Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

A high-nuclearity Cd(II)-Nd(III) nanocage for the rapid ratiometric fluorescent detection of quercetin

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Contents

1. General Procedures

All chemicals were purchased from commercial sources and directly used without further purified. The lanthanide complexes were synthesized using Schlenk system. 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 spectrum was recorded 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) spectrum was measured on a Malvern Zetasizer zs90. Scanning electron microscopy (SEM) images were obtained from a Nova NanoSEM 200 microscope. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-1200EX transmission electron microscope. UV-vis absorbance spectra were determined on an UV-3600 spectrophotometer. Excitation and emission spectra were carried out on a FLS 980 fluorimeter. Emission quantum yields were measured using an integrating sphere, and emission lifetimes were obtained by the attached storage digital oscilloscope.

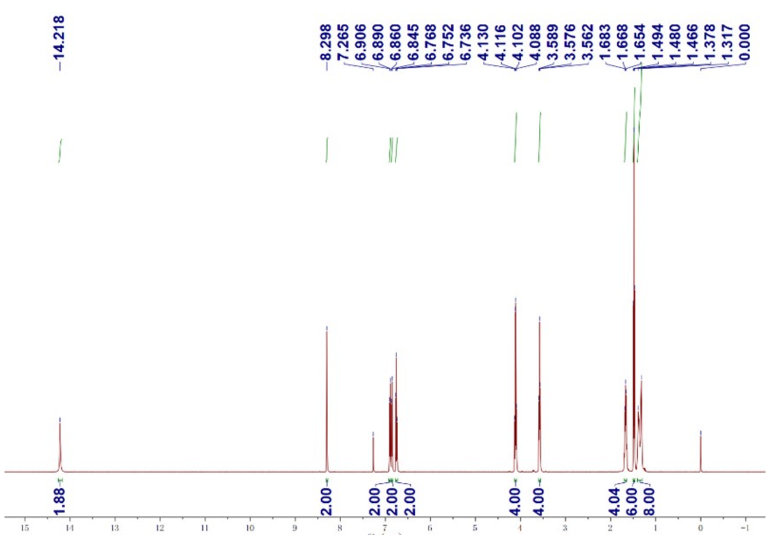
Photophysical Studies Visible and NIR luminescence spectra were recorded on a FLS 980 fluorimeter. The light source for the spectra was a 450 W xenon arc lamp with continuous spectral distribution from 190 to 2600 nm. Liquid nitrogen cooled Ge PIN diode detector was used to detect the NIR emissions from 800 nm to 1700 nm. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. The quantum yields (Φ_{em}) were obtained by using an integrating sphere, according to eqn $\Phi_{em} = N_{em} / N_{abs}$, where N_{em} and N_{abs} are the numbers of emitted and absorbed photons, respectively. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

2. Synthesis of the Gd(III) analogue

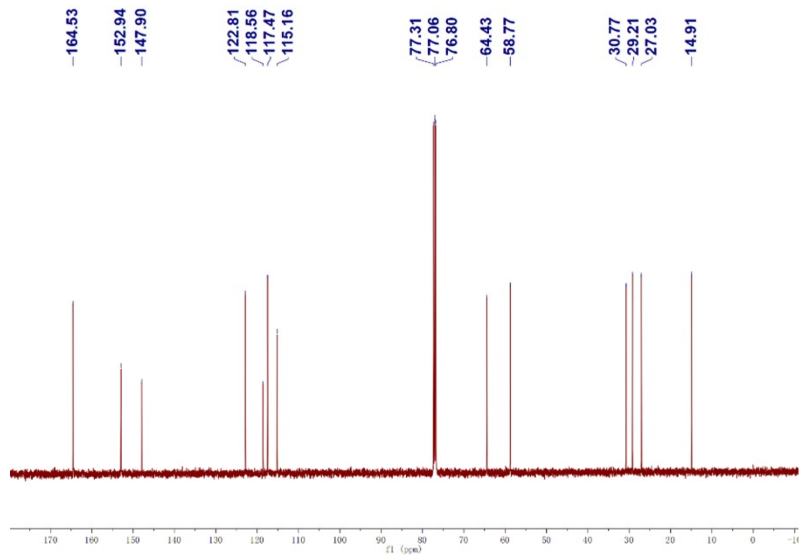
Synthesis of the Gd(III) analogue [$Cd_{24}Gd_8L_{12}(OAc)_{48}$]

$Gd(OAc)_3 \cdot 4H_2O$ (0.20 mmol, 0.0812 g), $Cd(OAc)_2 \cdot 2H_2O$ (0.60 mmol, 0.1595 g) and H_2L (0.40 mmol, 0.1770 g) were dissolved in 20 mL EtOH at room temperature, and a solution of triethylamine in MeOH (1.0 mol/L, 1 ml) was then added. The resulting solution was stirred and heated under reflux for 30 mins. It was allowed to cool and was then filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature and straw yellow powders were obtained after two weeks. The crystals were filtered off, washed with EtOH (3×5 ml) and dried in the air for one week. Yield (based on $Gd(OAc)_3 \cdot 6H_2O$): 0.1115 g (37%). IR (KBr, cm^{-1}): 2937 (m), 2852 (m), 1535 (s), 1394 (s), 1313 (w), 1206 (s), 1010 (s), 877 (m), 834 (w), 732 (s), 657 (s). m. p. > 280 ^{o}C (dec.).

3. ^1H NMR and ^{13}C NMR spectra of the ligand H_2L



(a)



(b)

Figure S1. (a) ^{1}H NMR spectrum of the ligand H_2L in $CDCl_3$; (b) ^{13}C NMR spectrum of the ligand H_2L in $CDCl_3$.

4. IR spectra of the ligand H_2L, Gd(III) analogue and 1

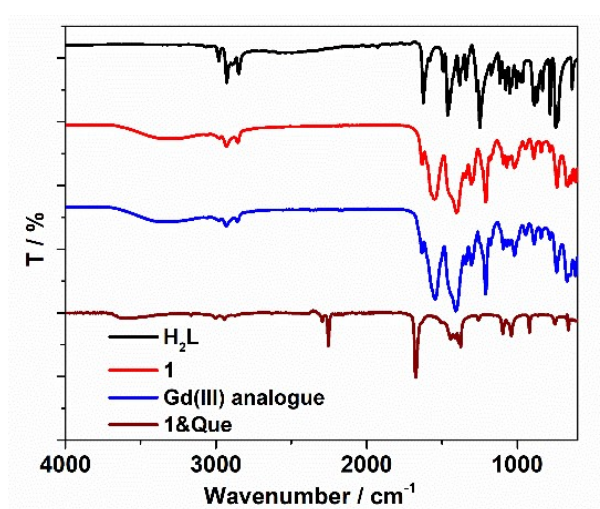


Figure S2. IR spectra of the ligand H_2L, Gd(III) analogue and **1**.

5. The thermogravimetric analysis of 1

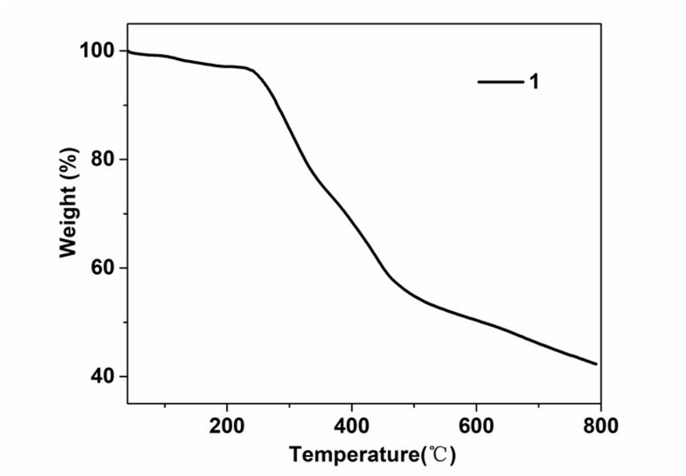


Figure S3. The thermogravimetric analysis of **1**.

6. Powder XRD patterns of 1

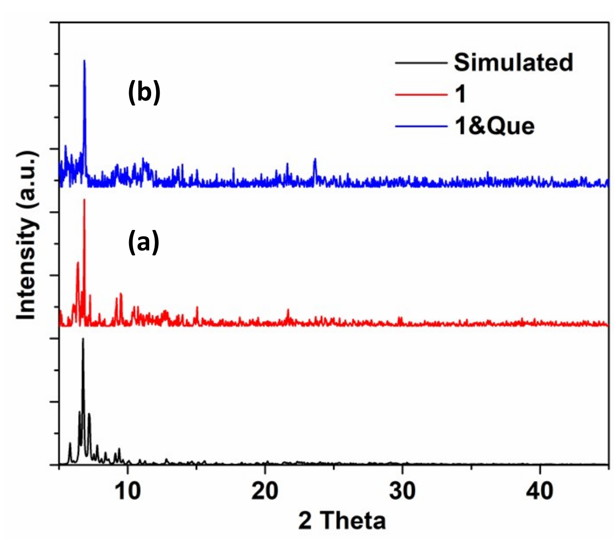


Figure S4. Powder XRD patterns of **1** before (a) and after (b) treated with Que.

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

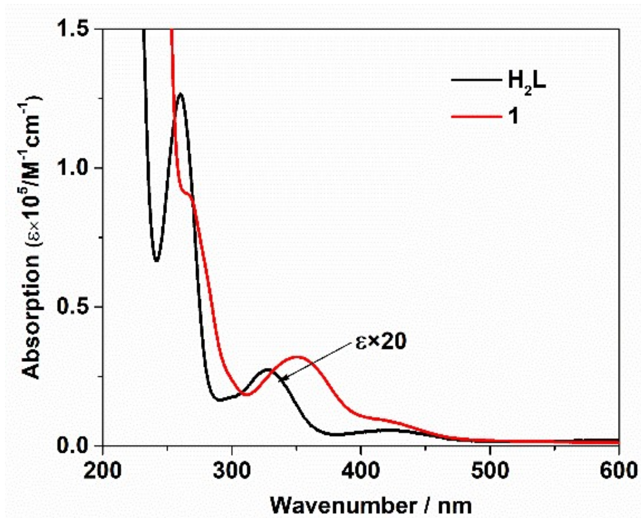


Figure S5. UV-vis absorption spectra of the free ligand H_2L and **1** in CH_3CN.

8. The excitation and emission spectra of the free ligand H_2L

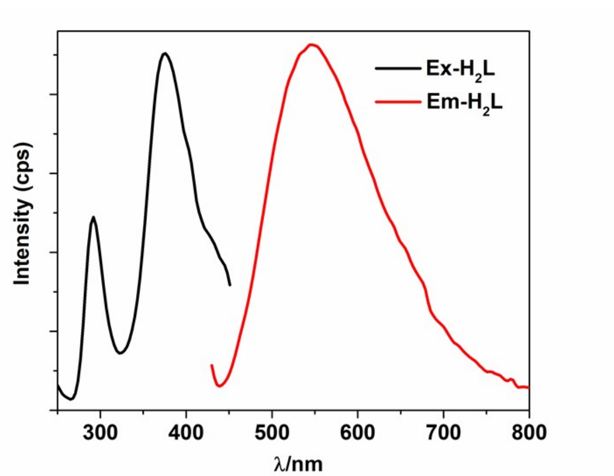


Figure S6. The excitation (λ_{em} = 643 nm) and visible emission (λ_{ex} = 368 nm) spectra of the free ligand H_2L in CH_3CN.

9. The excitation and NIR luminescence spectra of 1

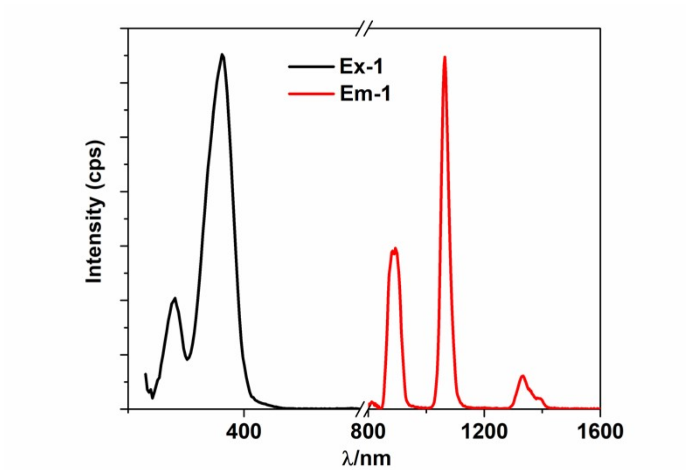


Figure S7. The excitation (λ_{em} = 1064 nm) and NIR luminescence (λ_{ex} = 371 nm) spectra of **1** (10 μM) in CH_3CN.

10. The NIR emission lifetime of 1

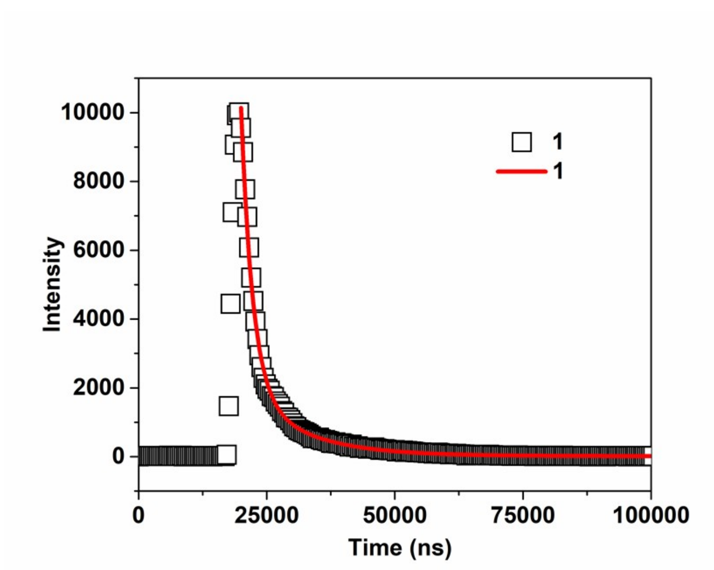
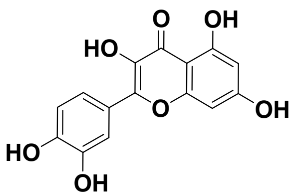
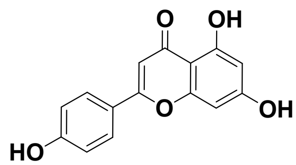


Figure S8. The NIR emission lifetime of **1** (10 μM) in CH_3CN.

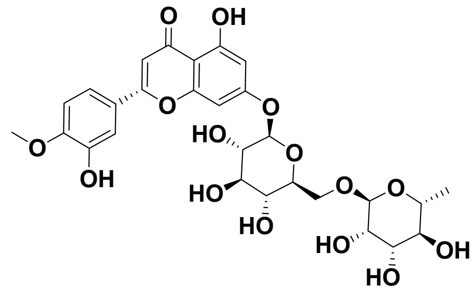
11. Chemical structures of analytes



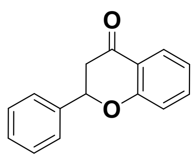
Quercetin **(Que)**



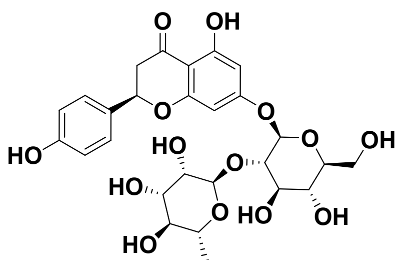
Apigenin **(Api)**



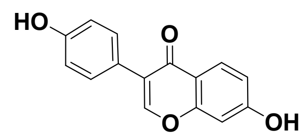
Hesperidin **(Hes)**



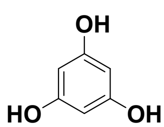
Flavanone **(Fla)**



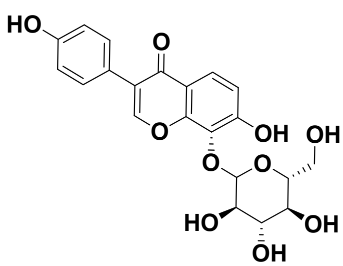
Naringin **(Nar)**



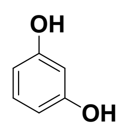
Daidzein **(Dai)**



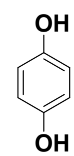
Phloroglucinol **(Phl)**



Puerarin **(Pue)**



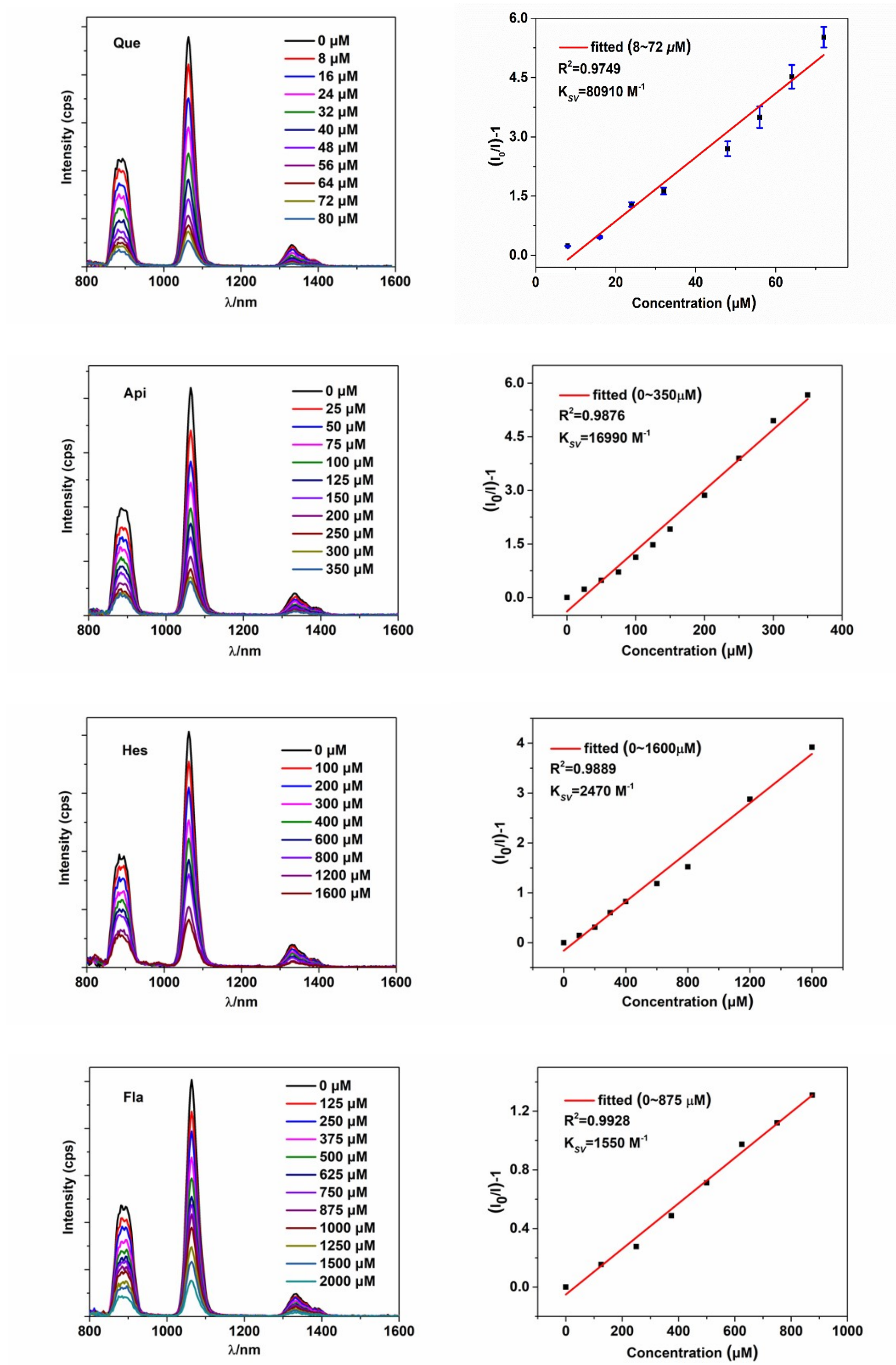
Resorcinol **(Res)**

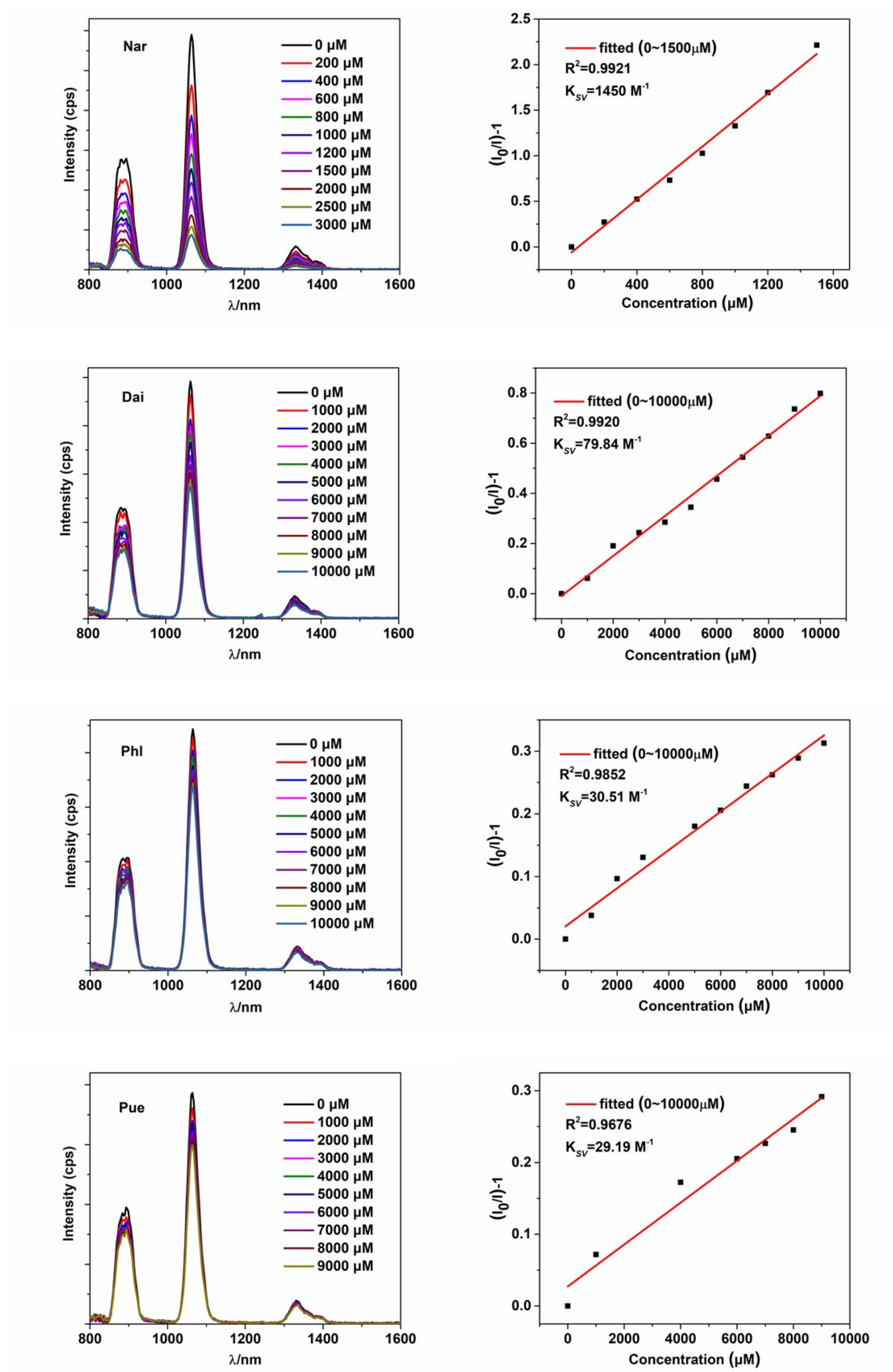


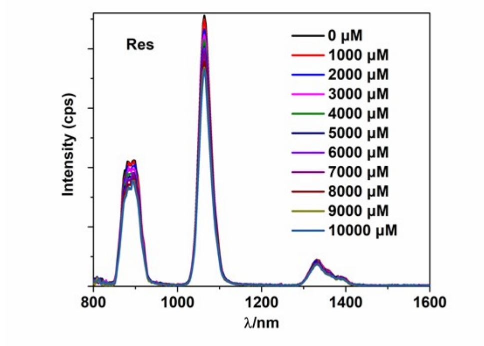
Hydroquinone **(Hyd)**

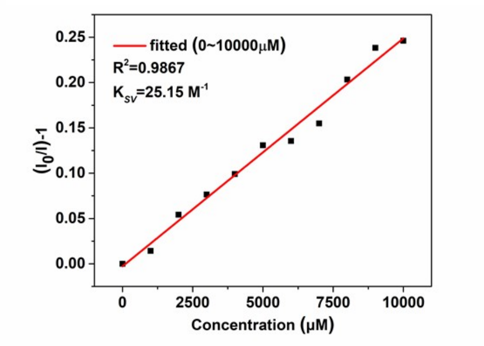
Scheme S1. Chemical structures of analytes.

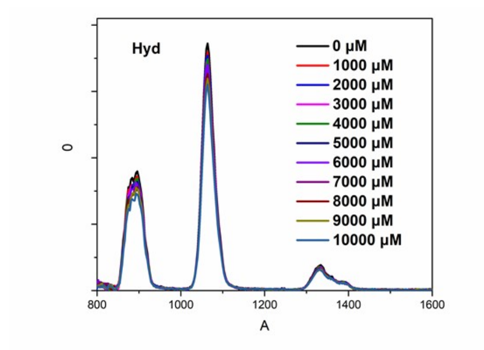
12. The NIR luminescent sensing of 1 to analytes

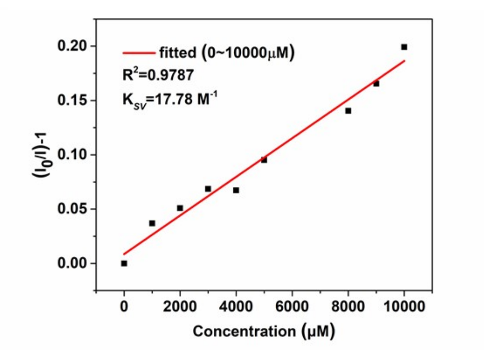


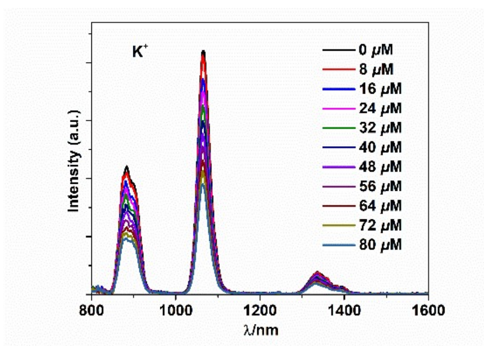

Nar
0 μM
200 μM
400 μM
600 μM
800 μM
1000 μM
1200 μM
1500 μM
2000 μM
2500 μM
3000 μM
Intensity (cps)
λ/nm
fitted (0~1500μM)
R²=0.9921
K_SV=1450 M⁻¹
(I_0/I)-1
Concentration (μM)
Dai
0 μM
1000 μM
2000 μM
3000 μM
4000 μM
5000 μM
6000 μM
7000 μM
8000 μM
9000 μM
10000 μM
Intensity (cps)
λ/nm
fitted (0~10000μM)
R²=0.9920
K_SV=79.84 M⁻¹
(I_0/I)-1
Concentration (μM)
Phl
0 μM
1000 μM
2000 μM
3000 μM
4000 μM
5000 μM
6000 μM
7000 μM
8000 μM
9000 μM
10000 μM
Intensity (cps)
λ/nm
fitted (0~10000μM)
R²=0.9852
K_SV=30.51 M⁻¹
(I_0/I)-1
Concentration (μM)
Pue
0 μM
1000 μM
2000 μM
3000 μM
4000 μM
5000 μM
6000 μM
7000 μM
8000 μM
9000 μM
Intensity (cps)
λ/nm
fitted (0~10000μM)
R²=0.9676
K_SV=29.19 M⁻¹
(I_0/I)-1
Concentration (μM)

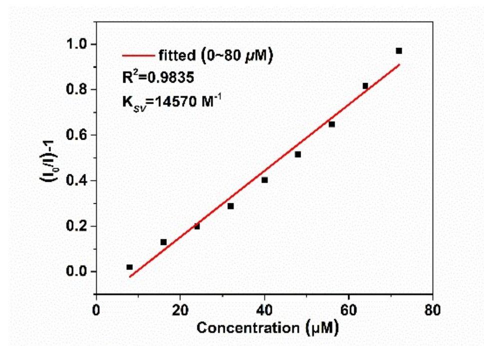

Res
0 μM
1000 μM
2000 μM
3000 μM
4000 μM
5000 μM
6000 μM
7000 μM
8000 μM
9000 μM
10000 μM
Intensity (cps)
800
1000
1200
1400
1600
λ/nm

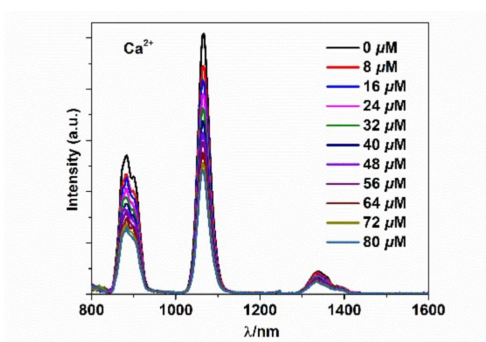

fitted (0~10000μM)
R²=0.9867
K_SV=25.15 M⁻¹
(I0/I)-1
0.25
0.20
0.15
0.10
0.05
0.00
0
2500
5000
7500
10000
Concentration (μM)

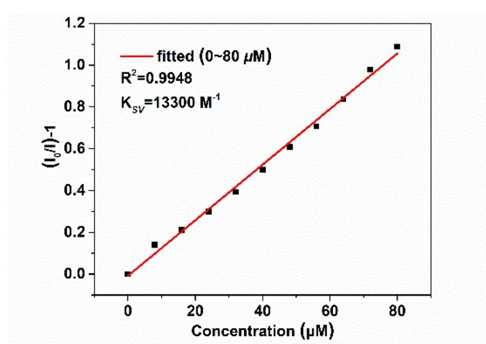

Hyd
0 μM
1000 μM
2000 μM
3000 μM
4000 μM
5000 μM
6000 μM
7000 μM
8000 μM
9000 μM
10000 μM
0
800
1000
1200
1400
1600
A

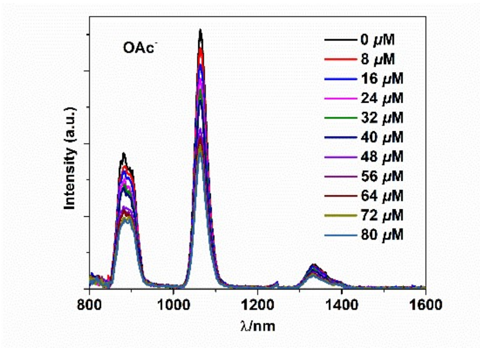

fitted (0~10000μM)
R²=0.9787
K_SV=17.78 M⁻¹
(I0/I)-1
0.20
0.15
0.10
0.05
0.00
0
2000
4000
6000
8000
10000
Concentration (μM)

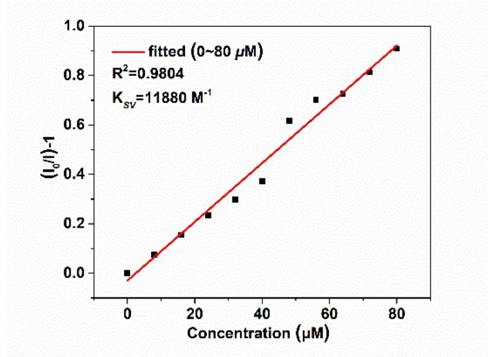

K⁺
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
Intensity (a.u.)
800
1000
1200
1400
1600
λ/nm

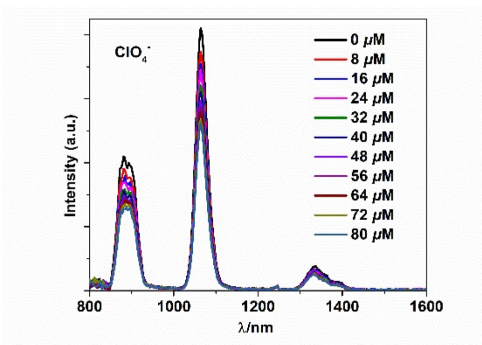

fitted (0~80 μM)
R²=0.9835
K_SV=14570 M⁻¹
(I0/I)-1
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Concentration (μM)

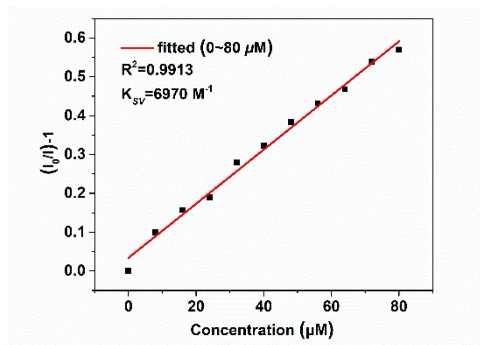

Ca²⁺
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
Intensity (a.u.)
800
1000
1200
1400
1600
λ/nm

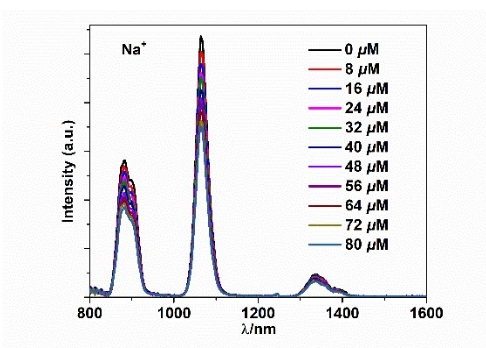

fitted (0~80 μM)
R²=0.9948
K_SV=13300 M⁻¹
(I0/I)-1
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Concentration (μM)

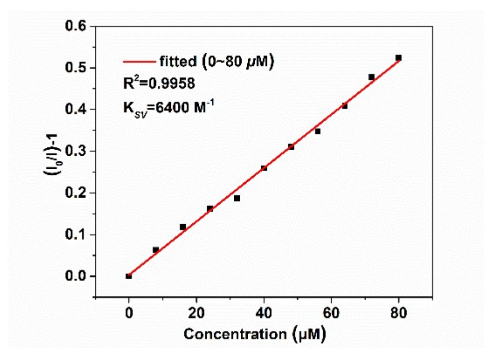

OAc⁻
Intensity (a.u.)
λ/nm
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
800 1000 1200 1400 1600


fitted (0~80 μM)
R²=0.9804
Ksv=11880 M⁻¹
(I0/I)-1
Concentration (μM)
0 20 40 60 80
0.0 0.2 0.4 0.6 0.8 1.0


ClO4⁻
Intensity (a.u.)
λ/nm
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
800 1000 1200 1400 1600


fitted (0~80 μM)
R²=0.9913
Ksv=6970 M⁻¹
(I0/I)-1
Concentration (μM)
0 20 40 60 80
0.0 0.1 0.2 0.3 0.4 0.5 0.6


Na⁺
Intensity (a.u.)
λ/nm
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
800 1000 1200 1400 1600


fitted (0~80 μM)
R²=0.9958
Ksv=6400 M⁻¹
(I0/I)-1
Concentration (μM)
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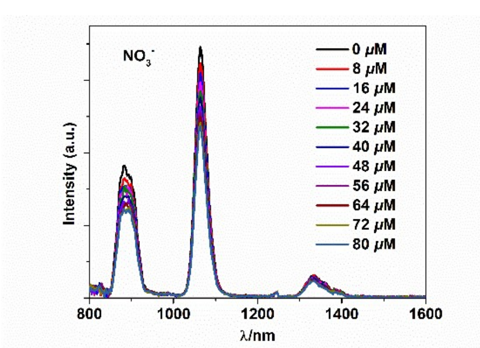
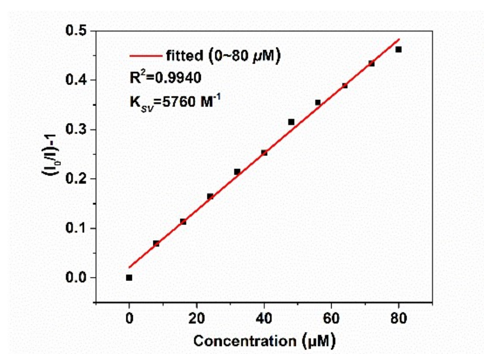
0.0 0.1 0.2 0.3 0.4 0.5 0.6


NO3⁻
Intensity (a.u.)
λ/nm
0 μM
8 μM
16 μM
24 μM
32 μM
40 μM
48 μM
56 μM
64 μM
72 μM
80 μM
800 1000 1200 1400 1600


fitted (0~80 μM)
R²=0.9940
Ksv=5760 M⁻¹
(I0/I)-1
Concentration (μM)
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0.0 0.1 0.2 0.3 0.4 0.5

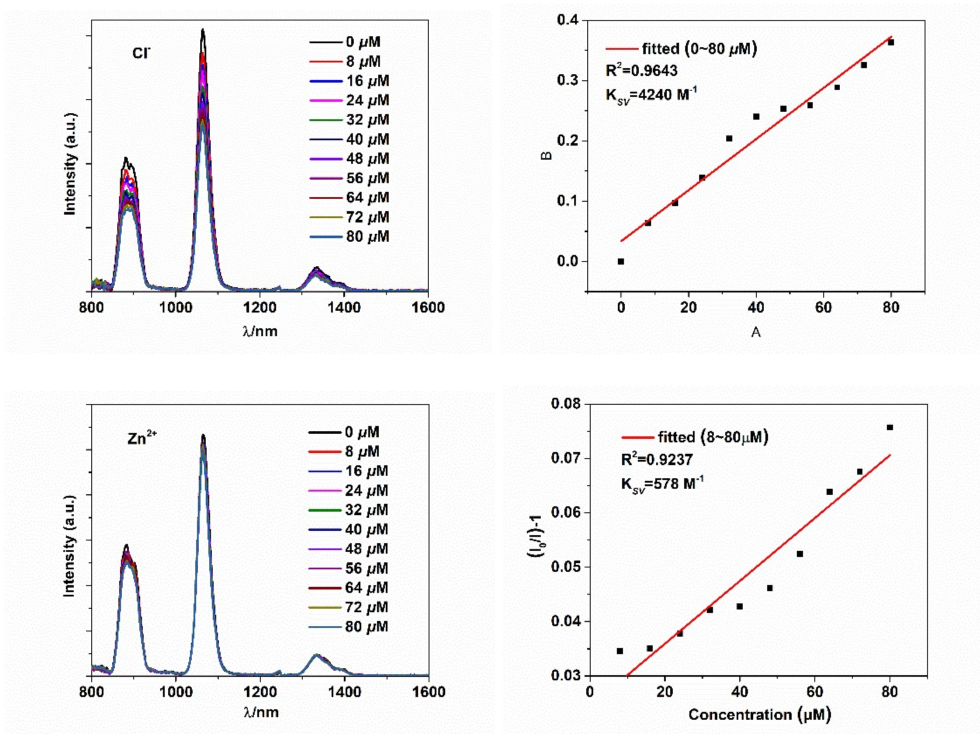

Figure S9. The NIR luminescent sensing of **1** (10 μM) to analytes in CH_3CN. (λ_{ex} = 371 nm)

13. The photostability of 1 with the addition of Que

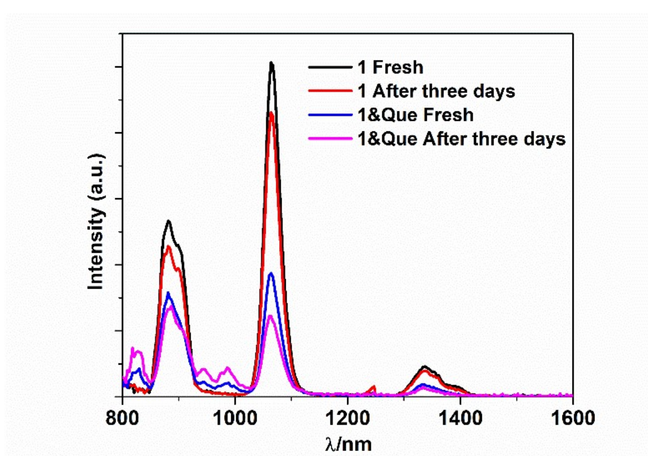

Figure S10. The NIR lanthanide luminescence spectra of **1** (10 μM) without and with the addition of Que (60 μM), and measured after three days. (λ_{ex} = 367 nm)

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

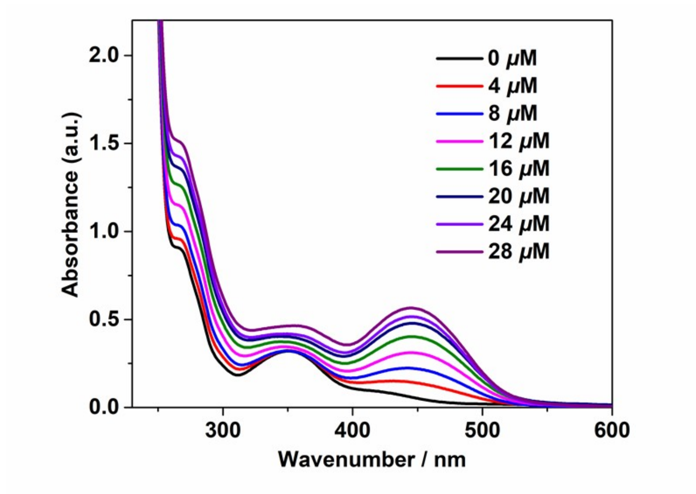

Figure S11. UV-vis titration of **1** (10 μM) to the addition of Que in CH_3CN.

15. The phosphorescence spectrum of the Gd(III) analogue

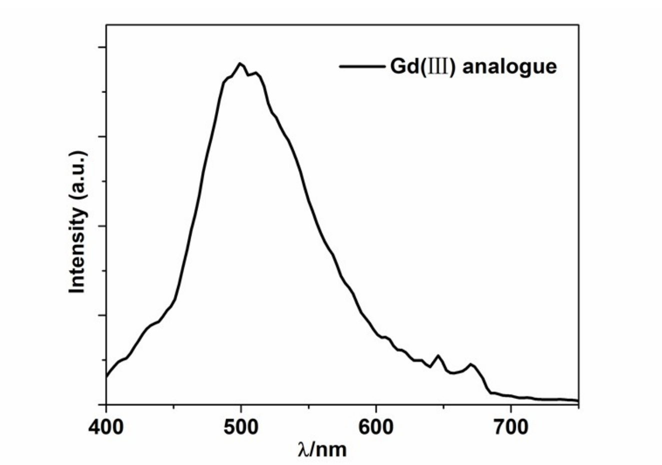

Figure S12. The phosphorescence spectrum of the Gd(III) analogue (10 μM) at 77 K. (λ_{ex} = 367 nm)

16. The UV-vis absorption spectra of analytes

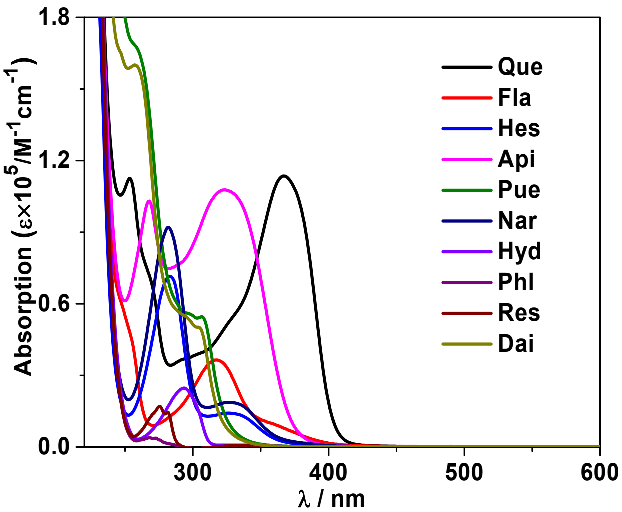

Figure S13. The UV-vis absorption spectra of analytes in CH_3CN at room temperature.

17. X-Ray Crystallography

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

Nd(1)-O(18)	2.369(11)	Cd(6)-O(4)	2.263(10)
Nd(1)-O(20)	2.383(9)	Cd(6)-O(13)	2.260(10)
Nd(1)-O(14)	2.400(12)	Cd(6)-O(17)	2.348(9)
Nd(1)-O(6)	2.401(8)	Cd(6)-O(3)	2.585(12)
Nd(1)-O(4)	2.437(9)	O(18)-Nd(1)-O(20)	74.3(3)
Nd(1)-O(17)	2.503(9)	O(18)-Nd(1)-O(14)	77.4(4)
Nd(1)-N(2)	2.650(12)	O(20)-Nd(1)-O(14)	143.7(3)
Nd(1)-O(5)	2.702(9)	O(18)-Nd(1)-O(6)	78.7(3)
Nd(2)-O(30)	2.350(8)	O(20)-Nd(1)-O(6)	86.8(3)
Nd(2)-O(28)	2.413(11)	O(14)-Nd(1)-O(6)	109.4(3)
Nd(2)-O(10)	2.413(8)	O(18)-Nd(1)-O(4)	148.6(4)
Nd(2)-O(12)	2.430(8)	O(20)-Nd(1)-O(4)	121.3(3)
Nd(2)-O(36)	2.434(9)	O(14)-Nd(1)-O(4)	75.7(3)
Nd(2)-O(27)	2.500(10)	O(6)-Nd(1)-O(4)	125.9(3)
Nd(2)-O(11)	2.658(9)	O(18)-Nd(1)-O(17)	88.9(3)
Nd(2)-N(5)	2.672(10)	O(20)-Nd(1)-O(17)	80.2(3)
Cd(1)-O(19)	2.249(9)	O(14)-Nd(1)-O(17)	77.1(3)
Cd(1)-O(23)	2.306(9)	O(6)-Nd(1)-O(17)	164.1(3)
Cd(1)-O(6)	2.315(8)	O(4)-Nd(1)-O(17)	69.3(3)
Cd(1)-O(21)	2.319(9)	O(18)-Nd(1)-N(2)	140.4(4)
Cd(1)-N(3)	2.355(12)	O(20)-Nd(1)-N(2)	76.5(4)
Cd(1)-O(26)	2.410(8)	O(14)-Nd(1)-N(2)	138.5(4)
Cd(2)-O(24)	2.292(9)	O(6)-Nd(1)-N(2)	73.5(3)
Cd(2)-O(22)	2.305(10)	O(4)-Nd(1)-N(2)	70.7(4)
Cd(2)-O(35)	2.331(9)	O(17)-Nd(1)-N(2)	111.7(3)
Cd(2)-O(8)	2.333(9)	O(18)-Nd(1)-O(5)	112.4(3)
Cd(2)-O(23)	2.518(8)	O(20)-Nd(1)-O(5)	141.9(3)
Cd(2)-O(7)	2.526(10)	O(14)-Nd(1)-O(5)	70.7(4)
Cd(2)-O(25)	2.557(13)	O(6)-Nd(1)-O(5)	59.7(3)
Cd(3)-N(4)	2.237(12)	O(4)-Nd(1)-O(5)	73.4(3)
Cd(3)-O(8)	2.255(9)	O(17)-Nd(1)-O(5)	135.5(3)
Cd(3)-O(35)	2.264(9)	N(2)-Nd(1)-O(5)	76.8(4)
Cd(3)-O(10)	2.326(9)	O(30)-Nd(2)-O(28)	76.7(3)
Cd(3)-O(27)	2.359(9)	O(30)-Nd(2)-O(10)	118.7(3)
Cd(3)-O(9)	2.520(8)	O(28)-Nd(2)-O(10)	146.6(3)
Cd(4)-O(29)	2.272(10)	O(30)-Nd(2)-O(12)	84.3(3)
Cd(4)-O(31)	2.290(8)	O(28)-Nd(2)-O(12)	79.1(3)
Cd(4)-O(12)	2.303(8)	O(10)-Nd(2)-O(12)	128.9(3)
Cd(4)-N(6)	2.314(12)	O(30)-Nd(2)-O(36)	143.8(3)
Cd(4)-O(32)	2.324(11)	O(28)-Nd(2)-O(36)	74.4(3)
Cd(4)-O(34)	2.346(8)	O(10)-Nd(2)-O(36)	77.9(3)
Cd(5)-O(33)#1	2.186(15)	O(12)-Nd(2)-O(36)	110.8(3)
Cd(5)-O(2)	2.253(10)	O(30)-Nd(2)-O(27)	79.1(3)
Cd(5)-O(15)	2.321(15)	O(28)-Nd(2)-O(27)	85.8(3)
Cd(5)-O(13)	2.326(10)	O(10)-Nd(2)-O(27)	70.1(3)
Cd(5)-O(16)	2.337(16)	O(12)-Nd(2)-O(27)	159.7(3)
Cd(5)-O(32)#1	2.486(10)	O(36)-Nd(2)-O(27)	77.4(3)
Cd(5)-O(1)	2.526(12)	O(30)-Nd(2)-O(11)	139.6(3)
Cd(6)-N(1)	2.218(13)	O(28)-Nd(2)-O(11)	112.1(3)
Cd(6)-O(2)	2.235(11)	O(10)-Nd(2)-O(11)	76.3(3)

O(12)-Nd(2)-O(11)	60.6(3)	O(10)-Cd(3)-O(27)	74.1(3)
O(36)-Nd(2)-O(11)	72.8(3)	N(4)-Cd(3)-O(9)	84.0(4)
O(27)-Nd(2)-O(11)	138.8(3)	O(8)-Cd(3)-O(9)	85.2(3)
O(30)-Nd(2)-N(5)	77.1(3)	O(35)-Cd(3)-O(9)	89.5(3)
O(28)-Nd(2)-N(5)	144.2(3)	O(10)-Cd(3)-O(9)	65.3(3)
O(10)-Nd(2)-N(5)	68.7(3)	O(27)-Cd(3)-O(9)	138.9(3)
O(12)-Nd(2)-N(5)	74.3(3)	O(29)-Cd(4)-O(31)	94.0(4)
O(36)-Nd(2)-N(5)	137.8(3)	O(29)-Cd(4)-O(12)	109.5(3)
O(27)-Nd(2)-N(5)	112.6(3)	O(31)-Cd(4)-O(12)	95.7(3)
O(11)-Nd(2)-N(5)	74.7(3)	O(29)-Cd(4)-N(6)	171.0(4)
O(19)-Cd(1)-O(23)	87.9(3)	O(31)-Cd(4)-N(6)	90.9(3)
O(19)-Cd(1)-O(6)	107.9(3)	O(12)-Cd(4)-N(6)	77.4(4)
O(23)-Cd(1)-O(6)	84.9(3)	O(29)-Cd(4)-O(32)	85.0(4)
O(19)-Cd(1)-O(21)	88.3(3)	O(31)-Cd(4)-O(32)	177.3(3)
O(23)-Cd(1)-O(21)	175.7(3)	O(12)-Cd(4)-O(32)	87.0(3)
O(6)-Cd(1)-O(21)	94.4(3)	N(6)-Cd(4)-O(32)	89.8(4)
O(19)-Cd(1)-N(3)	172.8(4)	O(29)-Cd(4)-O(34)	88.2(4)
O(23)-Cd(1)-N(3)	94.7(4)	O(31)-Cd(4)-O(34)	89.6(3)
O(6)-Cd(1)-N(3)	79.1(4)	O(12)-Cd(4)-O(34)	161.0(3)
O(21)-Cd(1)-N(3)	89.3(4)	N(6)-Cd(4)-O(34)	84.4(4)
O(19)-Cd(1)-O(26)	88.1(3)	O(32)-Cd(4)-O(34)	87.8(3)
O(23)-Cd(1)-O(26)	86.7(3)	O(33)#1-Cd(5)-O(2)	142.8(5)
O(6)-Cd(1)-O(26)	161.6(3)	O(33)#1-Cd(5)-O(15)	109.5(6)
O(21)-Cd(1)-O(26)	95.1(3)	O(2)-Cd(5)-O(15)	101.1(5)
N(3)-Cd(1)-O(26)	85.3(4)	O(33)#1-Cd(5)-O(13)	103.3(5)
O(24)-Cd(2)-O(22)	106.2(4)	O(2)-Cd(5)-O(13)	75.2(4)
O(24)-Cd(2)-O(35)	122.1(4)	O(15)-Cd(5)-O(13)	123.5(5)
O(22)-Cd(2)-O(35)	105.8(3)	O(33)#1-Cd(5)-O(16)	86.6(6)
O(24)-Cd(2)-O(8)	104.6(4)	O(2)-Cd(5)-O(16)	129.6(5)
O(22)-Cd(2)-O(8)	142.0(3)	O(15)-Cd(5)-O(16)	52.1(5)
O(35)-Cd(2)-O(8)	75.2(3)	O(13)-Cd(5)-O(16)	86.5(5)
O(24)-Cd(2)-O(23)	147.1(4)	O(33)#1-Cd(5)-O(32)#1	54.4(4)
O(22)-Cd(2)-O(23)	54.2(3)	O(2)-Cd(5)-O(32)#1	88.6(3)
O(35)-Cd(2)-O(23)	90.4(3)	O(15)-Cd(5)-O(32)#1	149.7(5)
O(8)-Cd(2)-O(23)	88.1(3)	O(13)-Cd(5)-O(32)#1	86.6(3)
O(24)-Cd(2)-O(7)	76.1(4)	O(16)-Cd(5)-O(32)#1	137.4(5)
O(22)-Cd(2)-O(7)	101.5(4)	O(2)-Cd(5)-O(1)	65.8(4)
O(35)-Cd(2)-O(7)	139.9(3)	O(15)-Cd(5)-O(1)	3.9(5)
O(8)-Cd(2)-O(7)	65.2(3)	O(13)-Cd(5)-O(1)	140.1(4)
O(23)-Cd(2)-O(7)	82.3(3)	O(16)-Cd(5)-O(1)	124.7(5)
O(24)-Cd(2)-O(25)	52.8(4)	N(1)-Cd(6)-O(2)	85.8(4)
O(22)-Cd(2)-O(25)	85.0(4)	N(1)-Cd(6)-O(4)	93.5(4)
O(35)-Cd(2)-O(25)	83.8(4)	O(2)-Cd(6)-O(4)	147.3(3)
O(8)-Cd(2)-O(25)	131.9(4)	N(1)-Cd(6)-O(13)	162.5(4)
O(23)-Cd(2)-O(25)	135.4(4)	O(2)-Cd(6)-O(13)	76.9(4)
O(7)-Cd(2)-O(25)	127.8(4)	O(4)-Cd(6)-O(13)	99.4(4)
N(4)-Cd(3)-O(8)	82.7(4)	N(1)-Cd(6)-O(17)	102.1(4)
N(4)-Cd(3)-O(35)	160.1(4)	O(2)-Cd(6)-O(17)	137.0(3)
O(8)-Cd(3)-O(35)	78.0(3)	O(4)-Cd(6)-O(17)	75.1(3)
N(4)-Cd(3)-O(10)	92.6(4)	O(13)-Cd(6)-O(17)	92.7(3)
O(8)-Cd(3)-O(10)	150.4(3)	N(1)-Cd(6)-O(3)	87.5(4)
O(35)-Cd(3)-O(10)	101.7(3)	O(2)-Cd(6)-O(3)	85.0(4)
N(4)-Cd(3)-O(27)	103.9(4)	O(4)-Cd(6)-O(3)	62.3(4)
O(8)-Cd(3)-O(27)	135.4(3)	O(13)-Cd(6)-O(3)	88.0(4)
O(35)-Cd(3)-O(27)	93.3(3)	O(17)-Cd(6)-O(3)	136.8(4)