Supporting Information

Construction of a Luminescent Eleven-metal Zn(II)-Tb(III) Nanocluster for Rapid and Quantitative Time-gated Detection of Guanosine-5-monophoshpate and RNA

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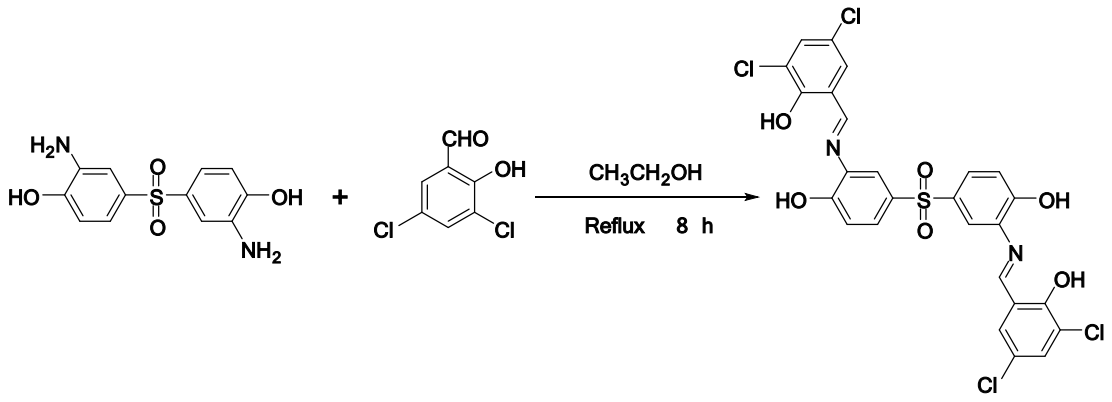
Contents

1. General Procedures

Metal salts and solvents were purchased from Meryer and used directly without further purification. All reactions were performed under dry oxygen-free dinitrogen atmospheres using standard Schlenk techniques. Physical measurements: NMR: AVANCE III AV500. 500 spectrometer at 298 K; Powder XRD: D8ADVANCE; IR: Nicolet IS10 spectrometer. Elemental analysis was performed on a EURO EA3000 with the solid sample after dried in the oven at 110°C for six hours. Melting points were obtained on an XT-4 electrothermal micromelting point apparatus. The thermogravimetric analyses were carried out on a TA Instruments Q600. Mass spectrometry (ESI-MS) was performed using a SCIEX Triple TOF 6600 system. Dynamic light scattering (DLS) spectrum was measured on a Malvern Zetasizer zs90. Field emission scanning electron microscopy (FESEM) images were recorded on a Nova NanoSEM 200 scanning electron microscope. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2100F transmission electron microscope with the sample after dried from the DMF solution. Absorption spectra were obtained on a UV-3600 spectrophotometer. Spectrophotometry analysis was carried out on a NanoDrop 2000 spectrophotometer.

2. Synthesis of the ligand H_4L



Scheme S1. Synthesis of the free ligand H_4L.

3,5-Dichloro-2-hydroxybenzaldehyde (20.0 mmol, 3.82 g) was dissolved in 30 mL EtOH, and a solution of 3,3'-diamino-4,4'-dihydroxydiphenyl sulfone (10.0 mmol, 2.80 g) in 30 mL EtOH was then added drop by drop. The resulting solution was stirred and heated under reflux for 8 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: 5.82 g (93%). EA: Calculated for $C_{26}H_{16}N_2O_6Cl_4S$ (%): C, 49.86; N, 4.47; H, 2.58. Found (%): C,49.67; N, 4.35; H, 2.64. ^{1}H NMR (DMSO-d_6, 500 MHz): 14.75(s, 2H), 11.23(s, 2H), 9.17(s, 2H), 8.08(d, J=2.2 Hz, 2H), 7.80 – 7.73(m, 4H), 7.71(d, J=2.6 Hz, 2H), 7.16(d, J=8.5 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 162.06, 157.04, 155.39, 135.55, 132.62, 132.43, 130.63, 128.05, 122.14, 121.44, 120.25, 118.95, 117.16. ESI-MS in DMF: 624 $[M+1]^+$. IR (KBr, cm^{-1}): 1633(s), 1508(s), 1439(w), 1366(w), 1293(m), 1216(s), 1143(s), 1085(m), 1026(w), 858(s), 826(m), 758(m), 700(s), 608(s), 513(s).

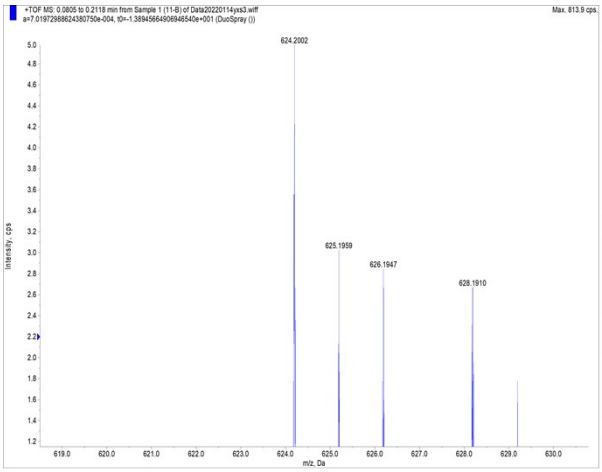


Figure S1. The mass spectra of the free H_4L ligand in DMF.

3. ^{1}H NMR and ^{13}C NMR spectra of the ligand H_4L

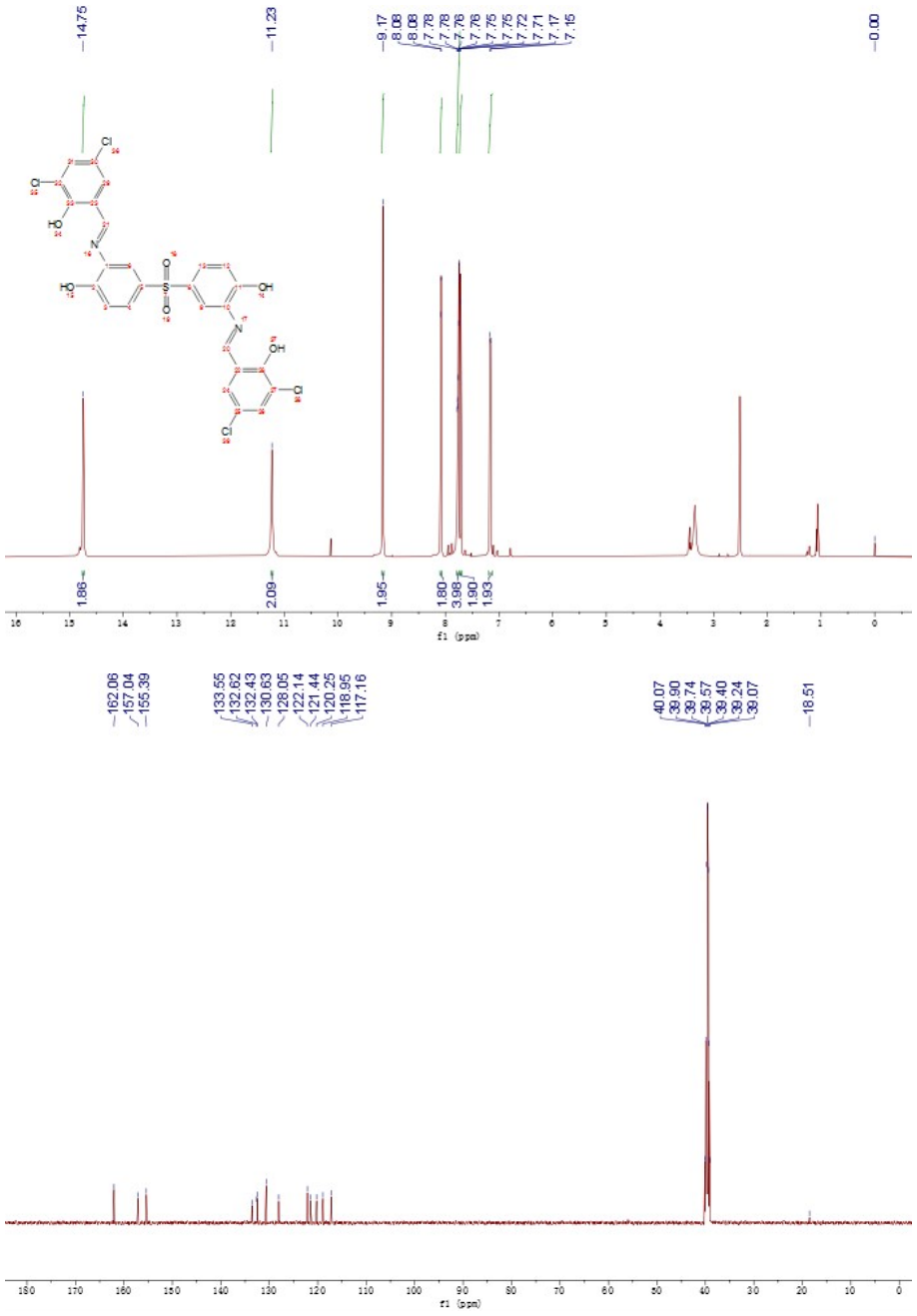


Figure S2. ^{1}H NMR and ^{13}C NMR spectra of the ligand H_4L in DMSO.

4. IR spectra of the ligand H_4L and 1

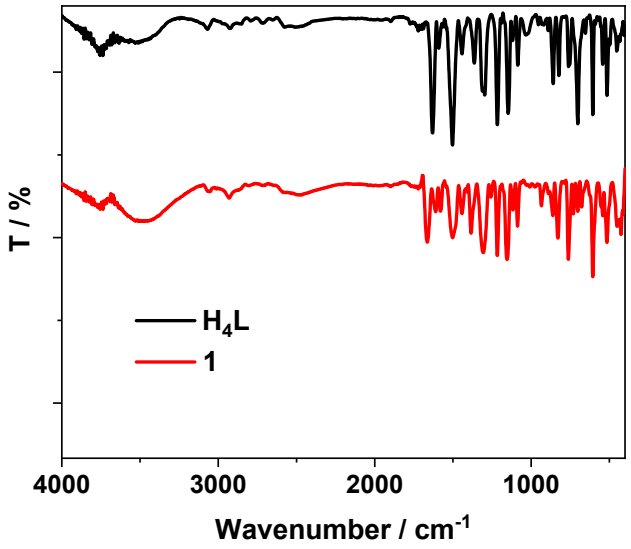


Figure S3. IR spectra of the ligand H_4L and **1**.

5. The coordination geometry of lanthanide ion

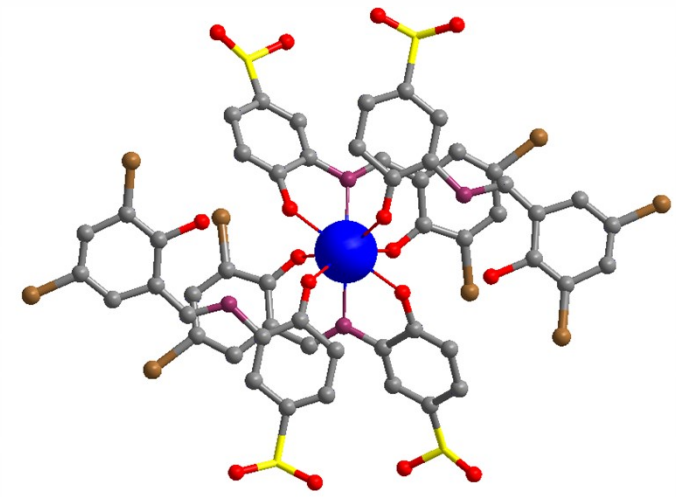
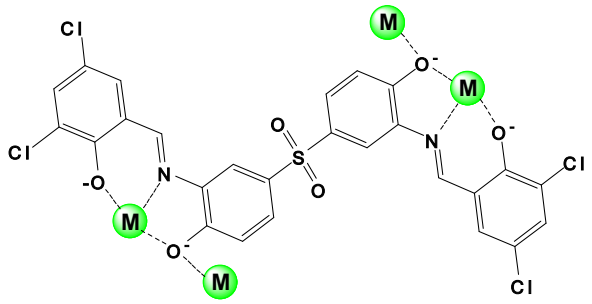


Figure S4. The eight-coordinated mode of Tb(III) in **1**.

6. The coordination mode of Schiff base ligand



M = Zn(II) or Tb(III)

Scheme S2. The coordination mode of Schiff base ligand in **1**.

7. The thermogravimetric analysis of 1

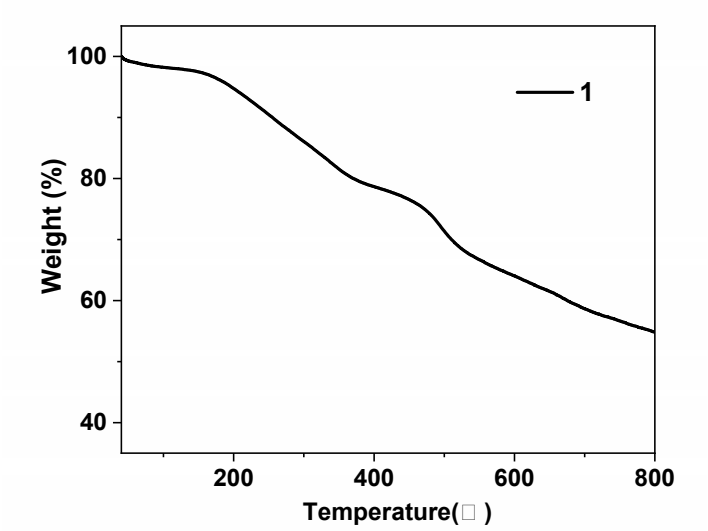


Figure S5. The thermogravimetric analysis of **1**.

8. Excitation and emission spectra of the free ligand H_4L and 1

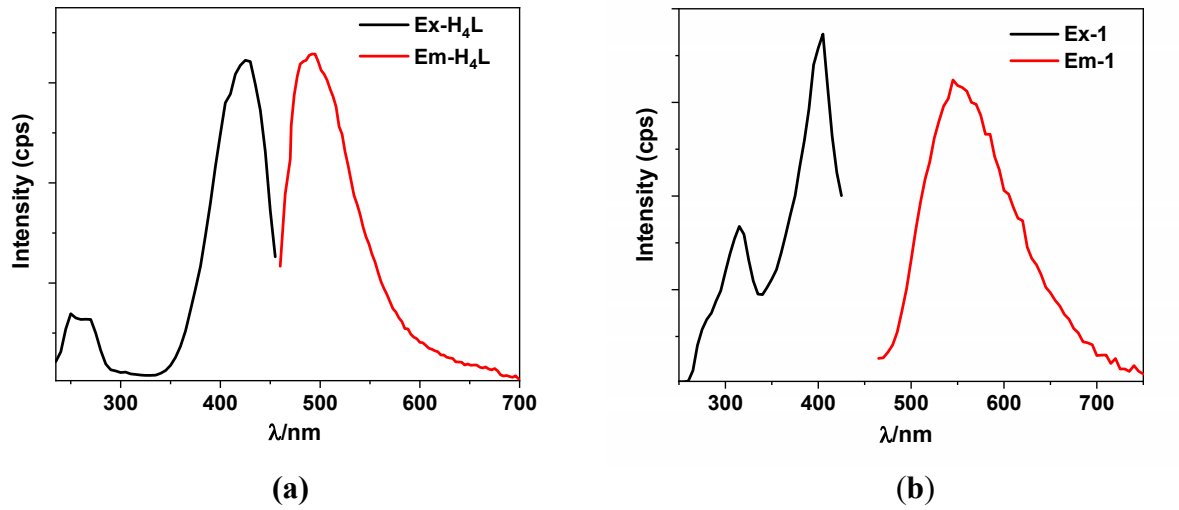


Figure S6. (**a**) The excitation (λ_{em} = 510 nm) and emission (λ_{ex} = 285 nm) spectra of the free ligand H_4L (10 μM) in DMF; (**b**) The excitation (λ_{em} = 550 nm) and emission (λ_{ex} = 285 nm) spectra of **1** (10 μM) in DMF.

9. The emission spectrum of GMP

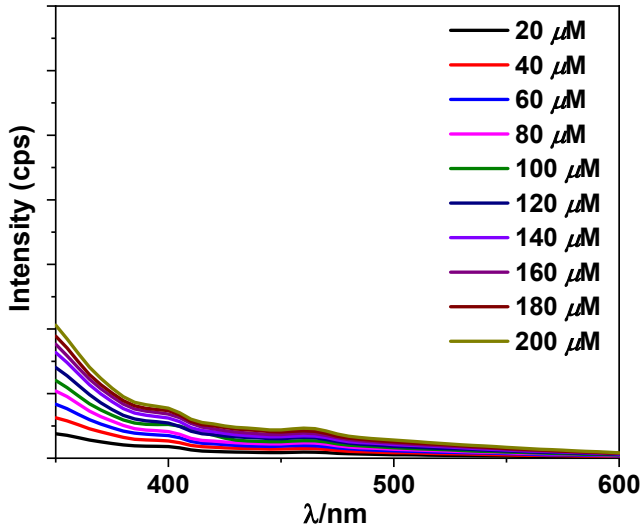


Figure S7. The emission spectra of GMP with different concentrations in DMF. (λ_{ex} = 285 nm)

10. The emission lifetimes of 1

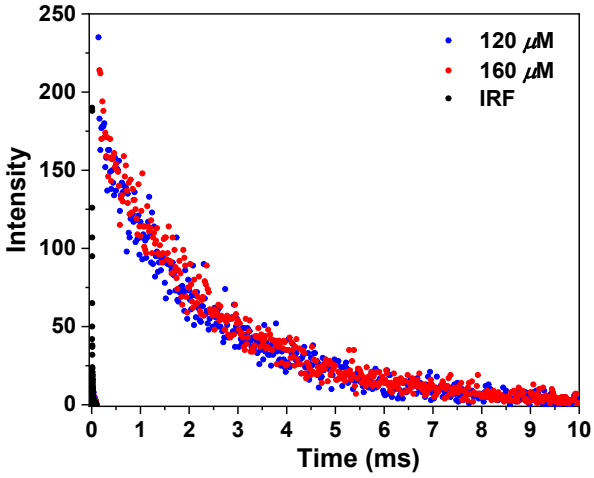
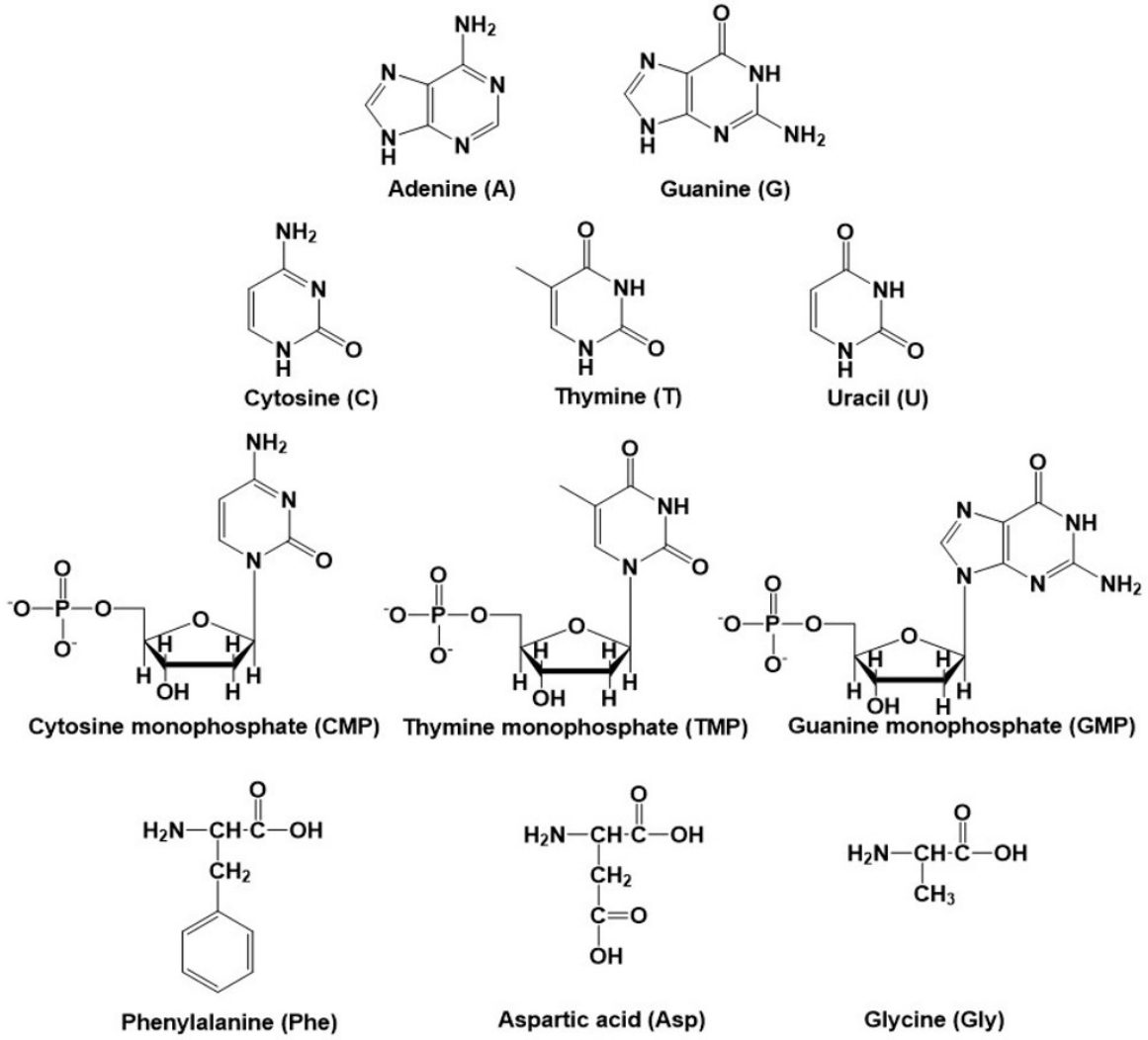


Figure S8. The emission lifetimes of **1** (10 μM) at 545 nm with the addition of GMP (λ_{ex} = 285 nm). The instrument response function (IRF) is obtained from 30% of silicon dioxide in H_2O with $\lambda_{ex} = \lambda_{em}$ = 285 nm.

11. Chemical structures of nitrogenous base, nucleotide and amino acids



Scheme S3. Chemical structures of nitrogenous base, nucleotide and amino acids.

12. Powder XRD patterns of 1

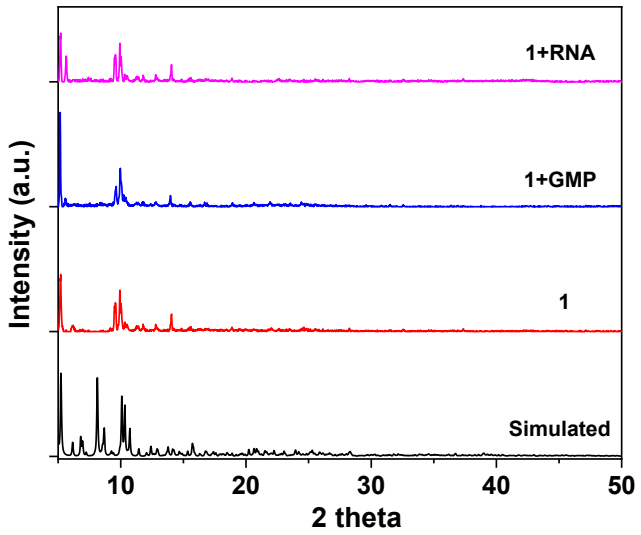


Figure S9. Powder XRD patterns of **1** before and after treated by GMP and RNA.

13. The emission spectra of the free Tb(III) with the addition of GMP

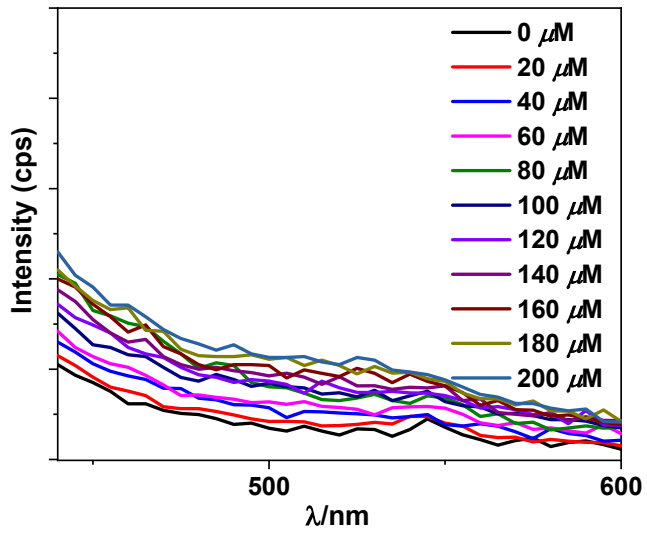


Figure S10. The emission spectra of $Tb(OAc)_3$ (10 μM) with the addition of GMP recorded by normal mode in DMF. (λ_{ex} = 285 nm)

14. UV-vis absorption spectra of the ligand H_4L and 1

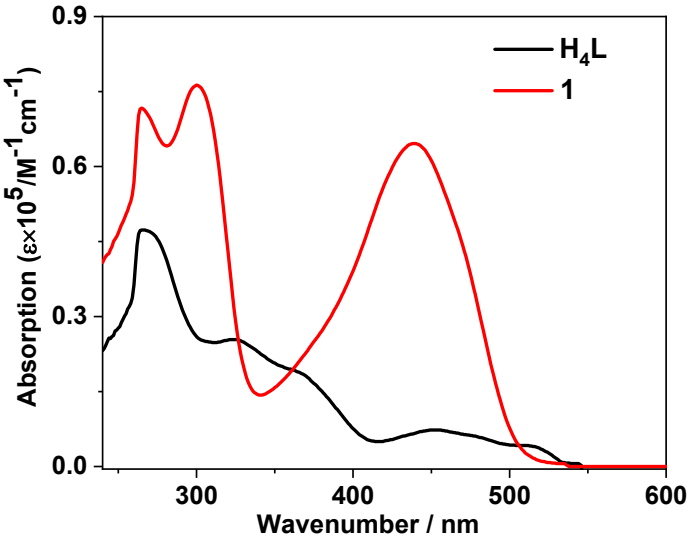


Figure S11. UV-vis absorption spectra of the free ligand H_4L and **1** in DMF. (c = 10 μM)

15. The emission spectrum of GMP at 77 K

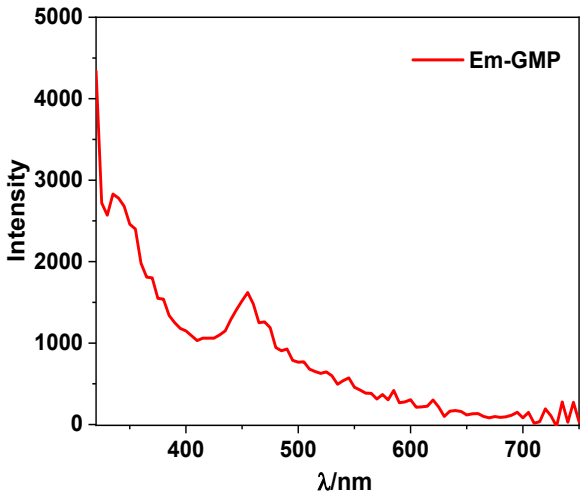
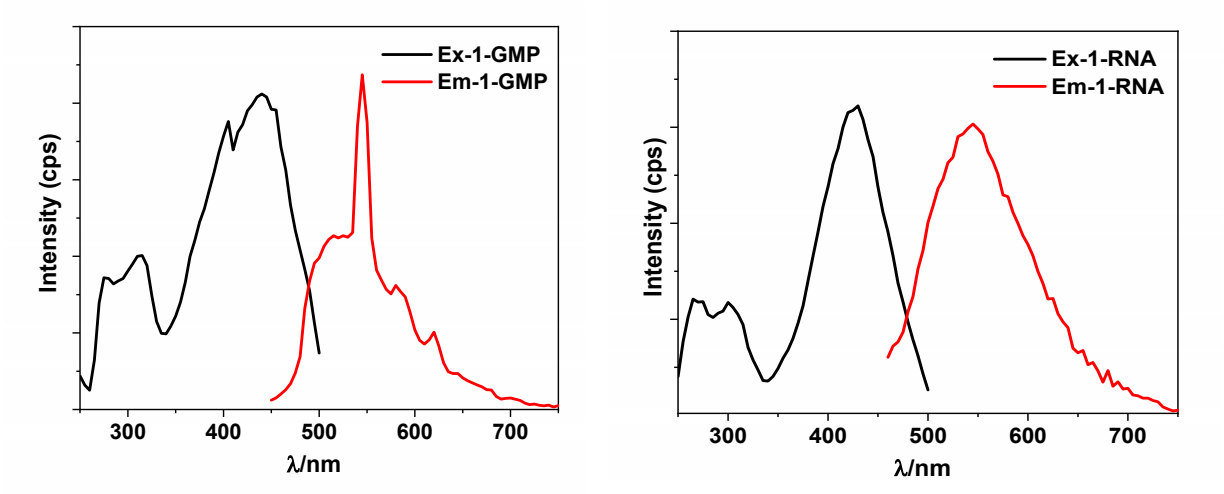


Figure S12. The emission spectrum of GMP in DMF at 77 K.

16. Excitation and emission spectra of 1 with the addition of GMP and RNA



(**a**) (**b**)

Figure S13. Excitation (λ_{em} = 545 nm) and emission (λ_{ex} = 285 nm) spectra of **1** (10 μM) with the addition of GMP (100 μM, **a**) and RNA (6.0 ng/μL, **b**) in DMF.

17. UV-vis absorption spectra of 1, GMP and RNA

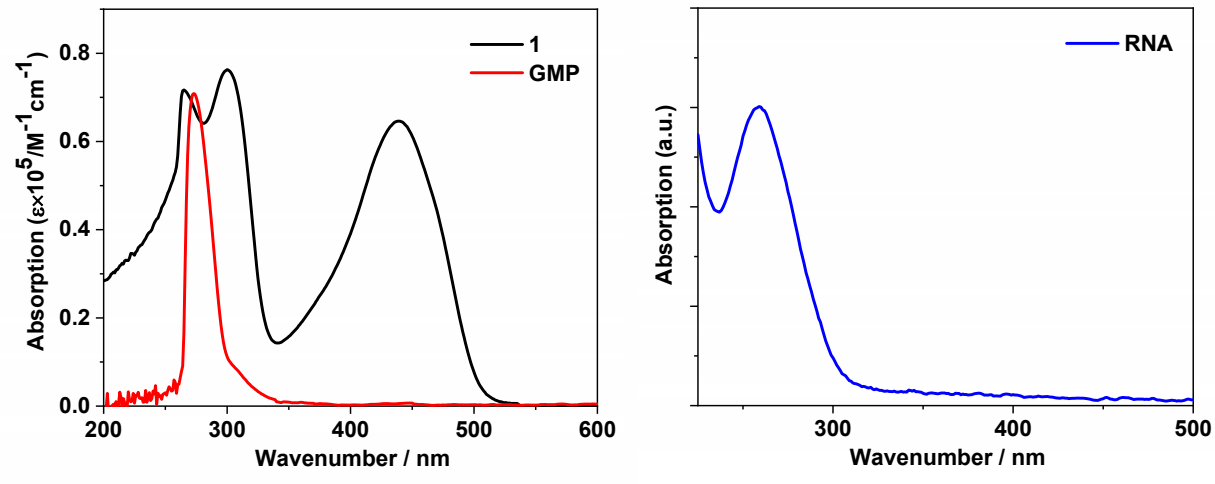


Figure S14. The UV-vis absorption spectra of **1**, GMP and RNA in DMF.

18. The emission spectra of 1 with the addition of GMP

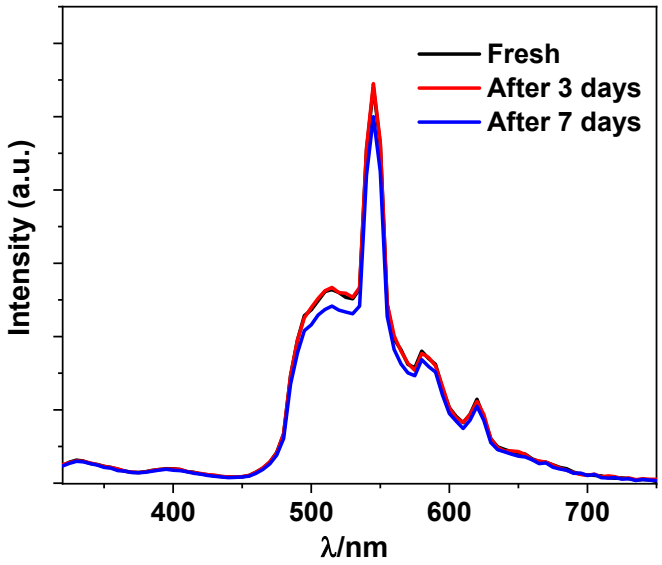


Figure S15. The emission spectra of **1** (10 μM) measured in different times with the addition of GMP (100 μM) in DMF.

19. X-Ray Crystallography

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

Zn(1)-O(31)	1.849(10)	O(6)-Zn(1)-O(1)#1	77.5(4)
Zn(1)-O(7)	2.001(12)	N(1)#1-Zn(1)-O(1)#1	76.3(4)
Zn(1)-O(6)	2.098(10)	O(32)-Zn(2)-O(5)	98.7(7)
Zn(1)-N(1)#1	2.086(15)	O(32)-Zn(2)-O(13)	100.5(6)
Zn(1)-O(1)#1	2.144(9)	O(5)-Zn(2)-O(13)	104.5(6)
Zn(2)-O(32)	1.888(9)	O(32)-Zn(2)-N(2)	108.9(7)
Zn(2)-O(5)	1.946(14)	O(5)-Zn(2)-N(2)	89.0(6)
Zn(2)-O(13)	2.042(12)	O(13)-Zn(2)-N(2)	145.3(5)
Zn(2)-N(2)	2.092(14)	O(32)-Zn(2)-O(4)	102.5(6)
Zn(2)-O(4)	2.140(11)	O(5)-Zn(2)-O(4)	158.0(6)
Zn(3)-O(11)	1.912(10)	O(13)-Zn(2)-O(4)	77.2(5)
Zn(3)-O(30)	1.990(10)	N(2)-Zn(2)-O(4)	78.8(5)
Zn(3)-O(28)	2.039(12)	O(11)-Zn(3)-O(30)	105.2(4)
Zn(3)-O(10)	2.075(9)	O(11)-Zn(3)-O(28)	99.8(5)
Zn(3)-N(4)	2.109(11)	O(30)-Zn(3)-O(28)	104.8(4)
Tb(1)-O(18)#1	2.218(10)	O(11)-Zn(3)-O(10)	163.6(4)
Tb(1)-O(18)	2.218(10)	O(30)-Zn(3)-O(10)	78.0(4)
Tb(1)-O(1)	2.327(10)	O(28)-Zn(3)-O(10)	94.8(4)
Tb(1)-O(1)#1	2.327(10)	O(11)-Zn(3)-N(4)	90.4(4)
Tb(1)-O(6)	2.428(10)	O(30)-Zn(3)-N(4)	141.8(4)
Tb(1)-O(6)#1	2.428(9)	O(28)-Zn(3)-N(4)	106.5(5)
Tb(1)-N(3)#1	2.455(13)	O(10)-Zn(3)-N(4)	78.1(4)
Tb(1)-N(3)	2.455(13)	O(18)#1-Tb(1)-O(18)	84.6(5)
Tb(2)-O(17)	2.221(12)	O(18)#1-Tb(1)-O(1)	101.0(4)
Tb(2)-O(29)	2.295(13)	O(18)-Tb(1)-O(1)	156.9(3)
Tb(2)-O(10)	2.304(10)	O(18)#1-Tb(1)-O(1)#1	156.9(3)
Tb(2)-O(30)	2.344(10)	O(18)-Tb(1)-O(1)#1	101.1(4)
Tb(2)-O(26)	2.393(12)	O(1)-Tb(1)-O(1)#1	82.6(5)
Tb(2)-N(6)	2.413(12)	O(18)#1-Tb(1)-O(6)	135.1(4)
Tb(2)-O(22)	2.433(14)	O(18)-Tb(1)-O(6)	77.7(3)
Tb(2)-O(23)	2.477(12)	O(1)-Tb(1)-O(6)	82.8(3)
Tb(2)-N(8)	2.83(2)	O(1)#1-Tb(1)-O(6)	67.8(3)
Tb(3)-O(12)	2.175(11)	O(18)#1-Tb(1)-O(6)#1	77.7(3)
Tb(3)-O(13)	2.289(10)	O(18)-Tb(1)-O(6)#1	135.1(4)
Tb(3)-O(4)	2.313(12)	O(1)-Tb(1)-O(6)#1	67.8(3)
Tb(3)-O(27)	2.324(12)	O(1)#1-Tb(1)-O(6)#1	82.8(3)
Tb(3)-O(19)	2.377(13)	O(6)-Tb(1)-O(6)#1	140.9(5)
Tb(3)-O(25)	2.396(15)	O(18)#1-Tb(1)-N(3)#1	80.2(4)
Tb(3)-N(5)	2.480(13)	O(18)-Tb(1)-N(3)#1	69.6(4)
Tb(3)-O(20)	2.493(14)	O(1)-Tb(1)-N(3)#1	133.3(4)
Tb(3)-N(7)	2.88(2)	O(1)#1-Tb(1)-N(3)#1	80.9(4)
O(31)-Zn(1)-O(7)	104.8(7)	O(6)-Tb(1)-N(3)#1	128.8(3)
O(31)-Zn(1)-O(6)	104.4(7)	O(6)#1-Tb(1)-N(3)#1	66.9(4)
O(7)-Zn(1)-O(6)	100.5(5)	O(18)#1-Tb(1)-N(3)	69.6(4)
O(31)-Zn(1)-N(1)#1	124.7(7)	O(18)-Tb(1)-N(3)	80.2(4)
O(7)-Zn(1)-N(1)#1	88.2(5)	O(1)-Tb(1)-N(3)	80.9(4)
O(6)-Zn(1)-N(1)#1	126.0(5)	O(1)#1-Tb(1)-N(3)	133.3(4)
O(31)-Zn(1)-O(1)#1	96.4(6)	O(6)-Tb(1)-N(3)	66.9(4)
O(7)-Zn(1)-O(1)#1	158.4(5)	O(6)#1-Tb(1)-N(3)	128.8(3)

N(3)#1-Tb(1)-N(3)	138.9(6)	O(12)-Tb(3)-O(13)	141.8(4)
O(17)-Tb(2)-O(29)	78.7(4)	O(12)-Tb(3)-O(4)	148.6(4)
O(17)-Tb(2)-O(10)	151.1(4)	O(13)-Tb(3)-O(4)	69.1(4)
O(29)-Tb(2)-O(10)	81.1(4)	O(12)-Tb(3)-O(27)	79.0(4)
O(17)-Tb(2)-O(30)	140.0(4)	O(13)-Tb(3)-O(27)	131.4(4)
O(29)-Tb(2)-O(30)	138.0(4)	O(4)-Tb(3)-O(27)	78.1(4)
O(10)-Tb(2)-O(30)	66.8(3)	O(12)-Tb(3)-O(19)	95.5(4)
O(17)-Tb(2)-O(26)	99.8(4)	O(13)-Tb(3)-O(19)	81.5(4)
O(29)-Tb(2)-O(26)	77.6(4)	O(4)-Tb(3)-O(19)	83.0(4)
O(10)-Tb(2)-O(26)	95.8(4)	O(27)-Tb(3)-O(19)	129.6(5)
O(30)-Tb(2)-O(26)	79.4(4)	O(12)-Tb(3)-O(25)	93.2(5)
O(17)-Tb(2)-N(6)	73.0(4)	O(13)-Tb(3)-O(25)	74.9(5)
O(29)-Tb(2)-N(6)	138.3(5)	O(4)-Tb(3)-O(25)	103.0(5)
O(10)-Tb(2)-N(6)	134.5(4)	O(27)-Tb(3)-O(25)	78.7(5)
O(30)-Tb(2)-N(6)	67.8(4)	O(19)-Tb(3)-O(25)	151.4(5)
O(26)-Tb(2)-N(6)	77.9(4)	O(12)-Tb(3)-N(5)	74.0(4)
O(17)-Tb(2)-O(22)	85.9(5)	O(13)-Tb(3)-N(5)	68.4(4)
O(29)-Tb(2)-O(22)	131.4(5)	O(4)-Tb(3)-N(5)	134.5(4)
O(10)-Tb(2)-O(22)	92.2(4)	O(27)-Tb(3)-N(5)	145.1(4)
O(30)-Tb(2)-O(22)	78.2(4)	O(19)-Tb(3)-N(5)	75.3(5)
O(26)-Tb(2)-O(22)	150.9(5)	O(25)-Tb(3)-N(5)	81.1(5)
N(6)-Tb(2)-O(22)	76.6(5)	O(12)-Tb(3)-O(20)	75.1(5)
O(17)-Tb(2)-O(23)	79.9(4)	O(13)-Tb(3)-O(20)	125.7(4)
O(29)-Tb(2)-O(23)	79.9(4)	O(4)-Tb(3)-O(20)	80.2(4)
O(10)-Tb(2)-O(23)	76.4(4)	O(27)-Tb(3)-O(20)	80.4(5)
O(30)-Tb(2)-O(23)	115.7(4)	O(19)-Tb(3)-O(20)	50.4(4)
O(26)-Tb(2)-O(23)	157.0(4)	O(25)-Tb(3)-O(20)	157.7(5)
N(6)-Tb(2)-O(23)	123.0(4)	N(5)-Tb(3)-O(20)	112.7(4)
O(22)-Tb(2)-O(23)	52.0(4)	O(12)-Tb(3)-N(7)	84.5(4)
O(17)-Tb(2)-N(8)	81.2(5)	O(13)-Tb(3)-N(7)	103.9(5)
O(29)-Tb(2)-N(8)	103.1(5)	O(4)-Tb(3)-N(7)	81.4(4)
O(10)-Tb(2)-N(8)	83.5(4)	O(27)-Tb(3)-N(7)	105.7(5)
O(30)-Tb(2)-N(8)	99.6(5)	O(19)-Tb(3)-N(7)	24.8(4)
O(26)-Tb(2)-N(8)	178.9(5)	O(25)-Tb(3)-N(7)	174.4(5)
N(6)-Tb(2)-N(8)	102.0(5)	N(5)-Tb(3)-N(7)	93.4(5)
O(22)-Tb(2)-N(8)	28.5(5)	O(20)-Tb(3)-N(7)	25.6(4)
O(23)-Tb(2)-N(8)	23.5(4)		