Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Construction of a luminescent square-like Cd_6Eu_2 nanocluster for the quantitative detection of 2,6-dipicolinic acid as an anthrax biomarker

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Contents

1. Reagent and instruments

All chemicals were purchased from commercial sources and directly used without further purified. The total protein content in fetal calf serum (FCS) is 35-45 g/L. Elemental analyses were 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. Scanning electron microscopy (SEM) image and energy dispersive X-ray (EDX) spectroscopy were obtained from a Nova NanoSEM 200 microscope. UV-vis absorption spectra were measured using an UV-3600 spectrophotometer. Excitation and emission spectra were obtained using a FLS 980 fluorimeter.

2. 1H NMR spectrum of the ligand H_4L^1

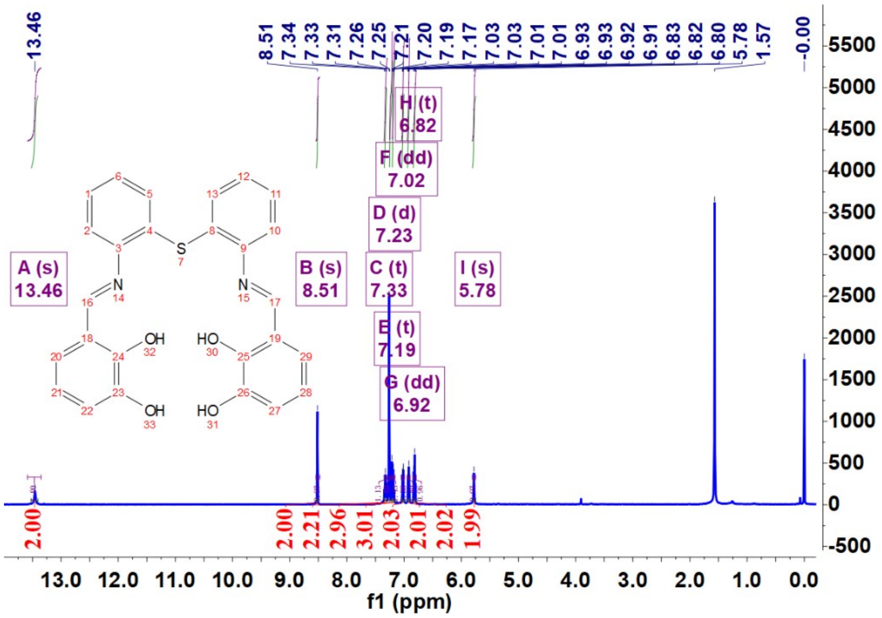


Figure S1. ^{1}H NMR spectrum of the Schiff base ligand H_4L^1 in $CDCl_3$.

3. IR spectra of the ligand H_4L^1, 1 and 2

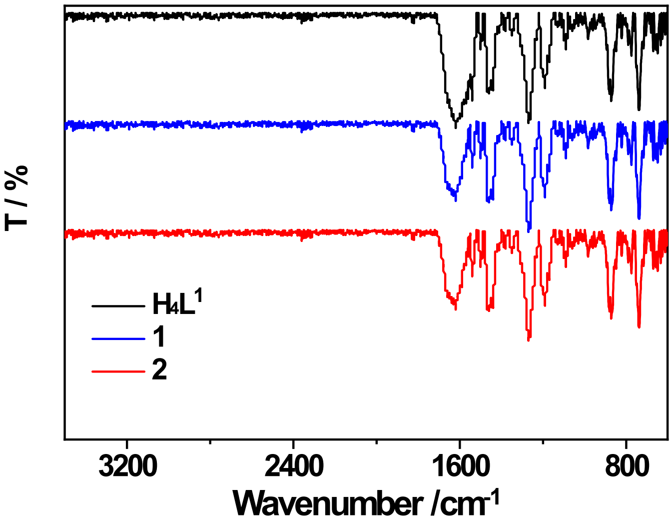


Figure S2. IR spectra of the ligand H_4L^1, **1** and **2**.

4. Powder XRD patterns of 1 and 2

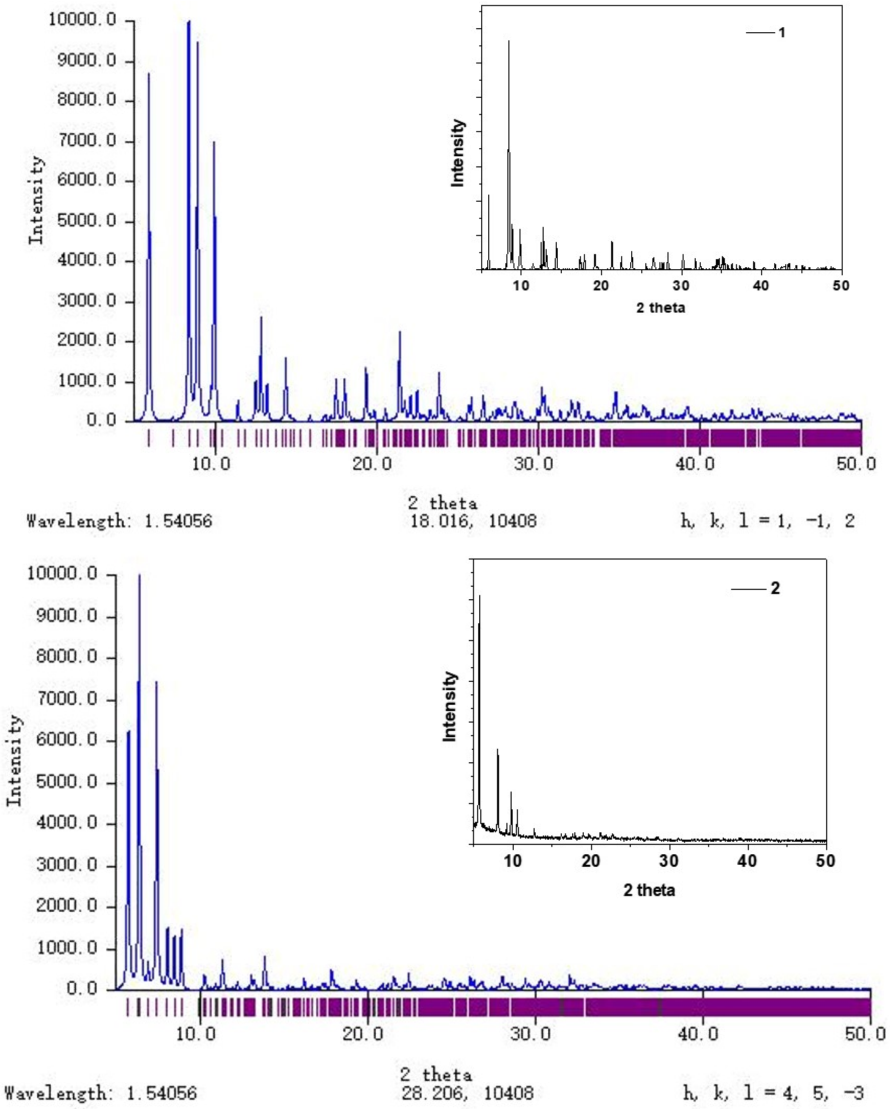


Figure S3. Powder XRD patterns of **1** and **2**.

5. UV-vis absorption spectra of the ligand H_4L^1, 1 and 2

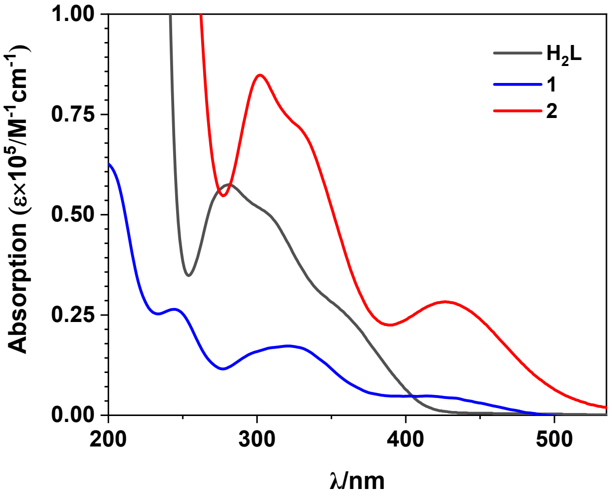


Figure S4. UV-vis absorption spectra of the ligand H_4L^1, **1** and **2** in CH_3CN.

6. The excitation and emission spectra of the ligand H_4L^1

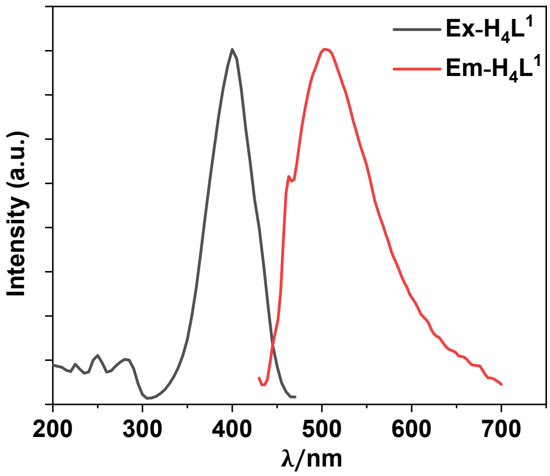
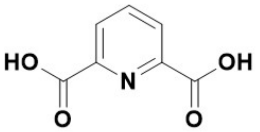
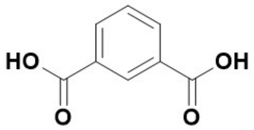


Figure S5. The excitation (λ_{em} =502 nm) and emission (λ_{ex} = 400 nm) spectra of the free ligand H_4L^1 (10 μM) in CH_3CN.

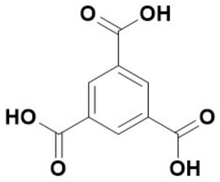
7. Chemical structures of DPA and carboxylic acids



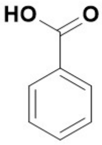
Dipicolinic acid **DPA**



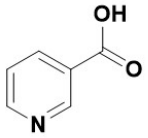
Isophthallc acid **IPA**



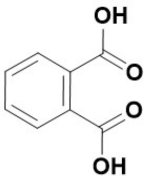
Trimesic acid **TA**



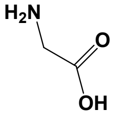
Benzoic acid **BA**



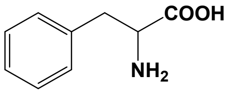
Nicotinic acid **NA**



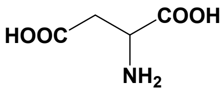
Phthalic acid **PA**



Glycine **Gly**



Phenylalanine **Phe**



Aspartic acid **Asp**

Scheme S1. Chemical structures of Chemical structures of DPA and carboxylic acids.

8. The excitation and emission spectra of 1 and 2

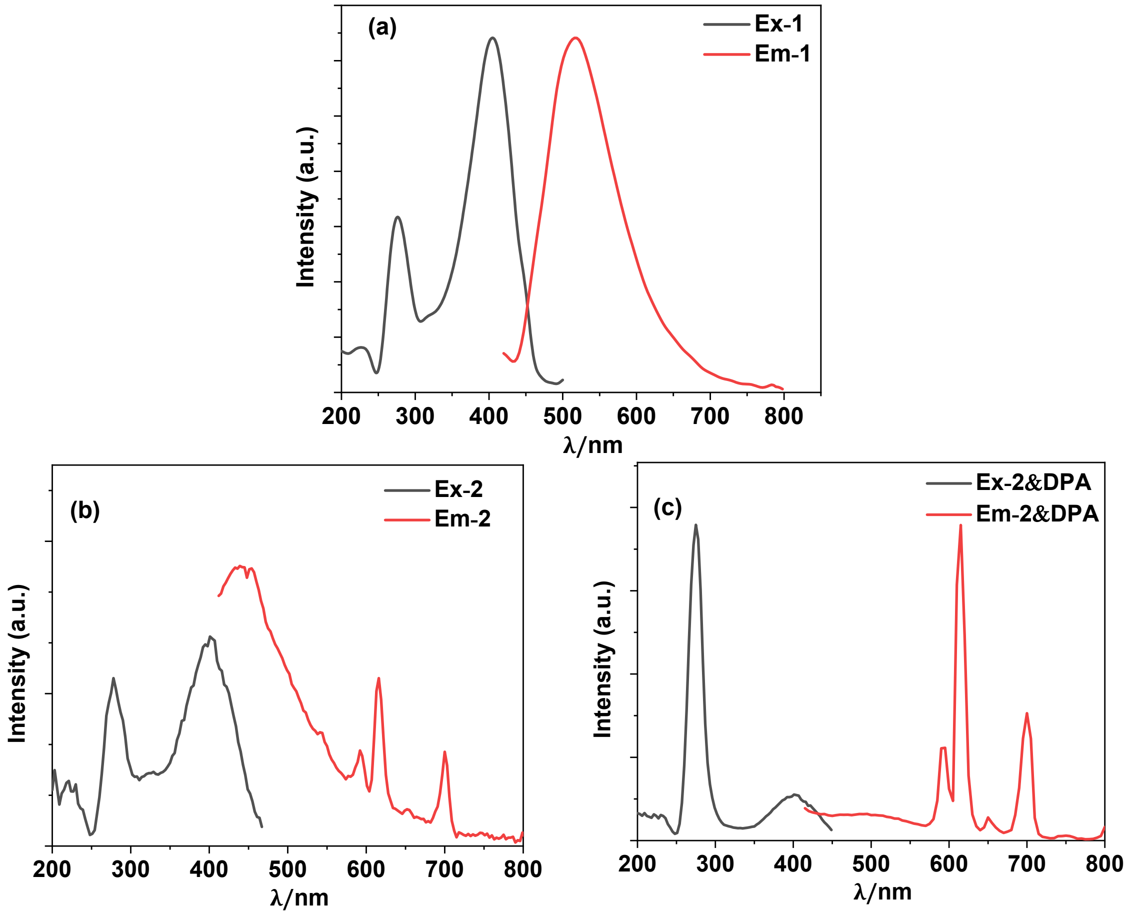


Figure S6. The excitation (λ_{em} = 520 nm) and emission (λ_{ex} = 402 nm) spectra of **1** (10 μM) in CH_3CN (**a**); and the excitation (λ_{em} = 615 nm) and emission (λ_{ex} = 275 nm) spectra of **2** (10 μM) before (**b**) and after (**c**) the addition of DPA (200 μM) in CH_3CN.

9. The enhancement of Eu(III) luminescence of 2 caused by DPA

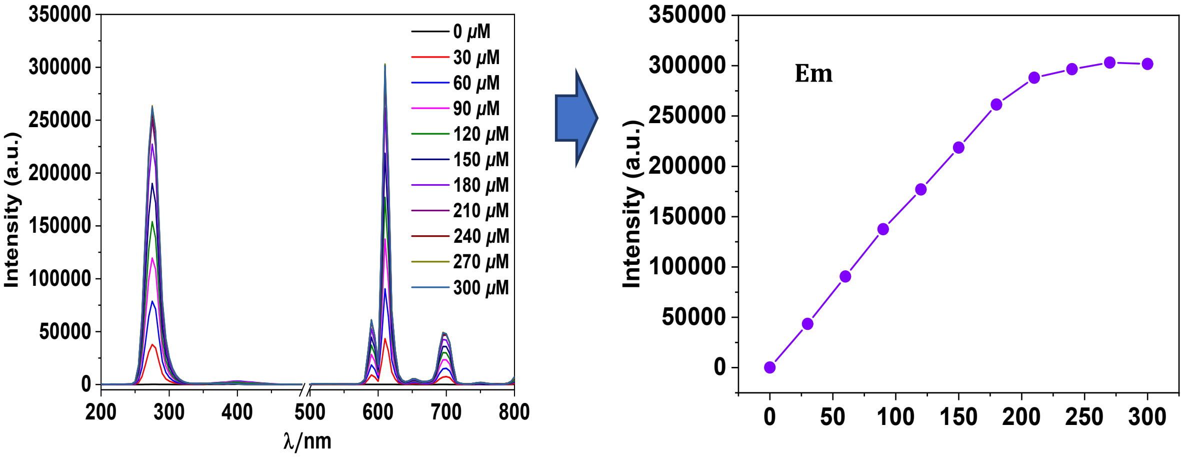


Figure S7. The excitation (λ_{em} = 615 nm) and emission (λ_{ex} = 275 nm) spectra of **2** (10 μM) with the addition of DPA in CH_3CN.

10. The color images of 2 under a UV lamp (365 nm) with addition of DPA

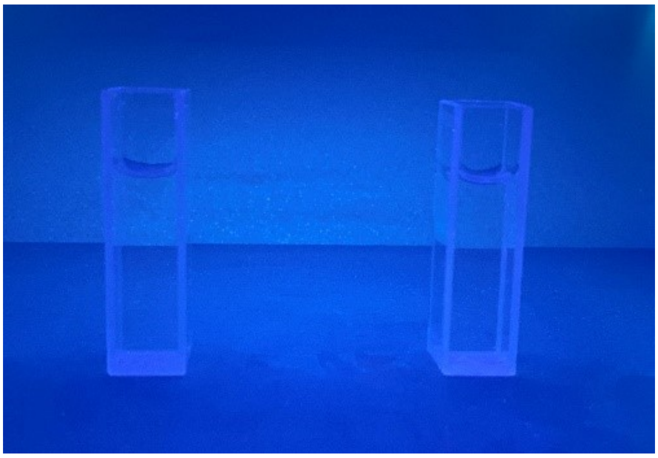
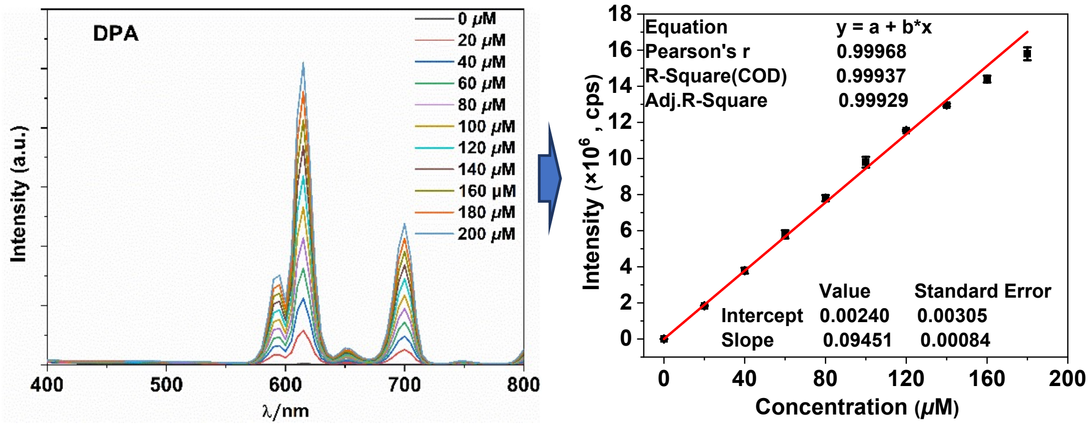
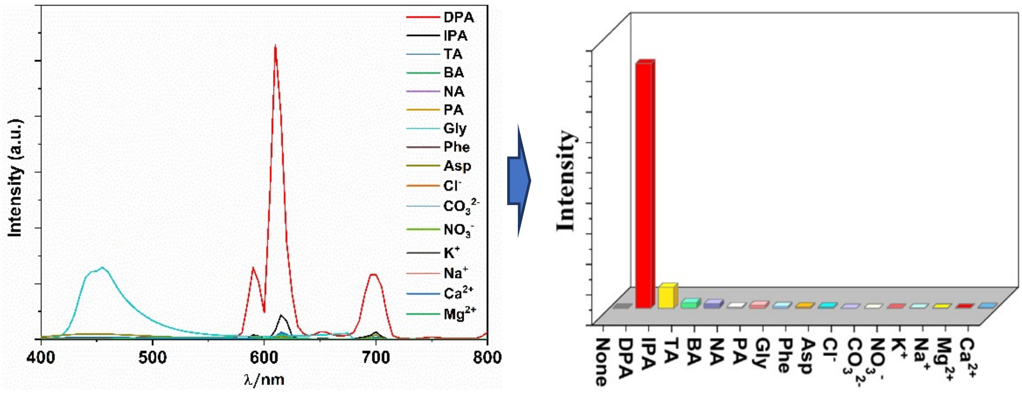


Figure S8. The color images of **2** (10 μM) under a UV lamp (365 nm) with addition of 100 μM (left) and 200 μM (right) DPA.

11. The fluorescent response of 2 to DPA and interferents



(a)



(b)

Figure S9. (**a**) The lanthanide luminescent response of **2** (10 μM) to the addition of different concentrations of DPA in CH_3CN ($\lambda_{ex} = 275$ nm, left), and relationship plot between luminescence intensities and concentrations of added DPA (right). (**b**) The emission response of **2** (10 μM) to DPA and various carboxylic acids and ions (200 μM) in CH_3CN ($\lambda_{ex} = 275$ nm, left), and the emission intensities of **2** at 615 nm (right).

12. The lanthanide luminescence response of the recycled sample of 2 to DPA

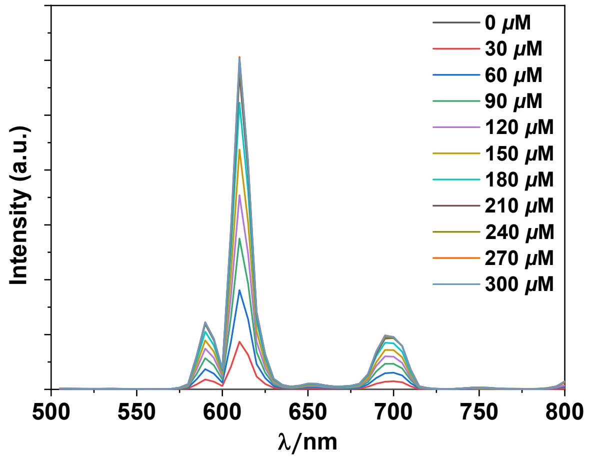


Figure S10. The lanthanide luminescence response of the recycled sample of **2** (10 μM) to DPA in CH_3CN (λ_{ex} = 275 nm).

13. The luminescence response of 2 to DPA in the presence of more interferents

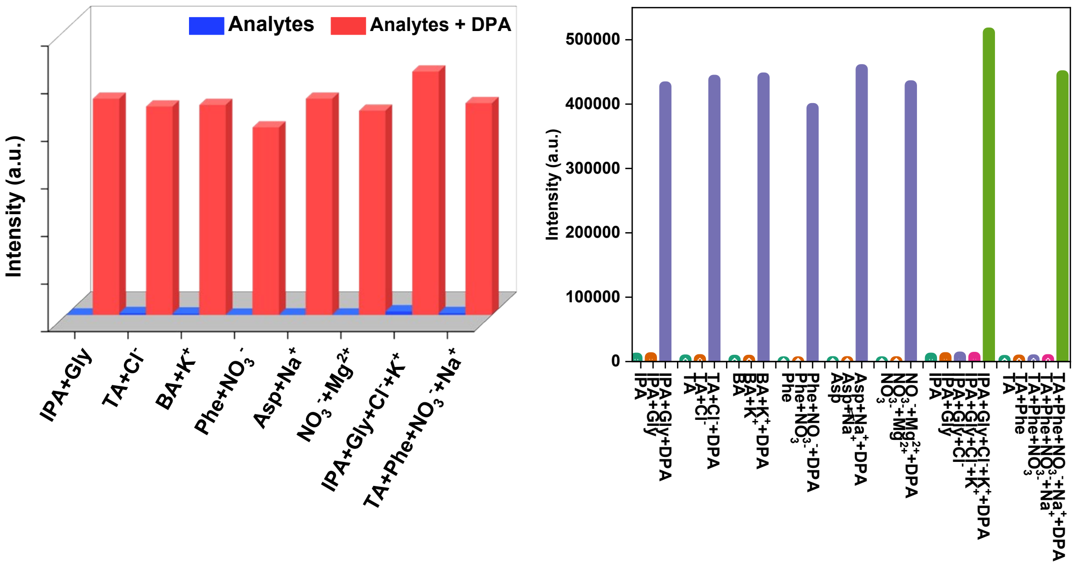


Figure S11. The luminescence intensity changes of **2** (10 μM) at 615 nm before and after the addition of DPA (60 μM) in the presence of two to five kinds of interferents (600 μM).

14. UV-vis titration of 2 to the addition of DPA

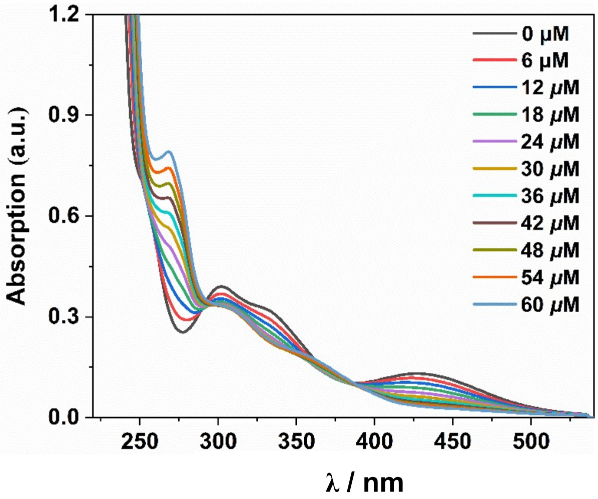


Figure S12. UV-vis titration of **2** (10 μM) with the addition of DPA in CH_3CN.

15. UV-vis absorption spectra of the PDA and carboxylic acids

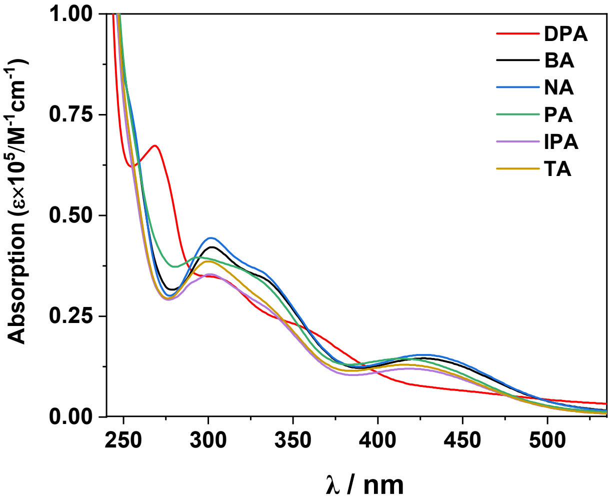


Figure S13. UV-vis absorption spectra of DPA and carboxylic acids in CH_3CN (c = 10 μM).

16. The lanthanide luminescence lifetimes of 2 with the addition of DPA

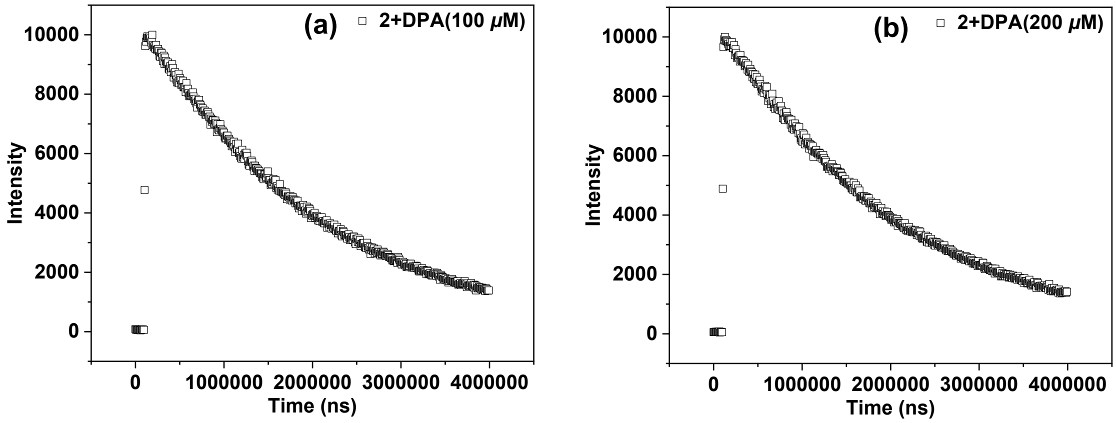


Figure S14. The lanthanide luminescence lifetimes **2** (10 μM) with the addition of 100 μM (**a**) and 200 μM (**b**) of DPA.

17. The lanthanide luminescence spectra of 2 with the addition of DPA

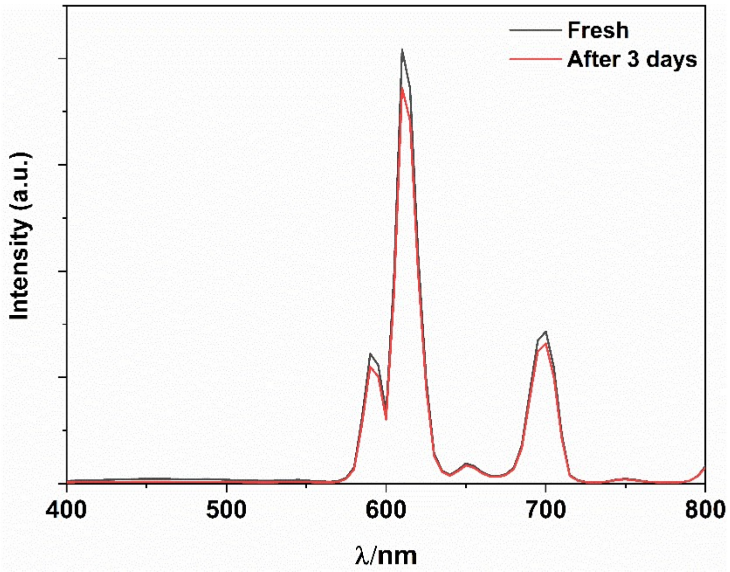


Figure S15. The emission spectra of **2** (10 μM) with the addition of DPA (60 μM).

18. X-ray crystallography

Table S1. Selected bond lengths (Å) and angles (°) for **1**

Ho(1)-O(13)	2.248(7)	O(13)-Ho(1)-O(14)	73.7(3)
Ho(1)-O(4)	2.269(9)	O(4)-Ho(1)-O(14)	95.9(3)
Ho(1)-O(3)	2.285(9)	O(3)-Ho(1)-O(14)	73.4(3)
Ho(1)-O(1)	2.310(8)	O(1)-Ho(1)-O(14)	91.7(3)
Ho(1)-O(9)	2.327(9)	O(9)-Ho(1)-O(14)	144.3(3)
Ho(1)-O(14)	2.333(7)	O(13)-Ho(1)-O(2)	131.2(3)
Ho(1)-O(2)	2.364(8)	O(4)-Ho(1)-O(2)	141.5(2)
Ho(1)-O(10)	2.398(8)	O(3)-Ho(1)-O(2)	69.9(3)
Ho(2)-O(12)	2.278(8)	O(1)-Ho(1)-O(2)	70.0(3)
Ho(2)-O(7)	2.248(7)	O(9)-Ho(1)-O(2)	75.4(3)
Ho(2)-O(8)	2.247(13)	O(14)-Ho(1)-O(2)	73.8(3)
Ho(2)-O(10)	2.309(8)	O(13)-Ho(1)-O(10)	72.4(3)
Ho(2)-O(6)	2.331(11)	O(4)-Ho(1)-O(10)	81.0(3)
Ho(2)-O(5)	2.383(11)	O(3)-Ho(1)-O(10)	135.2(3)
Ho(2)-O(13)	2.388(8)	O(1)-Ho(1)-O(10)	75.6(3)
Ho(2)-O(11)	2.578(14)	O(9)-Ho(1)-O(10)	69.5(3)
Cd(1)-O(15)	2.223(8)	O(14)-Ho(1)-O(10)	145.7(3)
Cd(1)-O(2)	2.254(7)	O(2)-Ho(1)-O(10)	127.9(3)
Cd(1)-O(3)	2.298(10)	O(12)-Ho(2)-O(7)	79.8(3)
Cd(1)-N(2)	2.377(10)	O(12)-Ho(2)-O(8)	96.7(4)
Cd(1)-O(16)	2.420(11)	O(7)-Ho(2)-O(8)	70.4(4)
Cd(1)-N(1)	2.425(12)	O(12)-Ho(2)-O(10)	141.1(3)
Cd(1)-S(1)	2.913(4)	O(7)-Ho(2)-O(10)	131.0(3)
Cd(2)-O(6)	2.292(9)	O(8)-Ho(2)-O(10)	77.5(4)
Cd(2)-N(4)	2.317(13)	O(12)-Ho(2)-O(6)	72.4(4)
Cd(2)-O(7)	2.357(9)	O(7)-Ho(2)-O(6)	72.4(3)
Cd(2)-N(3)	2.357(14)	O(8)-Ho(2)-O(6)	142.5(3)
Cd(2)-O(17)	2.368(7)	O(10)-Ho(2)-O(6)	133.1(3)
Cd(2)-O(18)	2.507(6)	O(12)-Ho(2)-O(5)	92.9(4)
Cd(2)-S(2)	2.867(4)	O(7)-Ho(2)-O(5)	142.6(4)
O(13)-Ho(1)-O(4)	77.2(3)	O(8)-Ho(2)-O(5)	146.9(4)
O(13)-Ho(1)-O(3)	131.3(3)	O(10)-Ho(2)-O(5)	75.2(3)
O(4)-Ho(1)-O(3)	71.7(3)	O(6)-Ho(2)-O(5)	70.5(3)
O(13)-Ho(1)-O(1)	75.7(3)	O(12)-Ho(2)-O(13)	69.6(3)
O(4)-Ho(1)-O(1)	148.4(3)	O(7)-Ho(2)-O(13)	132.8(3)
O(3)-Ho(1)-O(1)	139.7(3)	O(8)-Ho(2)-O(13)	78.3(4)
O(13)-Ho(1)-O(9)	141.8(3)	O(10)-Ho(2)-O(13)	71.5(3)
O(4)-Ho(1)-O(9)	96.9(3)	O(6)-Ho(2)-O(13)	126.7(3)
O(3)-Ho(1)-O(9)	79.2(3)	O(5)-Ho(2)-O(13)	75.6(4)
O(1)-Ho(1)-O(9)	94.5(3)	O(12)-Ho(2)-O(11)	145.1(4)

O(7)-Ho(2)-O(11)	72.4(4)	N(2)-Cd(1)-S(1)	65.2(3)
O(8)-Ho(2)-O(11)	93.6(5)	O(16)-Cd(1)-S(1)	82.0(3)
O(10)-Ho(2)-O(11)	73.8(4)	N(1)-Cd(1)-S(1)	71.7(2)
O(6)-Ho(2)-O(11)	79.2(4)	O(6)-Cd(2)-N(4)	146.5(4)
O(5)-Ho(2)-O(11)	96.4(4)	O(6)-Cd(2)-O(7)	71.1(3)
O(13)-Ho(2)-O(11)	145.3(4)	N(4)-Cd(2)-O(7)	76.4(4)
O(15)-Cd(1)-O(2)	89.5(3)	O(6)-Cd(2)-N(3)	79.1(4)
O(15)-Cd(1)-O(3)	93.7(3)	N(4)-Cd(2)-N(3)	133.1(4)
O(2)-Cd(1)-O(3)	71.6(3)	O(7)-Cd(2)-N(3)	150.2(3)
O(15)-Cd(1)-N(2)	79.4(4)	O(6)-Cd(2)-O(17)	85.8(3)
O(2)-Cd(1)-N(2)	147.9(3)	N(4)-Cd(2)-O(17)	97.2(4)
O(3)-Cd(1)-N(2)	79.2(3)	O(7)-Cd(2)-O(17)	80.6(3)
O(15)-Cd(1)-O(16)	172.9(3)	N(3)-Cd(2)-O(17)	97.1(3)
O(2)-Cd(1)-O(16)	83.7(3)	O(6)-Cd(2)-O(18)	59.6(3)
O(3)-Cd(1)-O(16)	82.0(3)	N(4)-Cd(2)-O(18)	107.7(4)
N(2)-Cd(1)-O(16)	105.3(4)	O(7)-Cd(2)-O(18)	81.4(3)
O(15)-Cd(1)-N(1)	84.6(4)	N(3)-Cd(2)-O(18)	84.1(4)
O(2)-Cd(1)-N(1)	80.2(3)	O(17)-Cd(2)-O(18)	144.7(3)
O(3)-Cd(1)-N(1)	151.8(3)	O(6)-Cd(2)-S(2)	142.9(3)
N(2)-Cd(1)-N(1)	127.7(4)	N(4)-Cd(2)-S(2)	69.0(3)
O(16)-Cd(1)-N(1)	96.4(4)	O(7)-Cd(2)-S(2)	134.7(2)
O(15)-Cd(1)-S(1)	105.0(3)	N(3)-Cd(2)-S(2)	71.7(3)
O(2)-Cd(1)-S(1)	146.7(2)	O(17)-Cd(2)-S(2)	75.81(18)
O(3)-Cd(1)-S(1)	135.1(3)	O(18)-Cd(2)-S(2)	136.3(2)

Table S2. Selected bond lengths (Å) and angles (°) for **2**

Eu(1)-O(11)	2.299(12)	O(4)-Eu(1)-O(3)	66.3(4)
Eu(1)-O(4)	2.334(12)	O(7)-Eu(1)-O(3)	87.0(4)
Eu(1)-O(7)	2.357(10)	O(10)-Eu(1)-O(3)	128.8(4)
Eu(1)-O(10)	2.352(11)	O(13)-Eu(1)-O(3)	143.8(4)
Eu(1)-O(13)	2.355(10)	O(8)-Eu(1)-O(3)	130.6(4)
Eu(1)-O(8)	2.380(10)	O(11)-Eu(1)-O(6)	80.7(4)
Eu(1)-O(3)	2.395(10)	O(4)-Eu(1)-O(6)	135.1(4)
Eu(1)-O(6)	2.552(10)	O(7)-Eu(1)-O(6)	72.5(3)
Cd(1)-O(4)#1	2.217(11)	O(10)-Eu(1)-O(6)	132.5(4)
Cd(1)-O(12)	2.242(13)	O(13)-Eu(1)-O(6)	73.7(4)
Cd(1)-O(10)	2.276(11)	O(8)-Eu(1)-O(6)	133.3(3)
Cd(1)-O(8)	2.299(10)	O(3)-Eu(1)-O(6)	70.2(4)
Cd(1)-O(9)	2.312(14)	O(4)#1-Cd(1)-O(12)	111.0(5)
Cd(1)-O(8)#1	2.475(11)	O(4)#1-Cd(1)-O(10)	158.3(4)
Cd(2)-O(2)	2.197(12)	O(12)-Cd(1)-O(10)	90.4(4)
Cd(2)-O(7)	2.242(10)	O(4)#1-Cd(1)-O(8)	107.4(4)
Cd(2)-N(3)	2.298(12)	O(12)-Cd(1)-O(8)	89.6(4)
Cd(2)-N(4)	2.302(14)	O(10)-Cd(1)-O(8)	75.2(4)
Cd(2)-O(6)	2.314(10)	O(4)#1-Cd(1)-O(9)	91.6(5)
Cd(2)-S(2)	2.878(5)	O(12)-Cd(1)-O(9)	99.6(5)
Cd(3)-O(3)	2.219(11)	O(10)-Cd(1)-O(9)	80.8(4)
Cd(3)-O(2)	2.328(11)	O(8)-Cd(1)-O(9)	154.3(4)
Cd(3)-N(1)	2.333(14)	O(4)#1-Cd(1)-O(8)#1	73.6(4)
Cd(3)-N(2)	2.330(15)	O(12)-Cd(1)-O(8)#1	171.7(4)
Cd(3)-O(5)	2.388(12)	O(10)-Cd(1)-O(8)#1	85.6(4)
Cd(3)-O(6)	2.430(11)	O(8)-Cd(1)-O(8)#1	82.3(3)
Cd(3)-S(1)	2.940(5)	O(9)-Cd(1)-O(8)#1	87.0(4)
O(11)-Eu(1)-O(4)	99.9(4)	O(2)-Cd(2)-O(7)	104.4(4)
O(11)-Eu(1)-O(7)	152.4(4)	O(2)-Cd(2)-N(3)	139.4(5)
O(4)-Eu(1)-O(7)	94.5(4)	O(7)-Cd(2)-N(3)	108.2(5)
O(11)-Eu(1)-O(10)	66.1(4)	O(2)-Cd(2)-N(4)	104.9(5)
O(4)-Eu(1)-O(10)	85.3(4)	O(7)-Cd(2)-N(4)	80.8(4)
O(7)-Eu(1)-O(10)	139.1(4)	N(3)-Cd(2)-N(4)	103.6(5)
O(11)-Eu(1)-O(13)	94.4(5)	O(2)-Cd(2)-O(6)	82.4(4)
O(4)-Eu(1)-O(13)	149.5(4)	O(7)-Cd(2)-O(6)	79.3(4)
O(7)-Eu(1)-O(13)	84.6(4)	N(3)-Cd(2)-O(6)	80.5(4)
O(10)-Eu(1)-O(13)	76.0(4)	N(4)-Cd(2)-O(6)	160.0(4)
O(11)-Eu(1)-O(8)	138.3(4)	O(2)-Cd(2)-S(2)	95.1(3)
O(4)-Eu(1)-O(8)	73.4(4)	O(7)-Cd(2)-S(2)	149.0(3)
O(7)-Eu(1)-O(8)	68.5(3)	N(3)-Cd(2)-S(2)	68.0(4)
O(10)-Eu(1)-O(8)	72.3(4)	N(4)-Cd(2)-S(2)	70.8(3)
O(13)-Eu(1)-O(8)	78.0(4)	O(6)-Cd(2)-S(2)	127.8(3)
O(11)-Eu(1)-O(3)	77.5(4)	O(3)-Cd(3)-O(2)	86.9(4)

O(3)-Cd(3)-N(1)	163.9(4)	O(2)-Cd(3)-O(6)	77.3(4)
O(2)-Cd(3)-N(1)	78.5(4)	N(1)-Cd(3)-O(6)	94.7(4)
O(3)-Cd(3)-N(2)	83.9(5)	N(2)-Cd(3)-O(6)	156.6(4)
O(2)-Cd(3)-N(2)	91.1(5)	O(5)-Cd(3)-O(6)	67.4(4)
N(1)-Cd(3)-N(2)	103.0(5)	O(3)-Cd(3)-S(1)	127.1(3)
O(3)-Cd(3)-O(5)	90.8(4)	O(2)-Cd(3)-S(1)	135.3(3)
O(2)-Cd(3)-O(5)	144.0(4)	N(1)-Cd(3)-S(1)	69.0(4)
N(1)-Cd(3)-O(5)	97.0(5)	N(2)-Cd(3)-S(1)	68.3(4)
N(2)-Cd(3)-O(5)	124.3(4)	O(5)-Cd(3)-S(1)	71.8(3)
O(3)-Cd(3)-O(6)	75.3(4)	O(6)-Cd(3)-S(1)	133.5(3)