Supporting Information

Rapid and sensitive detection of vanillylmandelic acid based on a luminescent fourteen-metal Tb(III) planar nanocluster

Yanheng Meng, Shiqing Wang, Xiaoli Lv, Xianfeng Huang, Weibin Zhang, Xiaojun Wu, Desmond Schipper, and Xiaoping Yang

Contents

1. General procedures

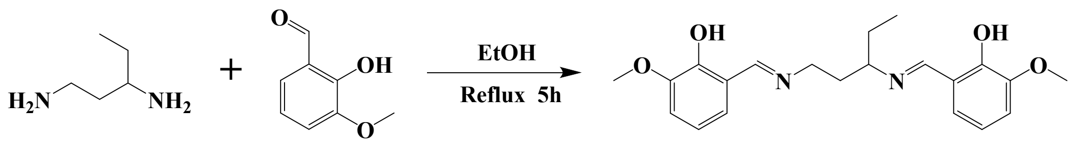
The metal salt is purchased from Meryer Company, and the reagent is from

Wenzhou Jinshan Chemical Reagent. NMR spectra were obtained on an AVANCE III AV500 at 298 K. IR spectra were determined on a FTIR-650 spectrometer. Powder XRD spectra were recorded on a D8 Advance. The thermogravimetric analyses were carried out on a Perking Elmer Diamond TG-DTA spectrum GX. The flow rate of N_2 is 200 ml min^{-1}, the temperature is heated from room temperature to 800 degrees, and the speed is 10°C min^{-1}. Elemental analyses were carried out on a EURO EA3000 with the solid sample after dried in the oven at 110°C for overnight. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova NanoSEM 200 scanning electron microscope.

Photophysical Studies. UV-vis absorption spectra were obtained on a UV-3600 spectrophotometer; Excitation and emission spectra 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. Systematic errors have been deducted through the standard instrument corrections. All the measurements were carried out at room temperature.

2. Synthesis of H_2L and 1

Synthesis of H_2L: 3-methoxysalicylaldehyde (20 mmol, 3.0430 g) was dissolved in 50 mL EtOH, and a solution of 1,3-diaminopentane (10 mmol, 1.0218 g) in 25 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 5 hours. It was allowed to cool and then filtered in vacuum. The solid was washed with EtOH (3 × 5 mL) and then dried under vacuum to give yellow product. Yield: 3.0138 g (81.35%). ^{1}H NMR (500 MHz, Chloroform-d) δ 14.08 (s, 1H), 13.99 (s, 1H), 8.33 (s, 1H), 8.29 (s, 1H), 6.94 (s, 2H), 6.88 (s, 2H), 6.81 (s, 2H), 3.92 (s, 6H), 3.60 (s, 2H), 3.32 (s, 1H), 2.01 (s, 2H), 1.69 (s, 2H), 0.88 (s, 3H). IR (KBr, cm^{-1}): 3465 (m), 3367 (s), 2935 (s), 2857 (w), 1607 (s), 1503 (s), 1460 (s), 1388 (m), 1345 (w), 1276 (s), 1227 (s), 1170 (w), 1142 (w), 1074 (m), 1040 (m), 994 (s), 896 (m), 779 (w), 723 (s), 606 (w).



Scheme S1. The synthesis route of H_2L.

Synthesis of 1: At room temperature, 3-methoxysalicylaldehyde (0.20 mmol, 3.043 g) and H_2L (0.20 mmol, 0.074 g) were dissolved in 8 mL EtOH and 4 mL MeOH, and then triethylamine in EtOH (1.0 mol/L, 1 ml) was added into the solution. $Tb(OAc)_3{\cdot}6H_2O$ (0.20 mmol, 0.0888 g) was added into the above solution, and the mixture was heated for 30 mins under reflux with stirring, and cooled to room temperature. The clear solution was obtained by filtered, and slow diffusion of diethyl ether into the solution for two weeks gave the yellow crystalline product of **1**. Yield (based on $Tb(OAc)_3{\cdot}6H_2O$): 22% (0.01644 g). Elemental analysis: Calcd for $C_{114}H_{146}N_4O_{82}Tb_{14}$: C, 26.80; H, 2.88; N, 1.10 %. Found: C, 26.57; H, 2.68; N, 1.25 %. IR (KBr, cm^{-1}): 1646 (m), 1552(s), 1444 (s), 1404 (s), 1342 (m), 1317 (m), 1242 (m), 1211 (s), 1170 (w) , 1071 (w), 1016 (m), 949 (m), 860 (w), 727 (s), 674 (s), 645 (m), 612 (m), 555 (w). m. p. > 210 °C (decompose).

3. ^{1}H NMR spectrum of H_2L

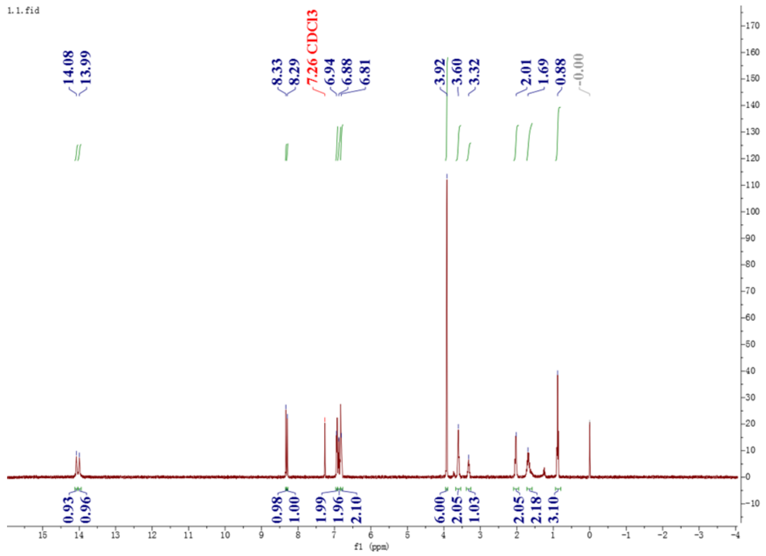


Figure S1. The ^{1}H NMR spectrum of H_2L.

4. IR spectra of H_2L and 1

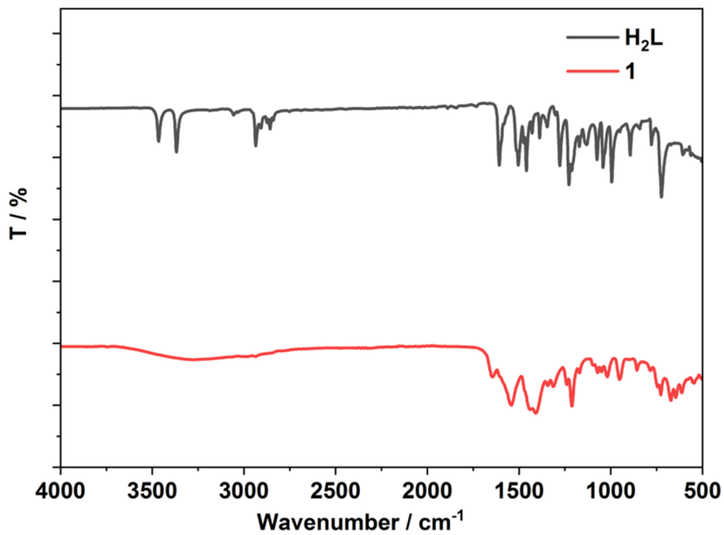


Figure S2. IR spectra of the ligand H_2L and **1**.

5. Coordination modes of Tb(III) ions with ligands

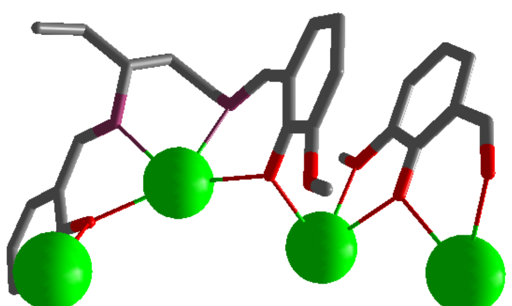


Figure S3. Coordination modes of Tb(III) ions with ligands in **1**.

6. The thermogravimetric analysis of 1

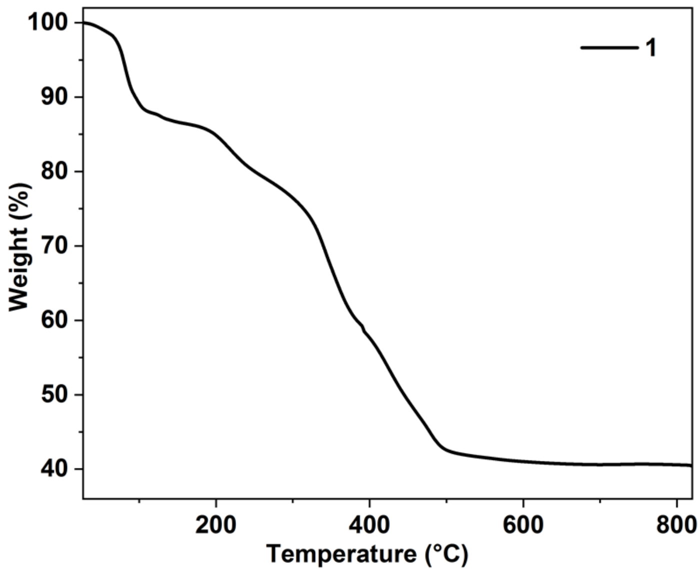


Figure S4. The thermogravimetric analysis of **1**.

7. UV-vis absorption spectra of H_2L, 1 and VMA

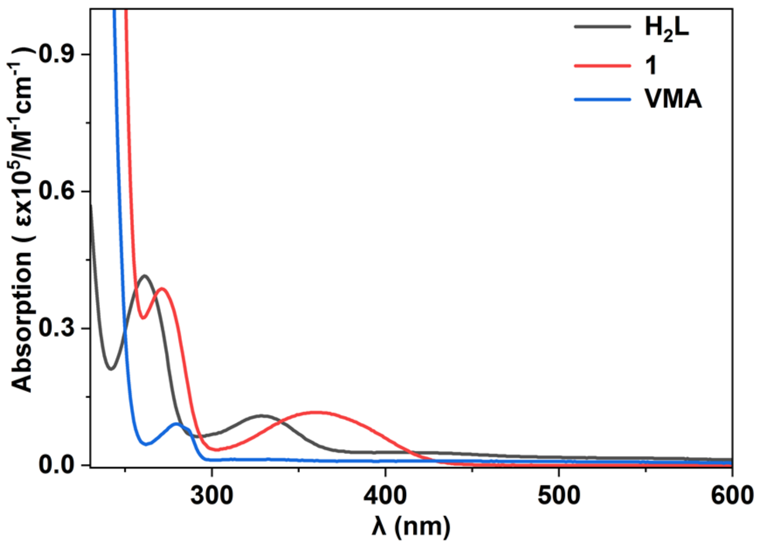


Figure S5. UV-vis absorption spectra of H_2L, **1** and VMA in CH_3CN. (c = 10 μM)

8. Excitation and emission spectra of H_2L and 1

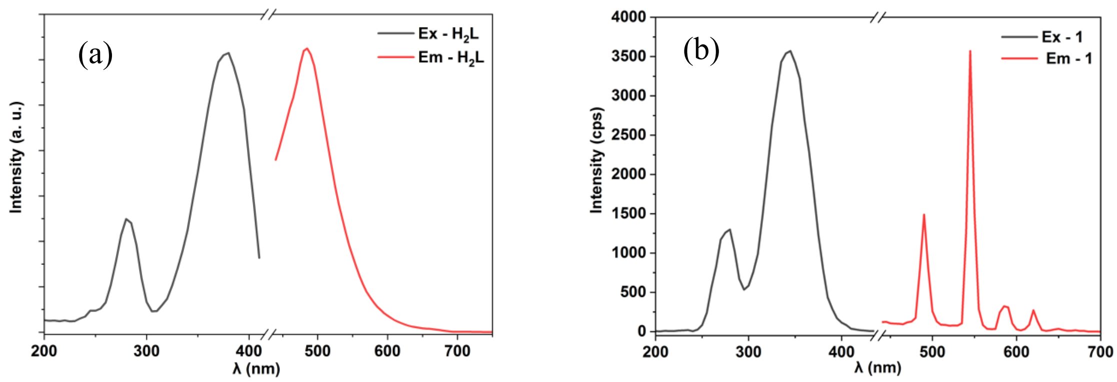


Figure S6. (a) Excitation (λ_{em} = 485 nm) and emission (λ_{ex} = 380 nm) spectra of H_2L (10 μM) in CH_3CN. (b) Excitation (λ_{em} = 545 nm) and emission (λ_{ex} = 345 nm) spectra of **1** (10 μM) at room temperature in CH_3CN.

9. The lanthanide luminescence lifetimes of 1

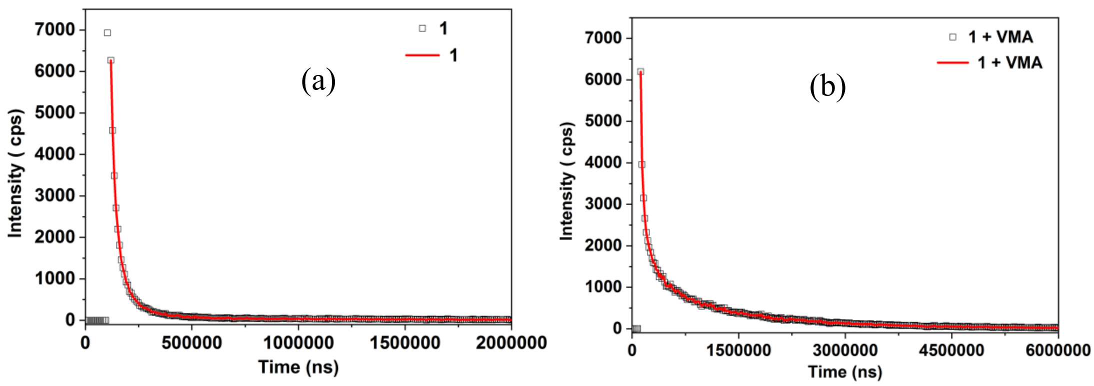


Figure S7. The lanthanide luminescence lifetimes of **1** (10 μM) without (a) and with (b) the addition of VMA (270 μM) in CH_3CN. (λ_{ex} = 285 nm)

10. The lanthanide luminescence spectra of 1

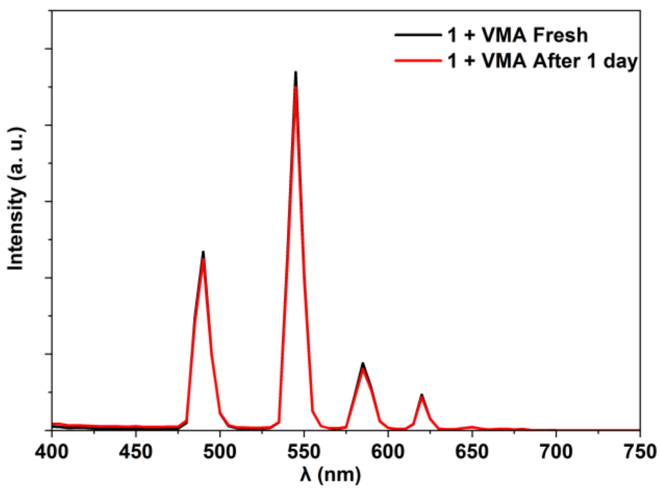
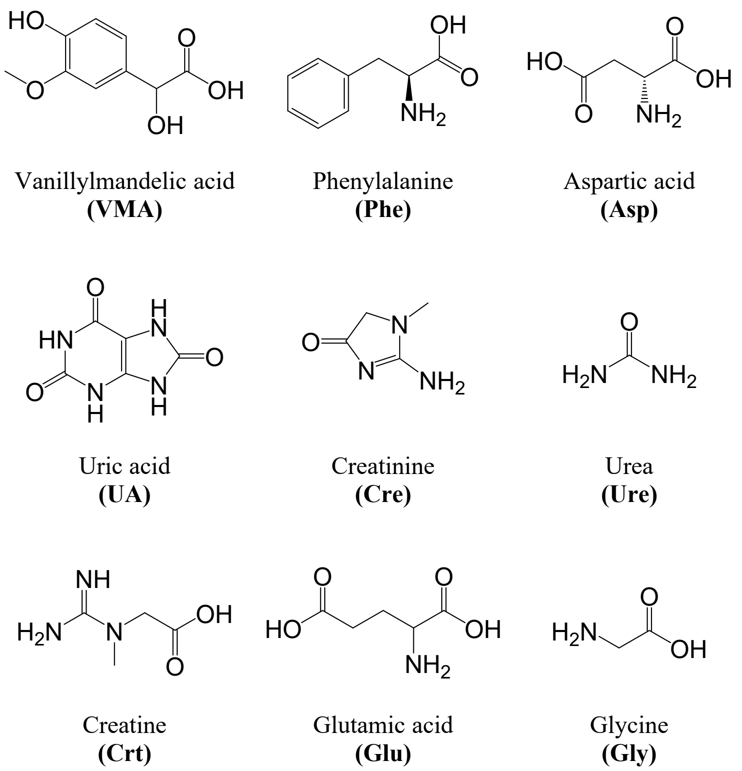


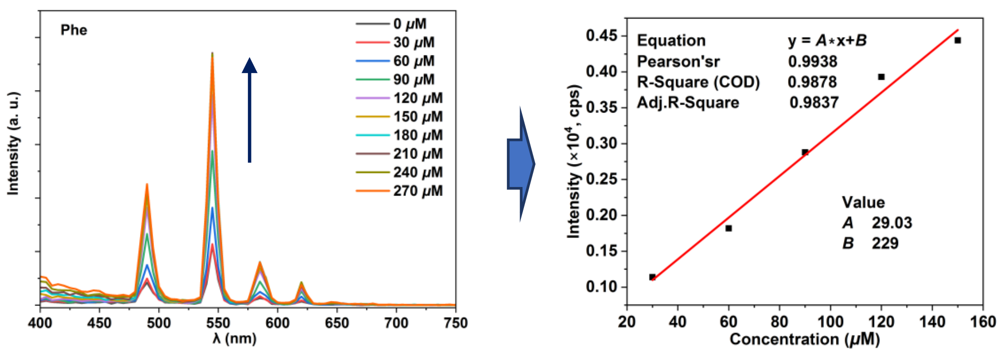
Figure S8. The lanthanide luminescence spectra (fresh and one day after) of **1** (10 μM) with the addition of VMA (270 μM). (λ_{ex} = 285 nm)

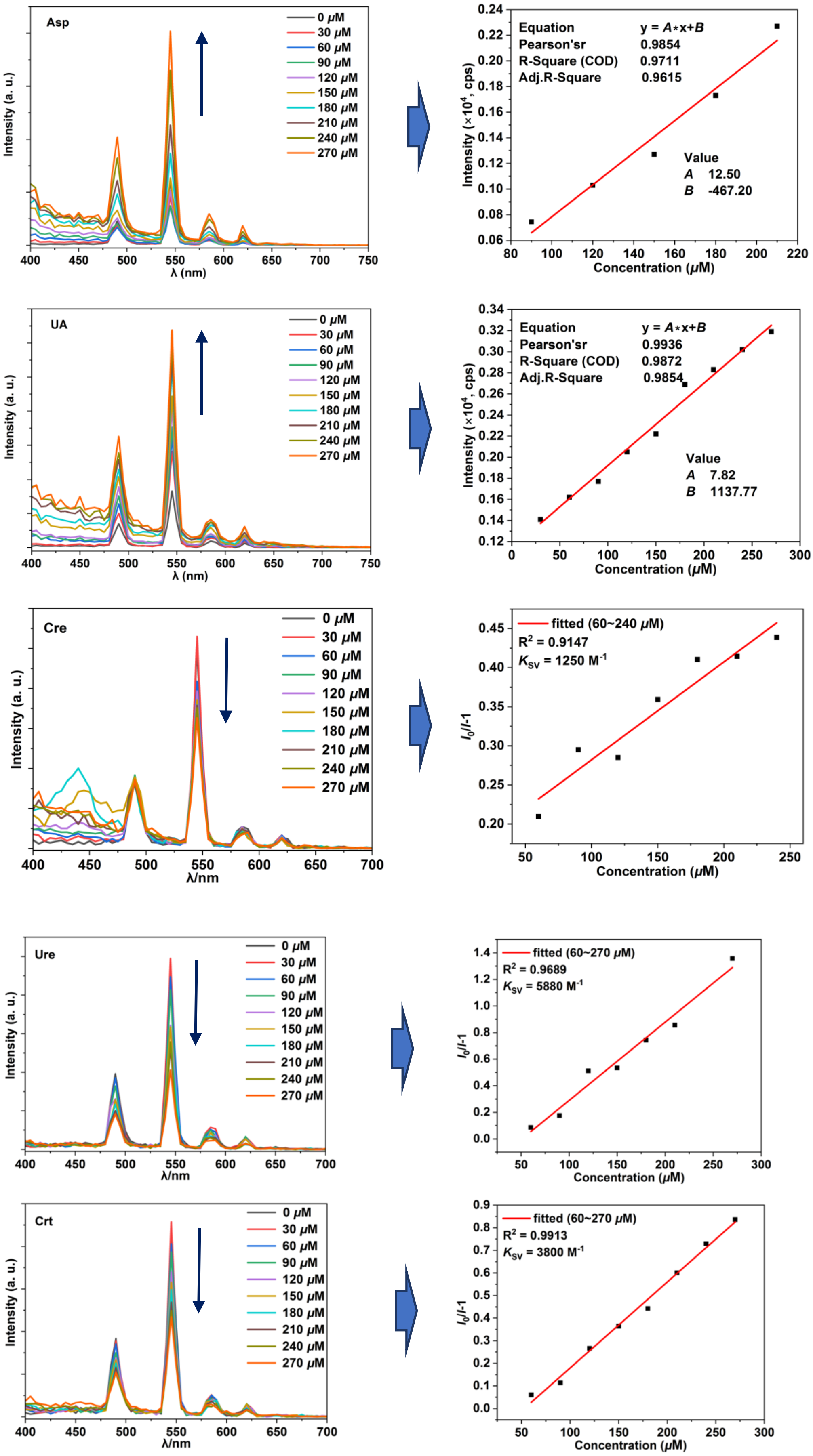
11. Chemical structures of urinary components

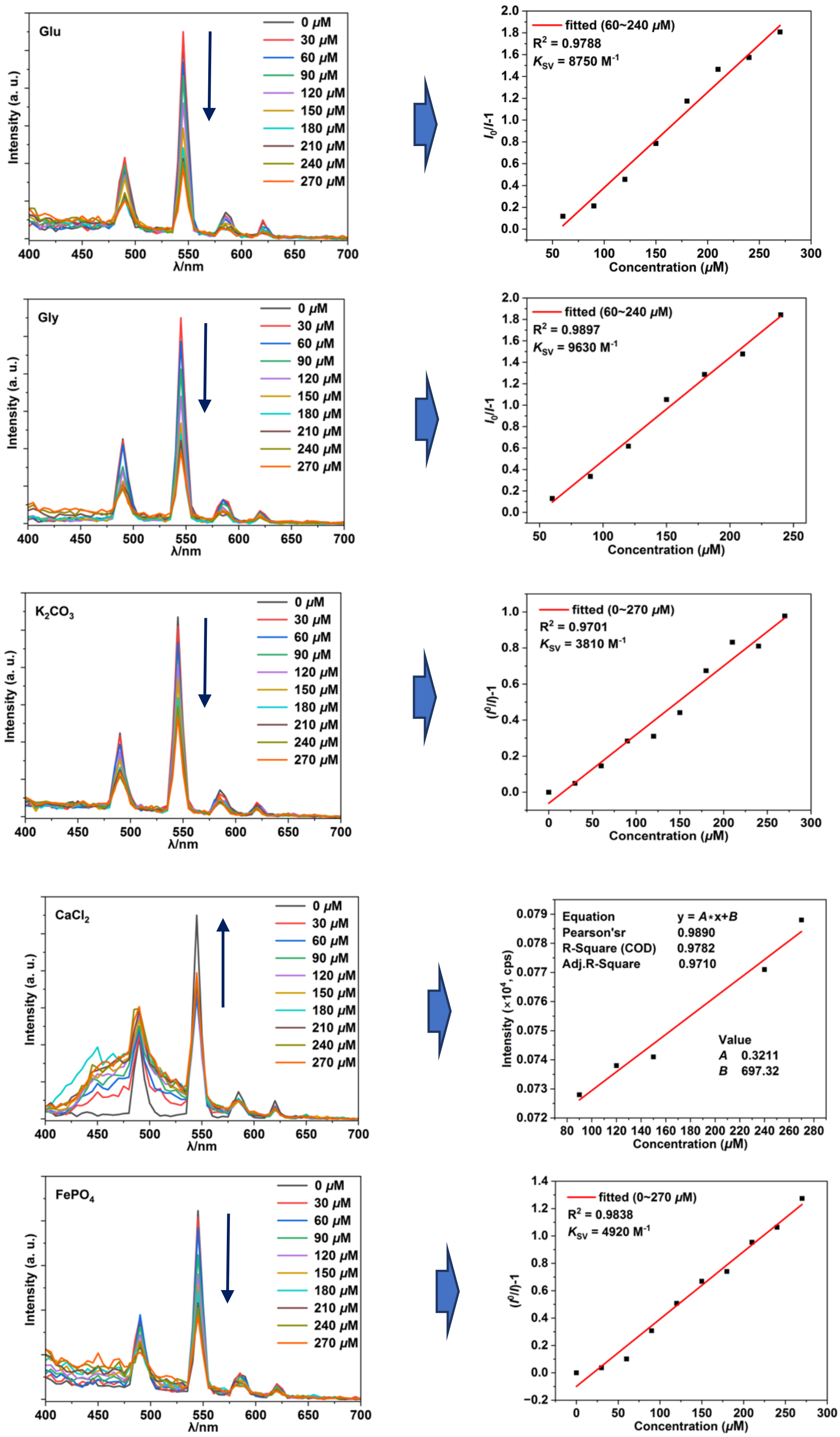


Scheme S2. Chemical structures of urinary components.

12. The luminescence response of 1 to urinary components




Asp
0 μM
30 μM
60 μM
90 μM
120 μM
150 μM
180 μM
210 μM
240 μM
270 μM
Intensity (a. u.)
λ (nm)
Equation y = A*x+B
Pearson'sr 0.9854
R-Square (COD) 0.9711
Adj.R-Square 0.9615
Value
A 12.50
B -467.20
Intensity (×10^4, cps)
Concentration (μM)
UA
Equation y = A*x+B
Pearson'sr 0.9936
R-Square (COD) 0.9872
Adj.R-Square 0.9854
Value
A 7.82
B 1137.77
Cre
λ/nm
fitted (60~240 μM)
R^2 = 0.9147
K_SV = 1250 M^-1
I_0/I-1
Ure
fitted (60~270 μM)
R^2 = 0.9689
K_SV = 5880 M^-1
Crt
fitted (60~270 μM)
R^2 = 0.9913
K_SV = 3800 M^-1


Glu
Gly
K2CO3
CaCl2
FePO4
0 μM
30 μM
60 μM
90 μM
120 μM
150 μM
180 μM
210 μM
240 μM
270 μM
Intensity (a. u.)
λ/nm
fitted (60~240 μM)
R2 = 0.9788
KSV = 8750 M-1
R2 = 0.9897
KSV = 9630 M-1
fitted (0~270 μM)
R2 = 0.9701
KSV = 3810 M-1
R2 = 0.9838
KSV = 4920 M-1
I0/I-1
(I0/I)-1
Concentration (μM)
Equation y = A*x+B
Pearson'sr 0.9890
R-Square (COD) 0.9782
Adj.R-Square 0.9710
Value
A 0.3211
B 697.32
Intensity (×10^4, cps)

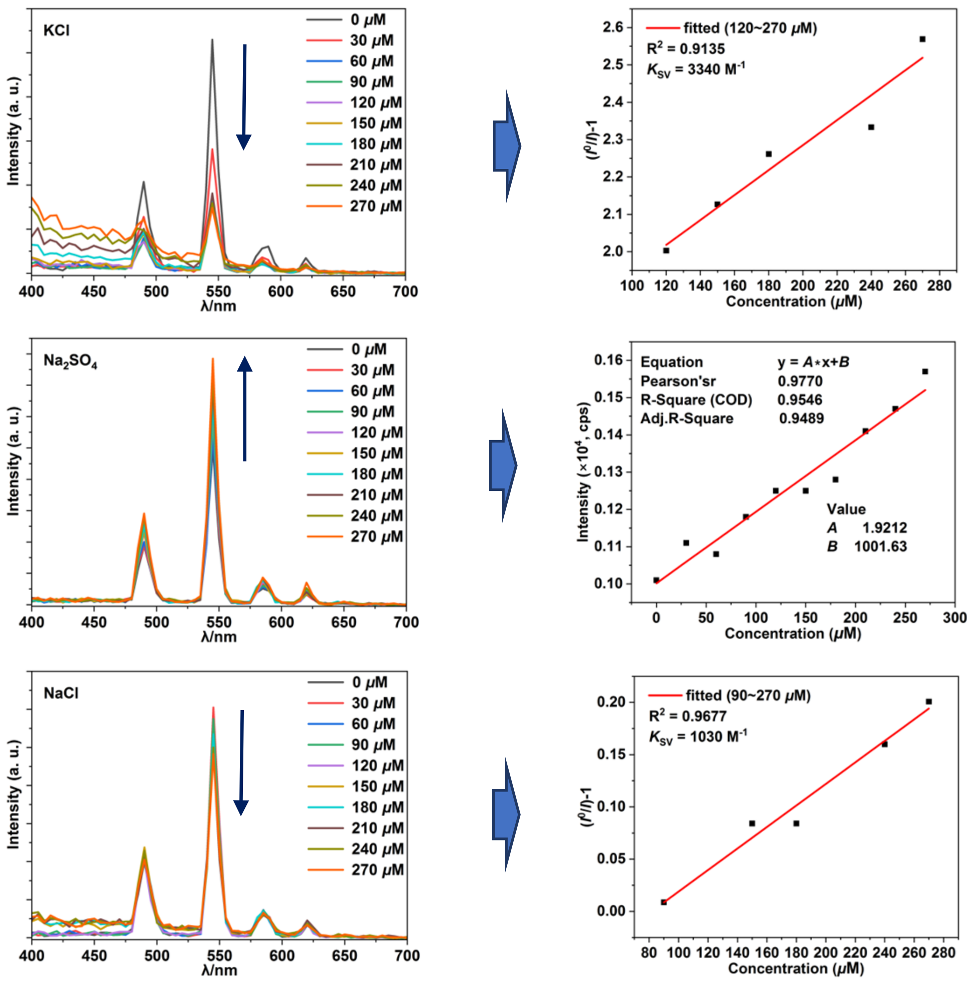


Figure S9. Luminescence spectra of **1** (10 μM) with the addition of urinary components in CH_3CN. (λ_{ex} = 285 nm)

13. The luminescence response of 1 to VMA in urine and FCS

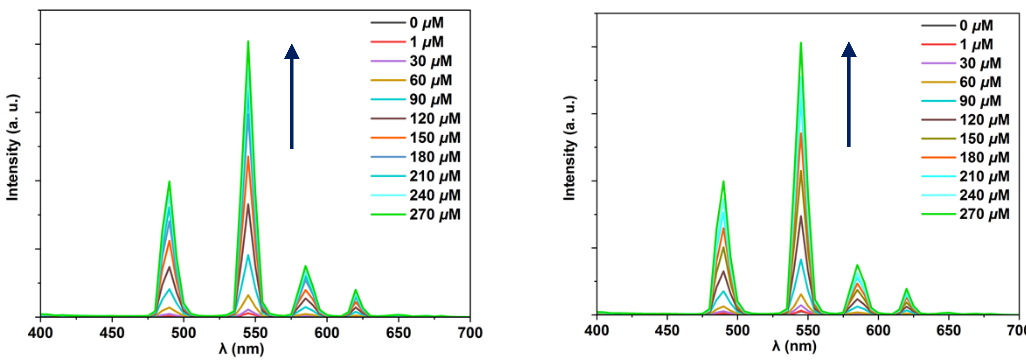


Figure S10. The luminescence spectra of **1** (10 μM) with the addition of VMA in FCS and urine. (λ_{ex} = 285 nm)

14. Powder XRD patterns of 1

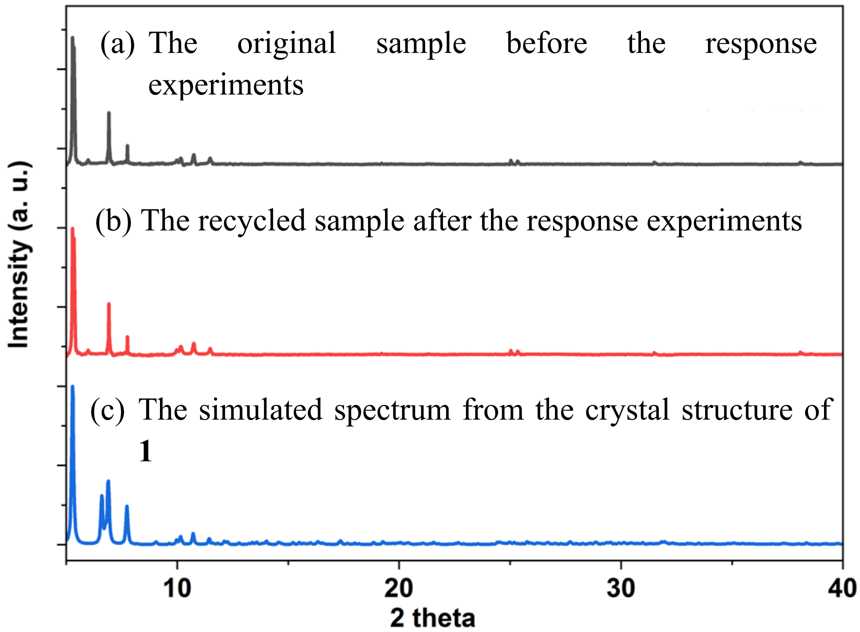


Figure S11. Powder XRD patterns of **1**.

15. UV-vis titration of 1 to the addition of VMA

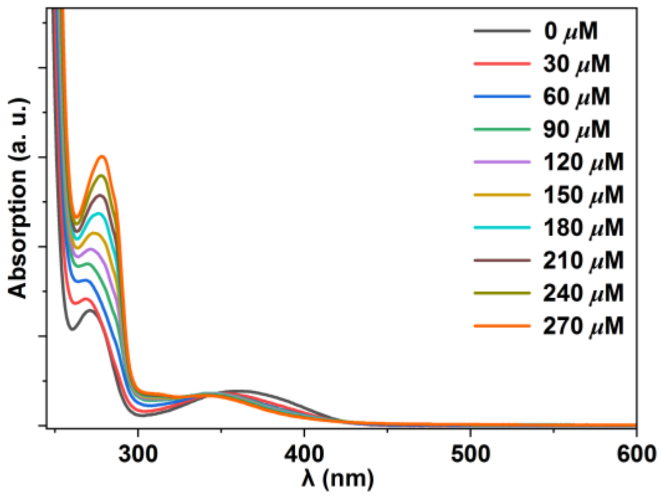


Figure S12. UV-vis titration of **1** (10 μM) with the addition of VMA in CH_3CN.

16. The emission spectrum of VMA at 77K

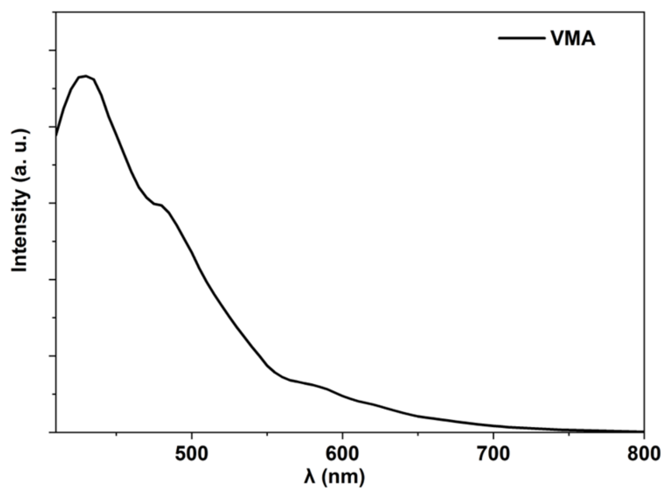


Figure S13. The emission spectrum of VMA at 77K.

17. UV-vis absorption spectra of VMA and urinary components

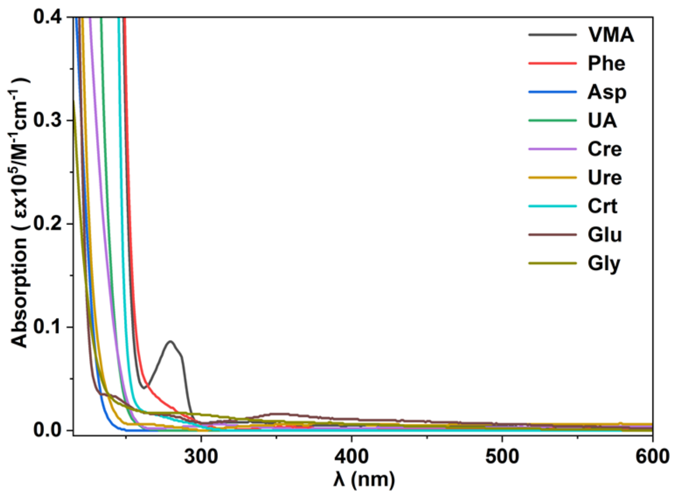


Figure S14. UV-vis absorption spectra of VMA and urinary components (10 μM) in CH_3CN.

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 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] Crystallographic data for **1** (CCDC reference number 2371789) are presented in Table S2, and selected bond lengths and angles are given in Table S3. See http://www.rsc.org/suppdata/cc/ for crystallographic data in CIF format.

1. DENZO-SMN. (**1997**). Otwinowski, Z.; Minor, W. *Methods in Enzymology*, 276: *Macromolecular Crystallography, Part A*, 307 – 326, Carter, C. W. J.; Simon, M. I.; Sweet, R. M. Editors, Academic Press.
2. Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, vol. 4, **1974**, Table 2.2A.

Table S2. Crystal data and structure refinement for **1**.

	1
Formula	$C_{114}H_{154}N_4Tb_{14}O_{86}$
Fw	5181.28
Crystal system	monoclinic
Space group	C2/c
a [Å]	33.4177(5)
b [Å]	14.6058(3)
c [Å]	43.1667(6)
α [deg]	90.00
β [deg]	91.3630(10)
γ [deg]	90.00
V / [Å^3]	21063.4(6)
d / [g/cm^3]	1.634

Z	4
T [K]	190
F(000)	9856
μ, mm^{-1}	4.707
θ rang, deg	1.798-25.000
reflns meads	86704
reflns used	18485
params	946
R1^a, wR2^a [$I > 2\sigma(I)$]	0.0422, 0.1084
R1, wR2 (all data)	0.0582, 0.1149
Quality of fit	1.037

^{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 S3. Selected Bond Lengths (Å) and angles (◦) for **1**.

Tb(1)-O(1)	2.455(6)	Tb(2)-O(41)	2.491(5)
Tb(1)-O(2)	2.467(5)	Tb(3)-O(10)#1	2.472(4)
Tb(1)-O(3)	2.434(5)	Tb(3)-O(11)	2.378(4)
Tb(1)-O(5)	2.459(5)	Tb(3)-O(14)	2.364(4)
Tb(1)-O(6)	2.591(4)	Tb(3)-O(18)#1	2.625(4)
Tb(1)-O(7)	2.363(5)	Tb(3)-O(19)	2.397(4)
Tb(1)-O(9)	2.392(4)	Tb(3)-O(19)#1	2.536(4)
Tb(1)-O(39)#1	2.583(4)	Tb(3)-O(23)	2.479(5)
Tb(1)-O(40)#1	2.490(5)	Tb(3)-O(24)	2.572(4)
Tb(2)-O(6)	2.458(4)	Tb(3)-O(25)	2.334(4)
Tb(2)-O(8)	2.338(5)	Tb(4)-O(12)	2.515(4)
Tb(2)-O(9)	2.533(4)	Tb(4)-O(13)	2.524(5)
Tb(2)-O(11)	2.486(4)	Tb(4)-O(14)	2.391(4)
Tb(2)-O(12)	2.441(4)	Tb(4)-O(16)	2.390(4)
Tb(2)-O(14)	2.507(4)	Tb(4)-O(17)	2.649(5)
Tb(2)-O(15)	2.479(5)	Tb(4)-O(18)#1	2.497(4)
Tb(2)-O(16)	2.445(4)	Tb(4)-O(20)	2.603(4)

Tb(4)-O(21)	2.347(4)	O(5)-Tb(1)-O(6)	50.95(15)
Tb(4)-O(37)	2.373(4)	O(5)-Tb(1)-O(39)#1	129.08(18)
Tb(5)-O(3)#1	2.481(4)	O(5)-Tb(1)-O(40)#1	82.14(18)
Tb(5)-O(4)#1	2.503(5)	O(7)-Tb(1)-O(1)	77.2(2)
Tb(5)-O(10)#1	2.679(4)	O(7)-Tb(1)-O(2)	127.4(2)
Tb(5)-O(24)	2.501(4)	O(7)-Tb(1)-O(3)	82.35(16)
Tb(5)-O(25)	2.423(4)	O(7)-Tb(1)-O(5)	85.45(18)
Tb(5)-O(26)	2.531(4)	O(7)-Tb(1)-O(6)	77.05(15)
Tb(5)-O(31)	2.388(4)	O(7)-Tb(1)-O(9)	82.33(15)
Tb(5)-O(33)	2.345(4)	O(7)-Tb(1)-O(39)#1	144.82(16)
Tb(5)-O(39)	2.418(5)	O(7)-Tb(1)-O(40)#1	149.74(16)
Tb(6)-O(20)	2.455(4)	O(9)-Tb(1)-O(1)	147.5(2)
Tb(6)-O(21)	2.728(5)	O(9)-Tb(1)-O(2)	149.16(19)
Tb(6)-O(22)	2.475(5)	O(9)-Tb(1)-O(3)	73.70(15)
Tb(6)-O(27)	2.345(4)	O(9)-Tb(1)-O(5)	116.85(16)
Tb(6)-O(35)	2.503(5)	O(9)-Tb(1)-O(6)	65.93(13)
Tb(6)-O(36)	2.451(5)	O(9)-Tb(1)-O(39)#1	76.03(13)
Tb(6)-O(37)	2.407(4)	O(9)-Tb(1)-O(40)#1	78.92(16)
Tb(6)-N(1)	2.578(5)	O(39)#1-Tb(1)-O(6)	117.13(15)
Tb(6)-N(2)	2.525(6)	O(40)#1-Tb(1)-O(6)	73.68(15)
Tb(7)-O(26)	2.380(4)	O(40)#1-Tb(1)-O(39)#1	50.57(15)
Tb(7)-O(27)	2.395(4)	O(6)-Tb(2)-O(9)	65.94(13)
Tb(7)-O(28)	2.613(5)	O(6)-Tb(2)-O(11)	97.26(13)
Tb(7)-O(29)	2.445(4)	O(6)-Tb(2)-O(14)	148.33(15)
Tb(7)-O(30)	2.411(5)	O(6)-Tb(2)-O(15)	76.44(14)
Tb(7)-O(31)	2.691(5)	O(6)-Tb(2)-O(41)	74.50(16)
Tb(7)-O(32)	2.469(5)	O(8)-Tb(2)-O(6)	75.51(16)
Tb(7)-O(34)	2.402(5)	O(8)-Tb(2)-O(9)	81.29(15)
Tb(7)-O(35)	2.469(5)	O(8)-Tb(2)-O(11)	129.10(15)
O(1)-Tb(1)-O(2)	52.5(2)	O(8)-Tb(2)-O(12)	78.26(16)
O(1)-Tb(1)-O(5)	86.6(2)	O(8)-Tb(2)-O(14)	136.05(14)
O(1)-Tb(1)-O(6)	131.4(2)	O(8)-Tb(2)-O(15)	78.93(18)
O(1)-Tb(1)-O(39)#1	107.6(2)	O(8)-Tb(2)-O(16)	75.69(15)
O(1)-Tb(1)-O(40)#1	129.1(2)	O(8)-Tb(2)-O(41)	143.55(16)
O(2)-Tb(1)-O(6)	123.3(2)	O(11)-Tb(2)-O(9)	51.41(13)
O(2)-Tb(1)-O(39)#1	73.96(17)	O(11)-Tb(2)-O(14)	66.32(12)
O(2)-Tb(1)-O(40)#1	76.7(2)	O(11)-Tb(2)-O(41)	75.17(15)
O(3)-Tb(1)-O(1)	78.7(2)	O(12)-Tb(2)-O(6)	134.23(15)
O(3)-Tb(1)-O(2)	99.7(2)	O(12)-Tb(2)-O(9)	73.55(13)
O(3)-Tb(1)-O(5)	162.64(18)	O(12)-Tb(2)-O(11)	71.80(14)
O(3)-Tb(1)-O(6)	136.50(14)	O(12)-Tb(2)-O(14)	68.53(14)
O(3)-Tb(1)-O(39)#1	65.22(15)	O(12)-Tb(2)-O(15)	133.46(15)
O(3)-Tb(1)-O(40)#1	114.33(16)	O(12)-Tb(2)-O(16)	67.36(14)
O(5)-Tb(1)-O(2)	78.1(2)	O(12)-Tb(2)-O(41)	138.14(15)

O(14)-Tb(2)-O(9)	114.14(12)	O(25)-Tb(3)-O(18)#1	71.31(14)
O(15)-Tb(2)-O(9)	140.78(14)	O(25)-Tb(3)-O(19)#1	113.25(14)
O(15)-Tb(2)-O(11)	149.43(16)	O(25)-Tb(3)-O(19)	139.07(13)
O(15)-Tb(2)-O(14)	103.56(14)	O(25)-Tb(3)-O(23)	91.00(15)
O(15)-Tb(2)-O(41)	74.32(17)	O(25)-Tb(3)-O(24)	67.71(13)
O(16)-Tb(2)-O(6)	137.57(14)	O(12)-Tb(4)-O(13)	51.35(15)
O(16)-Tb(2)-O(9)	137.69(15)	O(12)-Tb(4)-O(17)	91.24(15)
O(16)-Tb(2)-O(11)	125.11(13)	O(12)-Tb(4)-O(20)	136.58(13)
O(16)-Tb(2)-O(14)	65.53(13)	O(13)-Tb(4)-O(17)	68.20(17)
O(16)-Tb(2)-O(15)	67.95(15)	O(13)-Tb(4)-O(20)	129.33(15)
O(16)-Tb(2)-O(41)	115.11(16)	O(14)-Tb(4)-O(12)	69.15(14)
O(41)-Tb(2)-O(9)	104.55(15)	O(14)-Tb(4)-O(13)	119.17(15)
O(41)-Tb(2)-O(14)	75.11(15)	O(14)-Tb(4)-O(17)	130.18(15)
O(10)#1-Tb(3)-O(18)#1	84.55(14)	O(14)-Tb(4)-O(18)#1	74.10(13)
O(10)#1-Tb(3)-O(19)#1	76.23(13)	O(14)-Tb(4)-O(20)	84.70(13)
O(10)#1-Tb(3)-O(23)	114.72(15)	O(16)-Tb(4)-O(12)	67.00(14)
O(10)#1-Tb(3)-O(24)	64.15(14)	O(16)-Tb(4)-O(13)	96.10(17)
O(11)-Tb(3)-O(10)#1	139.40(13)	O(16)-Tb(4)-O(14)	68.20(14)
O(11)-Tb(3)-O(18)#1	94.17(14)	O(16)-Tb(4)-O(17)	61.98(16)
O(11)-Tb(3)-O(19)	72.45(13)	O(16)-Tb(4)-O(18)#1	130.39(13)
O(11)-Tb(3)-O(19)#1	72.38(13)	O(16)-Tb(4)-O(20)	134.49(15)
O(11)-Tb(3)-O(23)	87.14(15)	O(18)#1-Tb(4)-O(12)	70.20(13)
O(11)-Tb(3)-O(24)	130.72(14)	O(18)#1-Tb(4)-O(13)	75.17(16)
O(14)-Tb(3)-O(10)#1	144.57(12)	O(18)#1-Tb(4)-O(17)	142.78(16)
O(14)-Tb(3)-O(11)	70.33(13)	O(18)#1-Tb(4)-O(20)	69.57(13)
O(14)-Tb(3)-O(18)#1	72.17(13)	O(20)-Tb(4)-O(17)	131.39(14)
O(14)-Tb(3)-O(19)	140.26(13)	O(21)-Tb(4)-O(12)	134.18(17)
O(14)-Tb(3)-O(19)#1	105.98(13)	O(21)-Tb(4)-O(13)	83.09(17)
O(14)-Tb(3)-O(23)	78.03(15)	O(21)-Tb(4)-O(14)	150.99(16)
O(14)-Tb(3)-O(24)	115.52(14)	O(21)-Tb(4)-O(16)	131.65(15)
O(19)-Tb(3)-O(10)#1	75.06(13)	O(21)-Tb(4)-O(17)	73.36(16)
O(19)-Tb(3)-O(18)#1	124.38(13)	O(21)-Tb(4)-O(18)#1	96.33(14)
O(19)#1-Tb(3)-O(18)#1	49.86(12)	O(21)-Tb(4)-O(20)	66.35(15)
O(19)-Tb(3)-O(19)#1	74.96(15)	O(21)-Tb(4)-O(37)	76.48(16)
O(19)-Tb(3)-O(23)	86.76(14)	O(37)-Tb(4)-O(12)	145.25(14)
O(19)-Tb(3)-O(24)	79.64(13)	O(37)-Tb(4)-O(13)	147.95(15)
O(19)#1-Tb(3)-O(24)	137.20(13)	O(37)-Tb(4)-O(14)	89.17(14)
O(23)-Tb(3)-O(18)#1	147.74(14)	O(37)-Tb(4)-O(16)	80.01(14)
O(23)-Tb(3)-O(19)#1	155.75(14)	O(37)-Tb(4)-O(17)	82.30(16)
O(23)-Tb(3)-O(24)	50.94(15)	O(37)-Tb(4)-O(18)#1	131.00(14)
O(24)-Tb(3)-O(18)#1	135.00(13)	O(37)-Tb(4)-O(20)	63.14(13)
O(25)-Tb(3)-O(10)#1	68.93(13)	O(3)#1-Tb(5)-O(4)#1	51.52(16)
O(25)-Tb(3)-O(11)	148.30(13)	O(3)#1-Tb(5)-O(10)#1	86.90(14)
O(25)-Tb(3)-O(14)	78.32(13)	O(3)#1-Tb(5)-O(24)	106.42(14)

O(3)#1-Tb(5)-O(26)	136.12(14)
O(4)#1-Tb(5)-O(10)#1	111.28(15)
O(4)#1-Tb(5)-O(24)	78.93(16)
O(4)#1-Tb(5)-O(26)	146.72(15)
O(24)-Tb(5)-O(10)#1	62.20(13)
O(24)-Tb(5)-O(26)	115.76(13)
O(25)-Tb(5)-O(3)#1	150.28(15)
O(25)-Tb(5)-O(4)#1	144.14(15)
O(25)-Tb(5)-O(10)#1	64.27(13)
O(25)-Tb(5)-O(24)	67.60(13)
O(25)-Tb(5)-O(26)	51.38(13)
O(26)-Tb(5)-O(10)#1	101.87(13)
O(31)-Tb(5)-O(3)#1	82.11(16)
O(31)-Tb(5)-O(4)#1	85.28(17)
O(31)-Tb(5)-O(10)#1	147.45(15)
O(31)-Tb(5)-O(24)	150.35(16)
O(31)-Tb(5)-O(25)	118.06(14)
O(31)-Tb(5)-O(26)	67.44(15)
O(31)-Tb(5)-O(39)	79.69(15)
O(33)-Tb(5)-O(3)#1	126.32(17)
O(33)-Tb(5)-O(4)#1	77.55(16)
O(33)-Tb(5)-O(10)#1	132.21(14)
O(33)-Tb(5)-O(24)	74.73(15)
O(33)-Tb(5)-O(25)	81.45(16)
O(33)-Tb(5)-O(26)	78.15(15)
O(33)-Tb(5)-O(31)	77.46(16)
O(33)-Tb(5)-O(39)	150.96(14)
O(39)-Tb(5)-O(3)#1	67.07(16)
O(39)-Tb(5)-O(4)#1	118.17(16)
O(39)-Tb(5)-O(10)#1	67.81(13)
O(39)-Tb(5)-O(24)	129.92(14)
O(39)-Tb(5)-O(25)	93.86(15)
O(39)-Tb(5)-O(26)	76.67(14)
O(20)-Tb(6)-O(21)	62.97(14)
O(20)-Tb(6)-O(22)	80.86(15)
O(20)-Tb(6)-O(35)	75.50(15)
O(20)-Tb(6)-N(1)	155.54(17)
O(20)-Tb(6)-N(2)	124.65(16)
O(22)-Tb(6)-O(21)	49.03(15)
O(22)-Tb(6)-O(35)	136.63(16)
O(22)-Tb(6)-N(1)	79.76(18)
O(22)-Tb(6)-N(2)	93.83(19)
O(27)-Tb(6)-O(20)	90.91(14)
O(27)-Tb(6)-O(21)	121.41(15)
O(27)-Tb(6)-O(22)	77.12(17)
O(27)-Tb(6)-O(35)	67.58(15)
O(27)-Tb(6)-O(36)	94.50(17)
O(27)-Tb(6)-O(37)	146.97(14)
O(27)-Tb(6)-N(1)	70.31(17)
O(27)-Tb(6)-N(2)	141.81(16)
O(35)-Tb(6)-O(21)	136.93(13)
O(35)-Tb(6)-N(1)	109.53(17)
O(35)-Tb(6)-N(2)	129.51(18)
O(36)-Tb(6)-O(20)	120.04(16)
O(36)-Tb(6)-O(21)	144.06(17)
O(36)-Tb(6)-O(22)	157.97(16)
O(36)-Tb(6)-O(35)	52.68(16)
O(36)-Tb(6)-N(1)	78.23(18)
O(36)-Tb(6)-N(2)	80.1(2)
O(37)-Tb(6)-O(20)	64.99(13)
O(37)-Tb(6)-O(21)	69.03(14)
O(37)-Tb(6)-O(22)	117.78(16)
O(37)-Tb(6)-O(35)	83.99(15)
O(37)-Tb(6)-O(36)	80.20(16)
O(37)-Tb(6)-N(1)	138.29(17)
O(37)-Tb(6)-N(2)	69.81(16)
N(1)-Tb(6)-O(21)	112.97(16)
N(2)-Tb(6)-O(21)	72.31(17)
N(2)-Tb(6)-N(1)	71.58(19)
O(26)-Tb(7)-O(27)	80.62(14)
O(26)-Tb(7)-O(28)	77.36(14)
O(26)-Tb(7)-O(29)	148.11(17)
O(26)-Tb(7)-O(30)	147.13(17)
O(26)-Tb(7)-O(31)	64.88(14)
O(26)-Tb(7)-O(32)	113.98(15)
O(26)-Tb(7)-O(34)	90.55(15)
O(26)-Tb(7)-O(35)	72.06(14)
O(27)-Tb(7)-O(28)	62.04(15)
O(27)-Tb(7)-O(29)	74.88(16)

O(27)-Tb(7)-O(30)	88.73(17)
O(27)-Tb(7)-O(31)	132.84(15)
O(27)-Tb(7)-O(32)	138.90(16)
O(27)-Tb(7)-O(34)	143.69(16)
O(27)-Tb(7)-O(35)	67.39(15)
O(28)-Tb(7)-O(31)	79.09(14)
O(29)-Tb(7)-O(28)	73.27(17)
O(29)-Tb(7)-O(31)	120.01(17)
O(29)-Tb(7)-O(32)	74.70(17)
O(29)-Tb(7)-O(35)	115.25(17)
O(30)-Tb(7)-O(28)	124.38(16)
O(30)-Tb(7)-O(29)	52.97(18)
O(30)-Tb(7)-O(31)	137.27(18)
O(30)-Tb(7)-O(32)	94.44(19)
O(30)-Tb(7)-O(35)	75.13(17)
O(32)-Tb(7)-O(28)	83.09(17)
O(32)-Tb(7)-O(31)	49.60(14)
O(34)-Tb(7)-O(28)	149.85(15)
O(34)-Tb(7)-O(29)	121.23(17)
O(34)-Tb(7)-O(30)	79.81(17)
O(34)-Tb(7)-O(31)	70.78(15)
O(34)-Tb(7)-O(32)	76.74(18)
O(34)-Tb(7)-O(35)	76.36(16)
O(35)-Tb(7)-O(28)	123.95(16)
O(35)-Tb(7)-O(31)	124.39(14)
O(35)-Tb(7)-O(32)	152.47(17)