Supporting Information

Construction of a Cd_6Eu_4-containing coordination polymer for luminescence detection of ketoprofen as anti-inflammatory drug

Jinshuai Song, Shuhan Zhang, Shiqing Wang, Desmond Schipper, and Xiaoping Yang

Contents

1. General Procedures

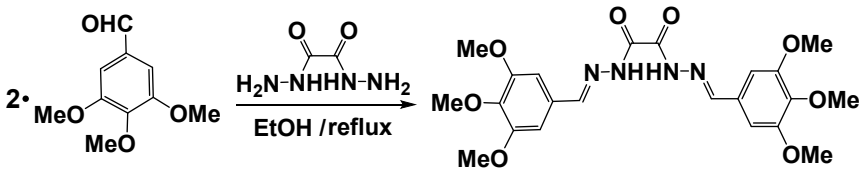
All chemicals and solvents were purchased from commercial sources. IR spectra were recorded using a Nicolet IS50 spectrometer. The sample is under a N_2 flow of 200 mL min^{-1}, and heated from room temperature to 900°C with a heating rate of 5°C min^{-1}; Elemental analysis was performed on a EURO EA3000 with the solid sample after dried in the oven at 110°C for six hours. The morphology of the sample was analyzed by Nova 200 NanoSEM scanning electron microscope (SEM) and an attached energy-dispersive x-ray spectrometer (EDX). The X-ray photoelectron spectroscopy (XPS) was performed on PHI5000 Versaprobe system. Molecular docking calculation was conducted by AutoDock Vina program.

Photophysical Studies. UV-vis absorption spectra were obtained on a UV-3600 spectrophotometer. Visible 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. The temporal decay curves of the fluorescence signals were stored by using the attached storage digital oscilloscope. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

Sensing experiments to KTP. The ground powder of **1** was dispersed in CH_3CN, and then sonicated for one hour to form homogeneous suspension of **1** (0.04 mg/mL). A quartz cell (sizes: 4.5 cm × 1.2 cm × 1.2 cm) was used in the sensing experiments. KTP in CH_3CN was added by a pipet with concentrations from 10 to 120 μM. Purchased FCS was diluted to 1% using PBS buffer solution (pH = 7.4) before the experiments. The KTP drug was dissolved in the PBS buffer solution. For the smartphone-based detection of KTP, a common smartphone (Redmi Note 12 Turbo) installed Color Picker APP was used as signal reader and analyzer. It is able to convert image color signals to digital format representing green (G), red (R) and blue (B) color by region of interest (ROI) averaging algorithm. The camera parameters such as ISO speed (5482), exposure time (1/15 s) and focus (24 mm) are fixed during the experiments. The samples in the quartz cell were placed in a commercial UV light box (ZF-20D Dark Box Type Ultraviolet Analyzer, sizes: 27 × 23 × 25 cm). The UV lamp is 6 cm directly above the quartz cell, and the light wavelength and power are 254 nm and 24 W, respectively. The shooting distance between the cell and camera is 10 cm.

2. Synthesis of H_2L and 1

Synthesis of H_2L: 3,4,5-trimethoxybenzaldehyde (3.92 g, 20 mmol) was dissolved in 20 mL of EtOH, and a solution of ethanedioic dihydrazide (1.18 g, 10 mmol) in 20 mL of EtOH was then added. The mixture was heated and stirred under reflux for 5 hrs. After cooling, the solution was filtered in vacuum to give white solid product (Scheme 2). It was washed with EtOH three times (5 mL per time), and dried in air for one day. Yield: 2.28 g (48%). ^{1}H NMR data in DMSO-d_6 (ppm): 12.29 (s, 2H), 8.55 (s, 2H), 7.03 (s, 4H), 3.86 (s, 12H), 3.74 (s, 6H). IR (KBr, cm^{-1}): 3455 (br, m), 3416 (w), 3036 (w), 2934 (w), 2829 (w), 1622 (s), 1576 (m), 1537 (m), 1502 (m), 1459 (m), 1415 (m), 1323 (s), 1214 (s), 1128 (s), 1064 (m), 1002 (m), 834 (m), 703 (w), 633 (w), 523 (w), 470 (w).



Scheme S1. Synthesis route of H_2L.

Synthesis of 1: $EuCl_3 \cdot 6H_2O$ (0.0733 g, 0.20 mmol), $Cd(OAc)_2 \cdot 2H_2O$ (0.0533 g, 0.20 mmol) and H_2L (0.0949 g, 0.20 mmol) were dissolved in 10 mL of DMF and EtOH (1:1) at room temperature, and 1 mL of triethylamine solution (1.0 mol/L) in EtOH was added. The mixed solution was stirred and heated under reflux for 20 minutes, and then filtered. The pale yellow crystals of **1** were obtained after two weeks by diffusing diethyl ether into the filtrate, and then collected. The crystalline product was dried in the oven at 110°C for six hours. Yield: 0.0265 g (22.21%, based on $Cd(OAc)_2 \cdot 2H_2O$). Elemental analysis: $C_{78}H_{130}Cd_6Cl_{12}N_{14}O_{38}Eu_4$: C, 26.17; H, 3.66; N, 5.48 %. Found: C, 26.09; H, 3.79; N, 5.60 %. FT-IR (KBr, ν/cm^{-1}): 3480 (br, s), 2942 (br, w), 1581 (s), 1551 (s), 1505 (m), 1453 (s), 1421 (s), 1333 (m), 1241 (m), 1157 (w), 1127 (s), 999 (br, w), 837 (w), 675 (w), 540 (br, w).

3. ^{1}H NMR spectrum of H_2L

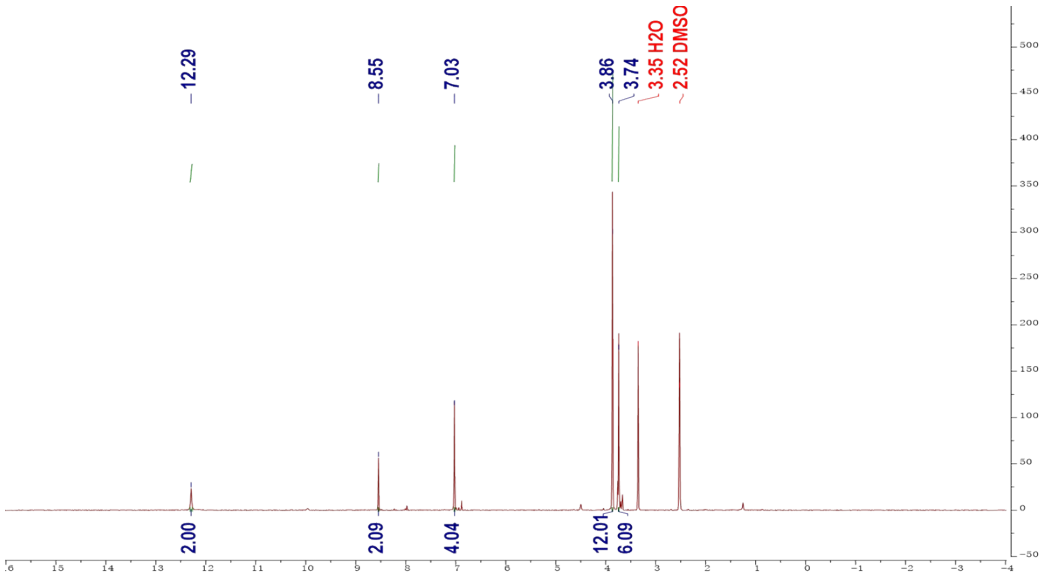


Figure S1. ^{1}H NMR spectrum of H_2L in DMSO-d_6.

4. IR spectra of H_2L and 1

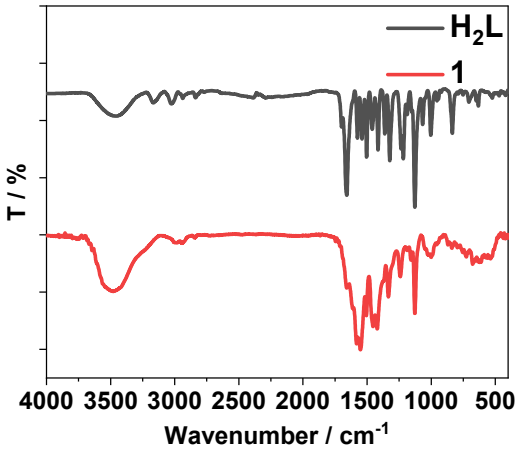


Figure S2. IR spectra of H_2L and **1**.

5. Repeating Cd_6Eu_4 unit and 1-D coordination polymeric structure of 1

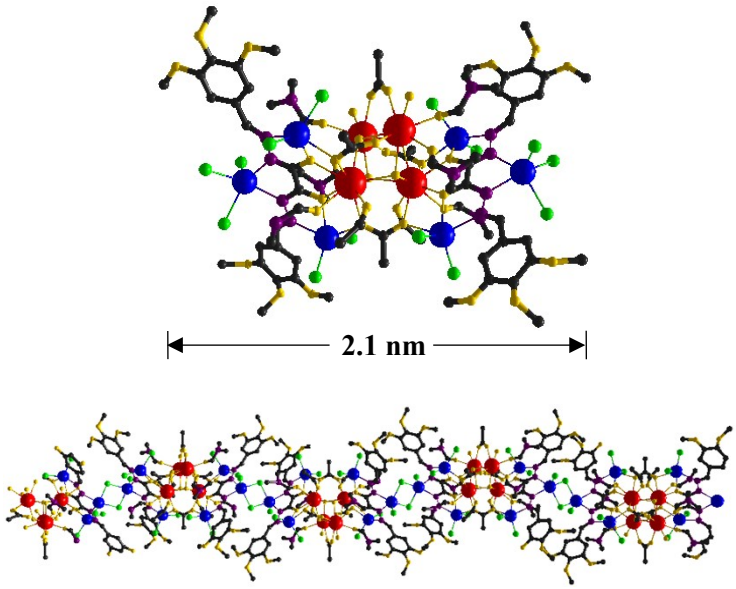
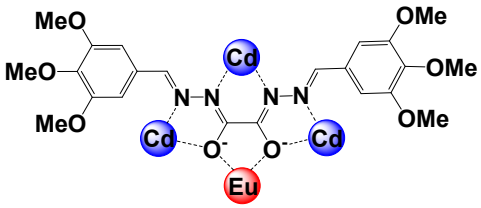


Figure S3. Repeating Cd_6Eu_4 unit and 1-D coordination polymeric structure of **1**.

6. Coordination mode of H_2L and intermolecular hydrogen bonds formed in 1

(a)



(b)

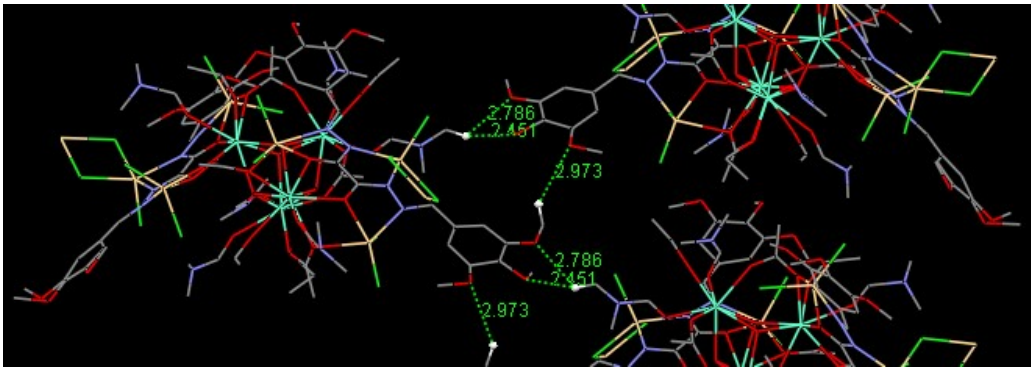


Figure S4. (a) Coordination mode of H_2L in **1**; (b) Intermolecular hydrogen bonds formed between H atoms of DMF (or $–OCH_3$ groups of L^{2-}) and O atoms of $–OCH_3$ groups from L^{2-} (H···O distances: 2.451 Å, 2.786 Å, and 2.973 Å) in **1**.

7. Characterization of 1

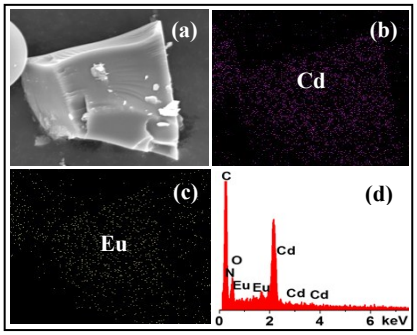


Figure S5. SEM image (a), elemental maps of Cd (b) and Eu (c), and EDX spectrum (d) of **1**.

8. UV-vis absorption spectra of H_2L and 1

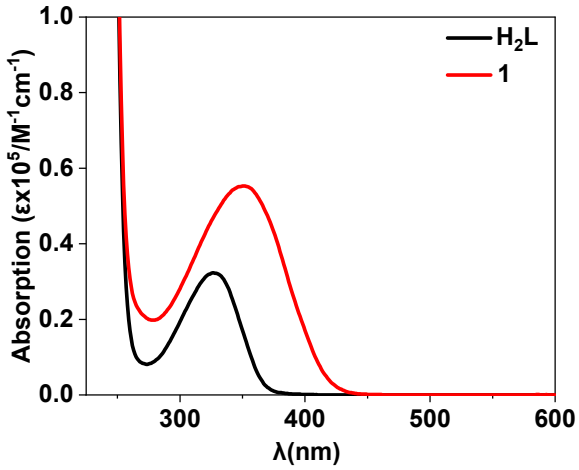


Figure S6. The UV-vis absorption spectra of H_2L and **1** in CH_3CN. (C = 10 μM).

9. Excitation and emission spectra of 1 before and after the addition of KTP

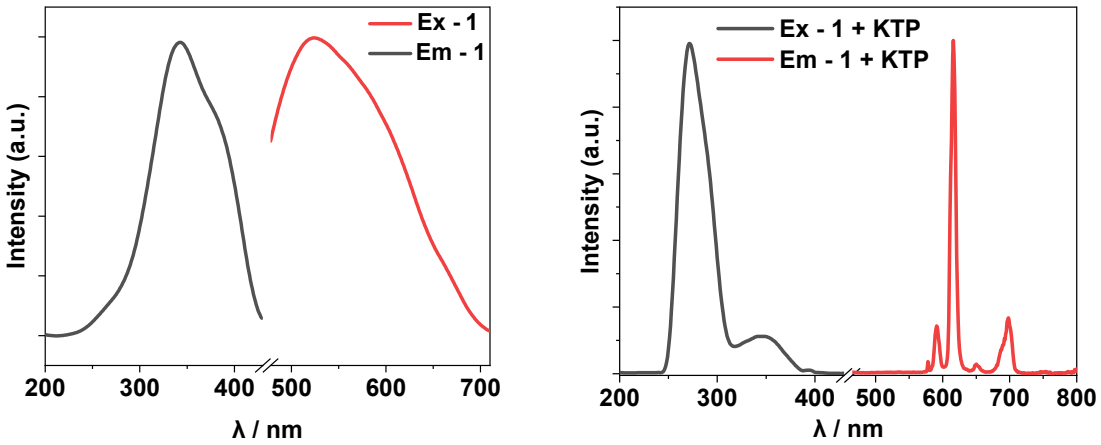


Figure S7. The excitation and emission spectra of **1** in CH_3CN: (a) Before the addition of KTP (λ_{em} = 525 nm, λ_{ex} = 340 nm); (b) After the addition of 100 μM KTP (λ_{em} = 615 nm, λ_{ex} = 270 nm).

10. The time scan of I_{615nm} upon the addition of KTP

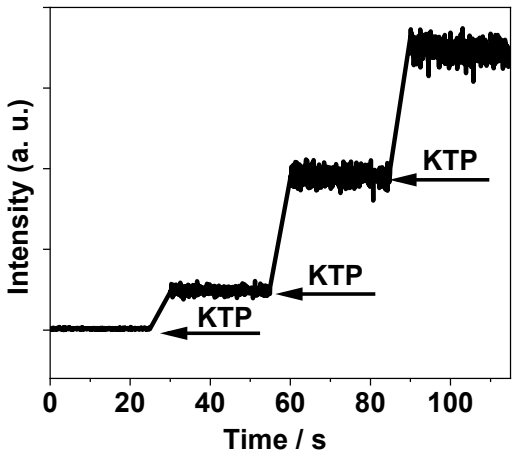


Figure S8. The time scan of I_{615nm} of **1** in CH_3CN upon the multiple additions of KTP (33 μM per time).

11. Lanthanide luminescence spectra of 1 with the addition of KTP

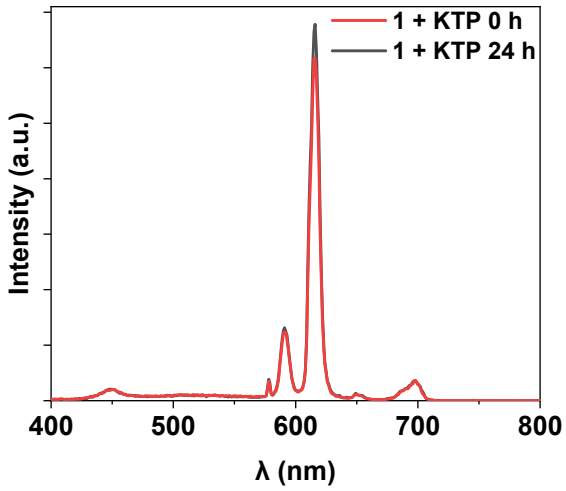
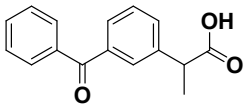
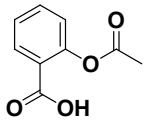


Figure S9. The emission spectra (fresh and after 24 hrs) of **1** with the addition of KTP (100 μM) in CH_3CN. (λ_{ex} = 270 nm)

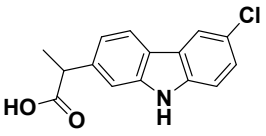
12. Chemical structures of KTP and interferences



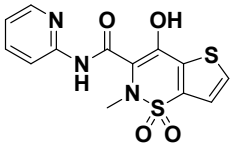
Ketoprofen (KTP)



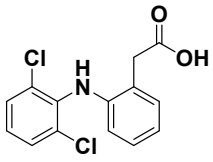
Acetylsalicylic acid (ASA)



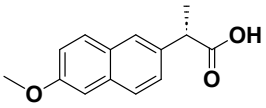
Carprofen (CPF)



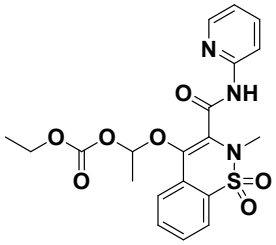
Tenoxicam (TNX)



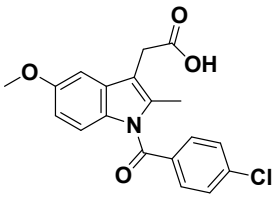
Diclofenac (DCF)



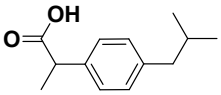
Naproxen (NAP)



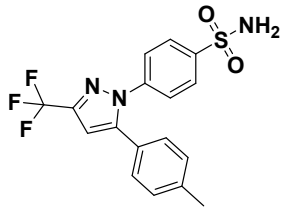
Ampiroxicam (APX)



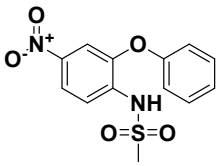
Indometacin (IND)



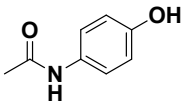
Ibuprofen (IBU)



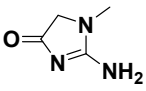
Celecoxib (CXB)



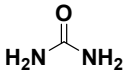
Nimesulide (NIM)



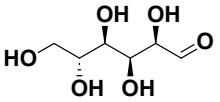
Acetaminophen (ACE)



Creatinine (CRE)



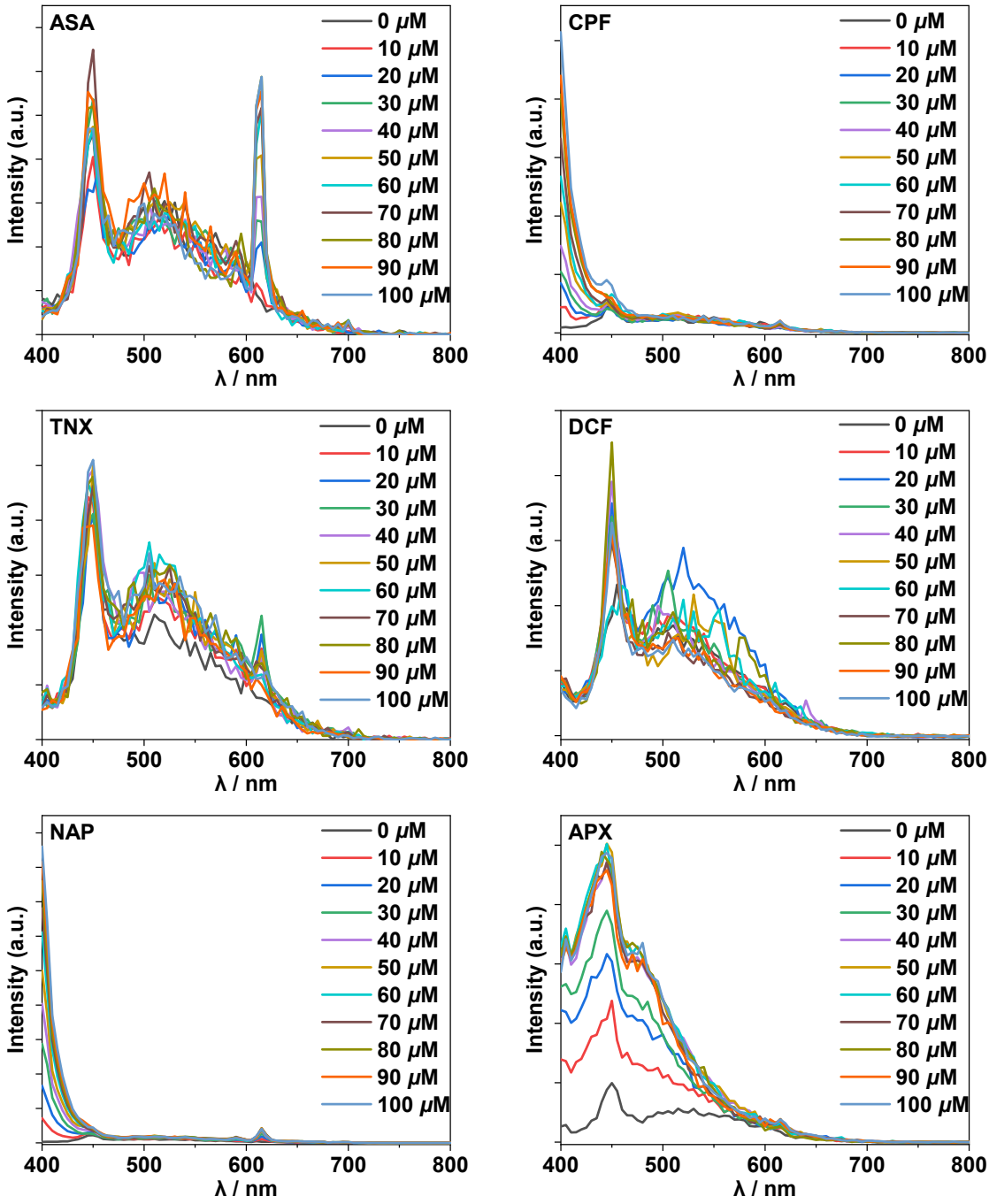
Urea (URE)

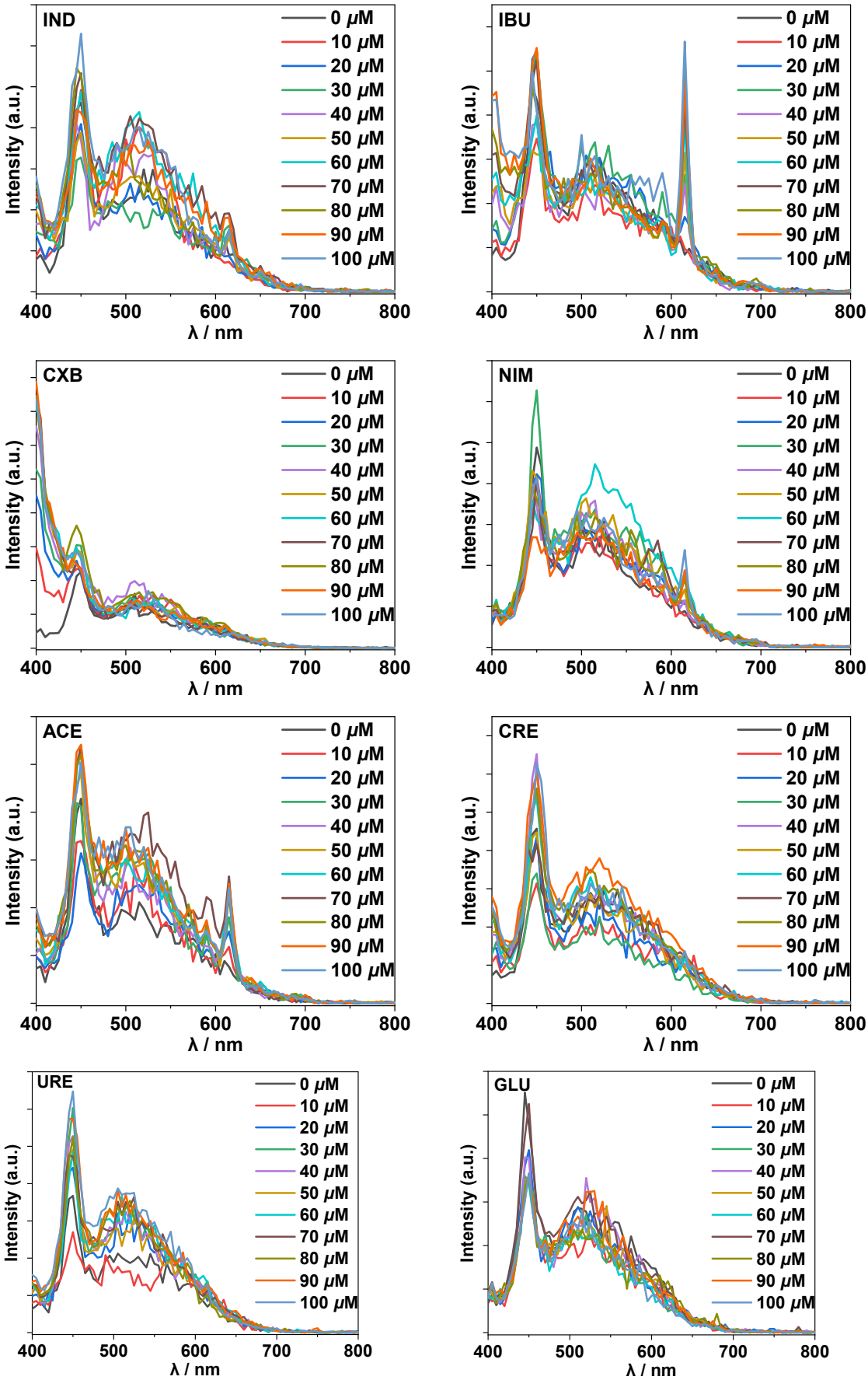


D(+)-Glucose (GLU)

Scheme S2. Chemical structures of **KTP** and other interferences.

13. Emission spectra of 1 with the addition of interferences




IND
IBU
CXB
NIM
ACE
CRE
URE
GLU
0 μM
10 μM
20 μM
30 μM
40 μM
50 μM
60 μM
70 μM
80 μM
90 μM
100 μM
Intensity (a.u.)
λ / nm
400
500
600
700
800

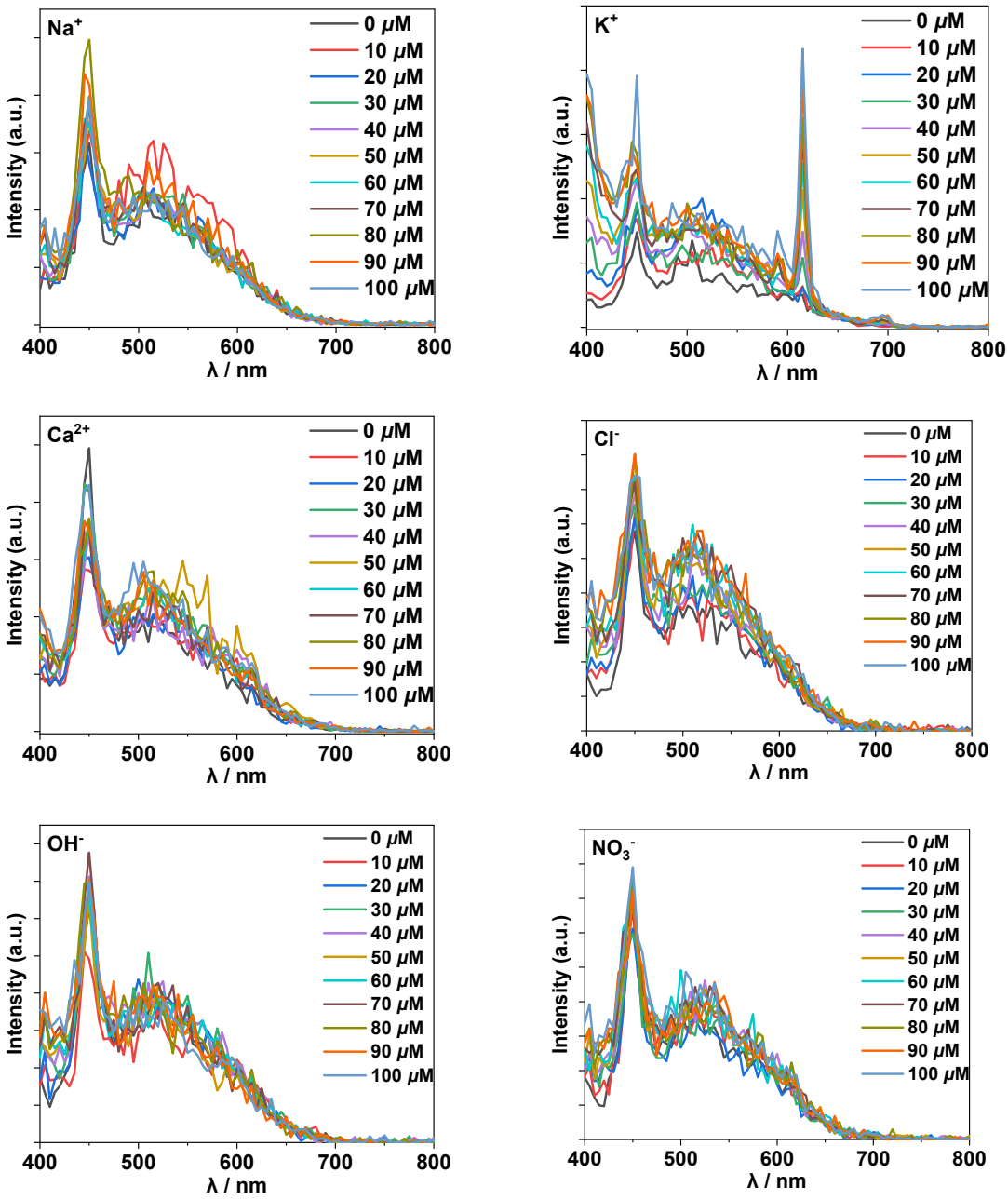


Figure S10. Emission spectra of **1** with the addition of interferences in CH_3CN.

14. CIE diagram of 1 with the addition of KTP

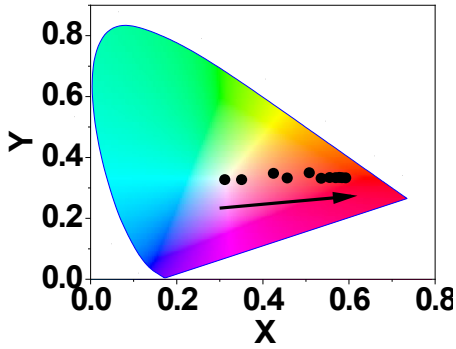


Figure S11. Corresponding CIE diagram of **1** with the addition of different concentrations of KTP in Figure 3 in the text.

15. Luminescence response of 1 to KTP in FCS and urine

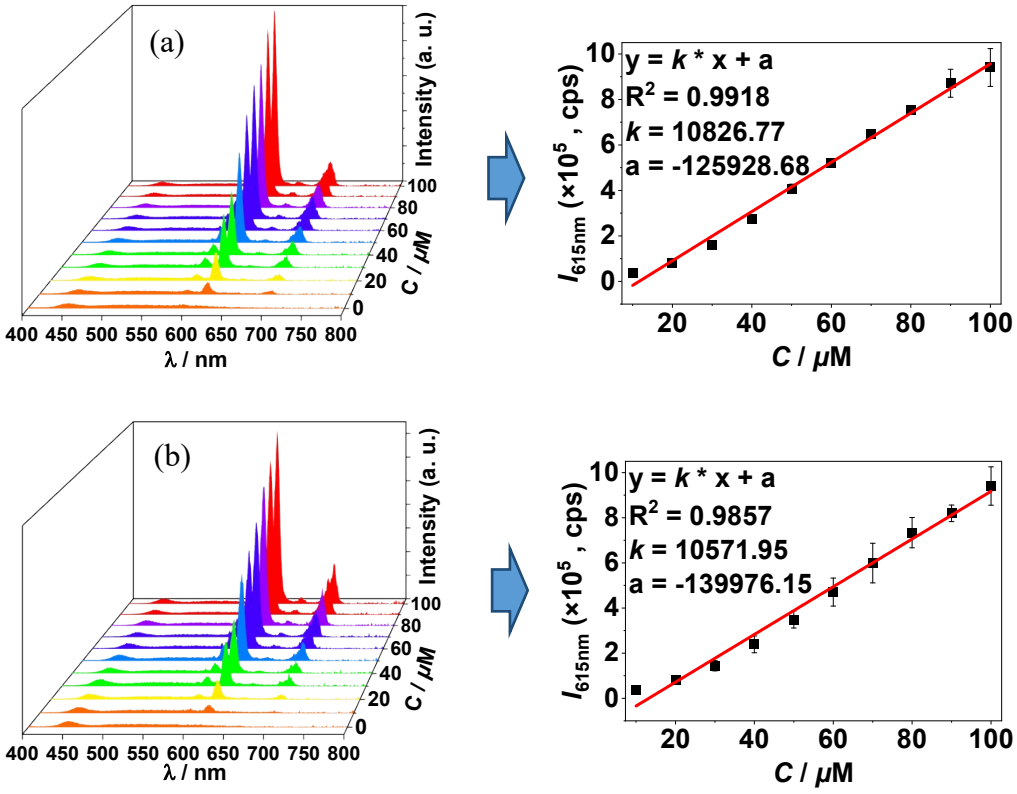


Figure S12. Left: The luminescence response of **1** to the addition of different concentrations of KTP in FCS (a) and urine (b). Right: The linear relationships between the luminescence intensities of **1** and the concentrations of KTP. (λ_{ex} = 270 nm)

16. UV-vis titration of 1 to the addition of KTP

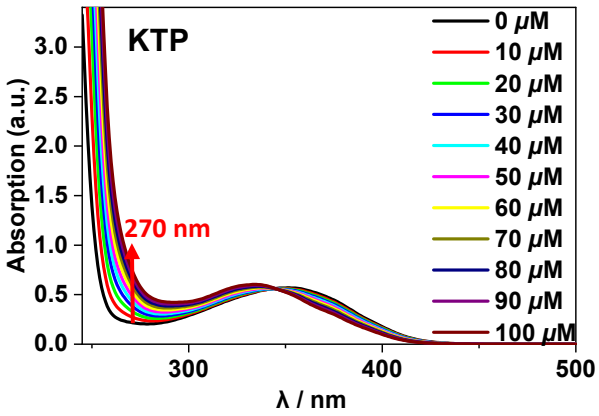


Figure S13. UV-vis titration of **1** to the addition of KTP in CH_3CN.

17. Emission spectrum of KTP at 77K

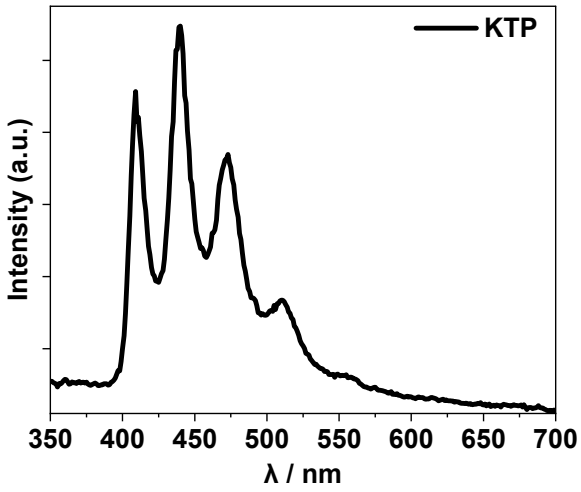


Figure S14. The emission spectrum of KTP at 77K.

18. Emission spectra of 1 and the Gd(III) analogue with the addition of KTP

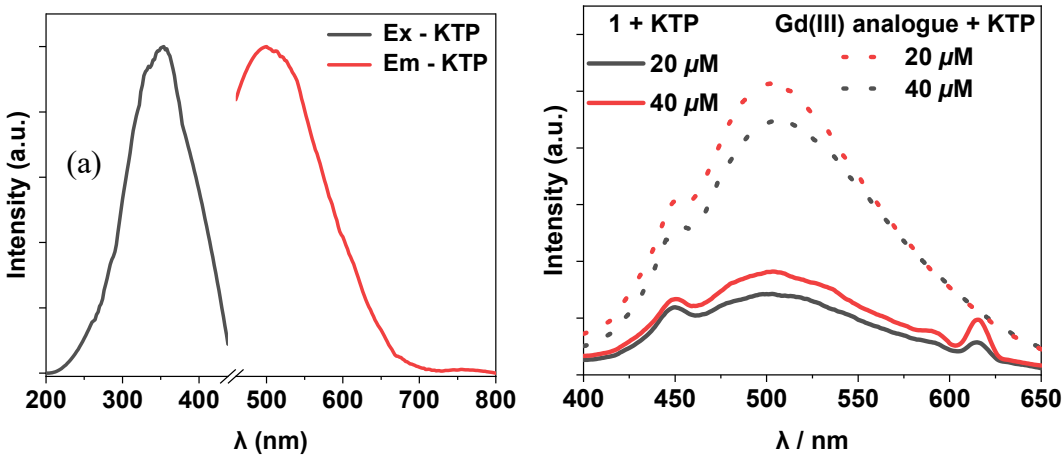


Figure S15. (a) The excitation (λ_{em} = 500 nm) and emission (λ_{ex} = 350 nm) spectra of KTP in CH_3CN; (b) The emission spectra of **1** (solid lines) and the Gd(III) analogue (dot lines) with the addition of different concentrations of KTP in CH_3CN. (λ_{ex} = 350 nm);

19. Lanthanide luminescence lifetimes of 1 with the addition of KTP

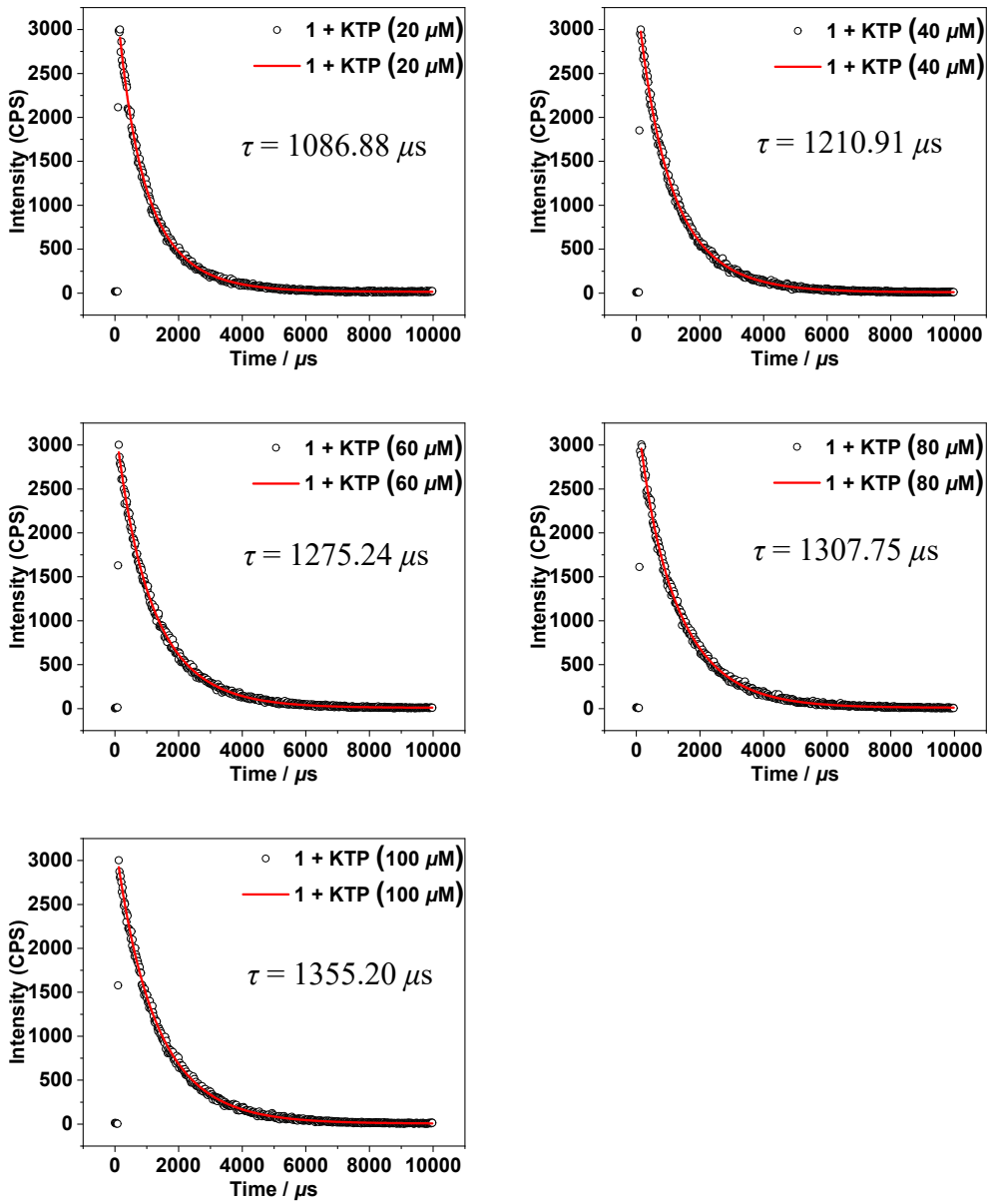
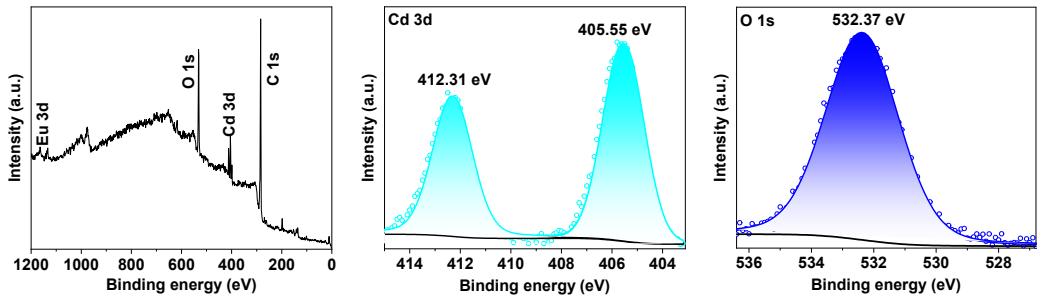
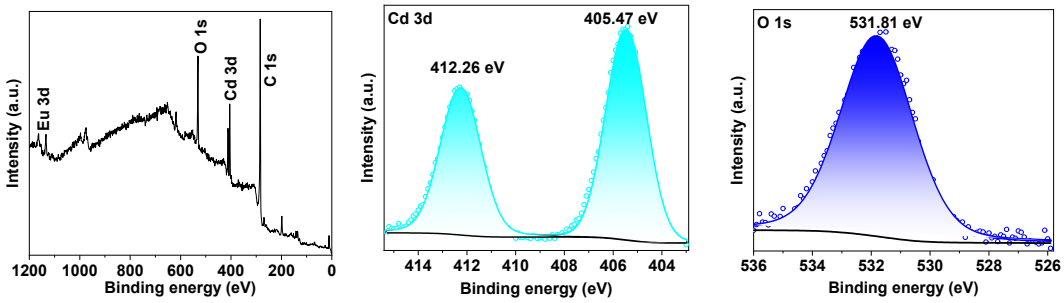


Figure S16. The lanthanide luminescence lifetimes of **1** with the addition of different concentrations of KTP in CH_3CN. (λ_{ex} = 270 nm)

20. High-resolution XPS spectra of 1



(a)



(b)

Figure S17. XPS spectra of **1** before (a) and after (b) the treatment with KTP.

21. X-Ray Crystallography

Data were collected on a Smart APEX CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) at 233 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 structure was solved by Olex2 program. 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.[2] Some uncoordinated solvent molecules such as EtOH and H_2O were found to be badly disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE (Sluis and Spek, 1990) in PLATON98 (Spek, 1998). PLATON98 was used as incorporated in WinGX (Farrugia, 1999). Crystallographic data for **1** are presented in Table S1 and selected bond lengths and angles are given in Table S2. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format (CCDC reference number 2529699).

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

Table S1. Crystal data and structure refinement for **1**.

	1
Formula	$C_{39}H_{65}Cd_3Cl_6Eu_2N_7O_{19}$
Fw	1789.80

Crystal system	Orthorhombic
Space group	Pbcn
a [Å]	12.5924(11)
b [Å]	29.4736(18)
c [Å]	36.5786(13)
α [deg]	90.00
β [deg]	90.00
γ [deg]	90.00
V / [Å^3]	13575.9(15)
d / [g/cm^3]	1.751
Z	8
T [K]	190(1)
F(000)	6976
μ, mm^{-1}	3.044
θ rang, deg	1.77-25.00
reflns meads	11814
reflns used	11814
params	687
R1[a], wR2[a] [$I > 2\sigma(I)$]	0.0903, 0.2220
R1, wR2 (all data)	0.1778, 0.2474
Quality of fit	1.046

[a] $R1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$. $wR2 = [\Sigma w[(F_o^2 - F_c^2)^2]/\Sigma|[w(F_o^2)^2]]^{1/2}$. $w=1/[\sigma^2(F_o^2)+(0.075P)^2]$, where $P = [\max(F_o^2,0)+2F_c^2]/3$.

Table S2. Selected Bond Lengths (Å) and angles (◦) for **1**.

Eu(1)-O(13)	2.385(10)	Eu(1)-O(4)	2.480(11)
Eu(1)-O(14)	2.405(11)	Eu(1)-O(11)	2.485(16)
Eu(1)-O(13)#1	2.426(11)	Eu(1)-O(19)	2.491(19)
Eu(1)-O(9)	2.467(17)	Eu(1)-O(10)	2.492(12)

Eu(1)-O(5)	2.539(11)	O(11)-Eu(1)-O(19)	72.3(6)
Eu(2)-O(17)	2.36(2)	O(13)-Eu(1)-O(10)	84.7(4)
Eu(2)-O(12)	2.385(17)	O(14)-Eu(1)-O(10)	138.6(4)
Eu(2)-O(15)	2.378(19)	O(13)#1-Eu(1)-O(10)	71.3(4)
Eu(2)-O(14)#1	2.403(12)	O(9)-Eu(1)-O(10)	78.3(5)
Eu(2)-O(14)	2.424(10)	O(4)-Eu(1)-O(10)	127.6(4)
Eu(2)-O(13)	2.434(11)	O(11)-Eu(1)-O(10)	143.3(5)
Eu(2)-O(16)	2.440(18)	O(19)-Eu(1)-O(10)	74.6(6)
Eu(2)-O(18)	2.57(2)	O(13)-Eu(1)-O(5)	133.8(4)
Cd(1)-O(4)	2.272(13)	O(14)-Eu(1)-O(5)	107.8(4)
Cd(1)-Cl(6)	2.324(13)	O(13)#1-Eu(1)-O(5)	70.3(4)
Cd(1)-N(1)	2.383(16)	O(9)-Eu(1)-O(5)	68.4(6)
Cd(1)-Cl(1)	2.456(7)	O(4)-Eu(1)-O(5)	62.9(4)
Cd(1)-O(11)	2.477(14)	O(11)-Eu(1)-O(5)	123.8(4)
Cd(2)-O(5)	2.216(12)	O(19)-Eu(1)-O(5)	126.2(5)
Cd(2)-Cl(3)	2.370(8)	O(10)-Eu(1)-O(5)	66.6(4)
Cd(2)-N(4)	2.401(17)	O(17)-Eu(2)-O(12)	142.1(7)
Cd(2)-Cl(2)	2.426(10)	O(17)-Eu(2)-O(15)	77.2(8)
Cd(2)-O(10)	2.511(12)	O(12)-Eu(2)-O(15)	113.2(6)
Cd(3)-N(2)	2.283(15)	O(17)-Eu(2)-O(14)#1	76.0(7)
Cd(3)-N(3)	2.327(16)	O(12)-Eu(2)-O(14)#1	139.6(4)
Cd(3)-Cl(4)	2.373(10)	O(15)-Eu(2)-O(14)#1	82.5(6)
Cd(3)-Cl(5)#2	2.557(8)	O(17)-Eu(2)-O(14)	139.3(7)
Cd(3)-Cl(5)	2.571(9)	O(12)-Eu(2)-O(14)	78.2(5)
O(13)-Eu(1)-O(14)	70.5(4)	O(15)-Eu(2)-O(14)	80.0(5)
O(13)-Eu(1)-O(13)#1	66.5(5)	O(14)#1-Eu(2)-O(14)	67.9(4)
O(14)-Eu(1)-O(13)#1	68.6(4)	O(17)-Eu(2)-O(13)	114.3(7)
O(13)-Eu(1)-O(9)	141.8(5)	O(12)-Eu(2)-O(13)	79.7(5)
O(14)-Eu(1)-O(9)	140.2(5)	O(15)-Eu(2)-O(13)	143.7(6)
O(13)#1-Eu(1)-O(9)	135.7(5)	O(14)#1-Eu(2)-O(13)	68.5(4)
O(13)-Eu(1)-O(4)	142.7(4)	O(14)-Eu(2)-O(13)	69.4(4)
O(14)-Eu(1)-O(4)	72.4(4)	O(17)-Eu(2)-O(16)	74.6(8)
O(13)#1-Eu(1)-O(4)	103.3(4)	O(12)-Eu(2)-O(16)	76.2(6)
O(9)-Eu(1)-O(4)	71.2(5)	O(15)-Eu(2)-O(16)	140.6(6)
O(13)-Eu(1)-O(11)	101.0(4)	O(14)#1-Eu(2)-O(16)	116.0(5)
O(14)-Eu(1)-O(11)	75.6(5)	O(14)-Eu(2)-O(16)	138.4(5)
O(13)#1-Eu(1)-O(11)	144.2(4)	O(13)-Eu(2)-O(16)	74.2(5)
O(9)-Eu(1)-O(11)	75.2(5)	O(17)-Eu(2)-O(18)	75.5(8)
O(4)-Eu(1)-O(11)	65.5(4)	O(12)-Eu(2)-O(18)	73.8(6)
O(13)-Eu(1)-O(19)	74.4(5)	O(15)-Eu(2)-O(18)	72.2(7)
O(14)-Eu(1)-O(19)	125.9(5)	O(14)#1-Eu(2)-O(18)	145.2(5)
O(13)#1-Eu(1)-O(19)	129.5(5)	O(14)-Eu(2)-O(18)	127.8(6)
O(9)-Eu(1)-O(19)	68.3(6)	O(13)-Eu(2)-O(18)	142.9(6)
O(4)-Eu(1)-O(19)	127.0(5)	O(16)-Eu(2)-O(18)	74.5(7)

O(4)-Cd(1)-Cl(6)	129.9(5)	N(4)-Cd(2)-Cl(2)	99.3(5)
O(4)-Cd(1)-N(1)	69.3(5)	O(5)-Cd(2)-O(10)	71.2(4)
Cl(6)-Cd(1)-N(1)	99.3(5)	Cl(3)-Cd(2)-O(10)	103.5(4)
O(4)-Cd(1)-Cl(1)	104.0(4)	N(4)-Cd(2)-O(10)	138.9(5)
Cl(6)-Cd(1)-Cl(1)	125.5(4)	Cl(2)-Cd(2)-O(10)	91.4(4)
N(1)-Cd(1)-Cl(1)	107.6(4)	N(2)-Cd(3)-N(3)	72.8(5)
O(4)-Cd(1)-O(11)	68.7(5)	N(2)-Cd(3)-Cl(4)	108.8(5)
Cl(6)-Cd(1)-O(11)	100.6(5)	N(3)-Cd(3)-Cl(4)	103.5(5)
N(1)-Cd(1)-O(11)	137.1(5)	N(2)-Cd(3)-Cl(5)#2	142.5(5)
Cl(1)-Cd(1)-O(11)	90.8(4)	N(3)-Cd(3)-Cl(5)#2	90.8(4)
O(5)-Cd(2)-Cl(3)	137.9(5)	Cl(4)-Cd(3)-Cl(5)#2	107.8(4)
O(5)-Cd(2)-N(4)	67.7(5)	N(2)-Cd(3)-Cl(5)	92.8(5)
Cl(3)-Cd(2)-N(4)	106.9(5)	N(3)-Cd(3)-Cl(5)	148.6(5)
O(5)-Cd(2)-Cl(2)	106.0(4)	Cl(4)-Cd(3)-Cl(5)	107.5(4)
Cl(3)-Cd(2)-Cl(2)	116.0(4)	Cl(5)#2-Cd(3)-Cl(5)	84.1(3)