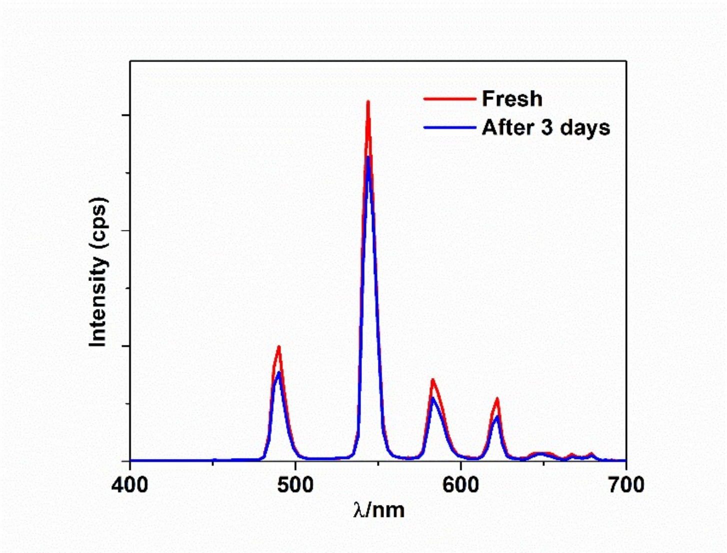


Figure S14. The emission spectra of **1** (10 μM) with the addition of DPA (120 μM).

18. X-Ray Crystallography

Data were collected on a Smart APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 190 K. The data set was corrected for absorption based on multiple scans and reduced using standard methods. Data reduction was performed using DENZO-SMN.[1] The structures were solved by direct methods and refined anisotropically using full-matrix least-squares methods with the SHELX 97 program package.[2] Coordinates of the non-hydrogen atoms were refined anisotropically, while hydrogen atoms were included in the calculation isotropically but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[3] PLATON98 was used as incorporated in WinGX (Farrugia, 1999). Selected bond lengths are given in Table S1. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format (CCDC reference number 2079048).

Ref. (1) DENZO-SMN. (**1997**). Z. Otwinowski, W. Minor, *Methods in Enzymology*, 276: *Macromolecular Crystallography, Part A*, 307 – 326, C. W. J. Carter, M. I. Simon, R. M. Sweet, Editors, Academic Press.

(2) G. H. Sheldrick, SHELX 97, *A software package for the solution and refinement of X-ray data*; University of Göttingen: Göttingen, Germany, **1997**.

(3) D. T. Cromer, J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, **1974**, Table 2.2A.

Table S1. Selected Bond Lengths (Å) and angles (◦) for **1**.

Tb(1)-O(15)	2.31(2)	O(15)-Tb(1)-O(7)	125.0(7)
Tb(1)-O(5)	2.327(19)	O(5)-Tb(1)-O(7)	103.5(6)
Tb(1)-O(14)	2.35(2)	O(14)-Tb(1)-O(7)	136.7(6)
Tb(1)-O(2)	2.396(18)	O(2)-Tb(1)-O(7)	64.1(6)
Tb(1)-O(11)	2.477(19)	O(11)-Tb(1)-O(7)	86.5(6)
Tb(1)-O(8)	2.524(15)	O(8)-Tb(1)-O(7)	57.8(5)
Tb(1)-O(12)	2.763(19)	O(12)-Tb(1)-O(7)	65.7(6)
Tb(1)-O(7)	2.80(2)	O(15)-Tb(1)-O(6)	87.9(6)
Tb(1)-O(6)	2.827(18)	O(5)-Tb(1)-O(6)	55.6(6)
Tb(1)-O(1)	2.857(19)	O(14)-Tb(1)-O(6)	70.8(6)
Cd(1)-O(13)	2.23(2)	O(2)-Tb(1)-O(6)	130.3(5)
Cd(1)-O(11)	2.276(18)	O(11)-Tb(1)-O(6)	70.2(6)
Cd(1)-N(4)	2.34(2)	O(8)-Tb(1)-O(6)	121.5(5)
Cd(1)-O(2)	2.358(17)	O(12)-Tb(1)-O(6)	71.3(6)
Cd(1)-N(1)	2.39(2)	O(7)-Tb(1)-O(6)	137.0(5)
Cd(1)-O(10)#1	2.543(18)	O(15)-Tb(1)-O(1)	68.4(6)
Cd(2)-N(3)	2.22(2)	O(5)-Tb(1)-O(1)	127.3(6)
Cd(2)-N(2)	2.23(2)	O(14)-Tb(1)-O(1)	87.3(6)
Cd(2)-O(8)	2.256(15)	O(2)-Tb(1)-O(1)	54.9(6)
Cd(2)-O(5)	2.32(2)	O(11)-Tb(1)-O(1)	122.2(6)
Cd(2)-O(16)	2.35(3)	O(8)-Tb(1)-O(1)	68.5(5)
Cd(2)-O(9)	2.489(17)	O(12)-Tb(1)-O(1)	137.8(6)
O(15)-Tb(1)-O(5)	73.8(7)	O(7)-Tb(1)-O(1)	72.1(6)
O(15)-Tb(1)-O(14)	77.7(7)	O(6)-Tb(1)-O(1)	150.9(5)
O(5)-Tb(1)-O(14)	119.0(7)	O(13)-Cd(1)-O(11)	111.3(8)
O(15)-Tb(1)-O(2)	116.0(7)	O(13)-Cd(1)-N(4)	103.4(8)
O(5)-Tb(1)-O(2)	167.0(6)	O(11)-Cd(1)-N(4)	81.7(7)
O(14)-Tb(1)-O(2)	72.8(6)	O(13)-Cd(1)-O(2)	87.9(7)
O(15)-Tb(1)-O(11)	147.4(7)	O(11)-Cd(1)-O(2)	71.3(7)
O(5)-Tb(1)-O(11)	109.6(7)	N(4)-Cd(1)-O(2)	153.1(7)
O(14)-Tb(1)-O(11)	72.6(6)	O(13)-Cd(1)-N(1)	135.6(8)
O(2)-Tb(1)-O(11)	67.3(6)	O(11)-Cd(1)-N(1)	102.2(7)
O(15)-Tb(1)-O(8)	72.8(6)	N(4)-Cd(1)-N(1)	109.6(8)
O(5)-Tb(1)-O(8)	66.0(6)	O(2)-Cd(1)-N(1)	75.9(7)
O(14)-Tb(1)-O(8)	147.0(6)	O(13)-Cd(1)-O(10)#1	81.1(7)
O(2)-Tb(1)-O(8)	107.5(5)	O(11)-Cd(1)-O(10)#1	150.2(7)
O(11)-Tb(1)-O(8)	139.2(6)	N(4)-Cd(1)-O(10)#1	68.8(7)
O(15)-Tb(1)-O(12)	139.0(7)	O(2)-Cd(1)-O(10)#1	137.8(6)
O(5)-Tb(1)-O(12)	65.2(6)	N(1)-Cd(1)-O(10)#1	84.0(7)
O(14)-Tb(1)-O(12)	124.2(6)	N(3)-Cd(2)-N(2)	112.1(8)
O(2)-Tb(1)-O(12)	104.2(6)	N(3)-Cd(2)-O(8)	78.0(7)
O(11)-Tb(1)-O(12)	56.7(6)	N(2)-Cd(2)-O(8)	102.7(6)
O(8)-Tb(1)-O(12)	88.3(6)	N(3)-Cd(2)-O(5)	148.4(8)

N(2)-Cd(2)-O(5)	79.0(8)	N(3)-Cd(2)-O(9)	70.3(7)
O(8)-Cd(2)-O(5)	70.6(6)	N(2)-Cd(2)-O(9)	86.6(7)
N(3)-Cd(2)-O(16)	101.0(9)	O(8)-Cd(2)-O(9)	148.2(6)
N(2)-Cd(2)-O(16)	136.5(9)	O(5)-Cd(2)-O(9)	141.2(7)
O(8)-Cd(2)-O(16)	111.3(9)	O(16)-Cd(2)-O(9)	78.7(9)
O(5)-Cd(2)-O(16)	87.4(9)		