Electronic Supplementary Material (ESI) for CrystEngComm.

Two Lanthanide Metal−Organic Frameworks as Sensitive Luminescence Sensor for the detection of Cr2+ and Cr2O72- in aqueous solutions

X.H. Huang,[a,b,c] L. Shi,[a] Y.P. Chen,[*a] L.H. Liu,[a] Y.Q. Sun[a] and S.M. Ying[b,c]

[a] *College of Chemistry, Fuzhou University, Fuzhou 350108, P. R. China*

[b] *College of Chemistry and Materials，Ningde Normal University, Ningde 352100, P. R. China*

[c] *Fujian Provincial Key Laboratory of Featured Materials in Biochemical Industry, Ningde Normal University, Ningde 352100, P. R. China*

E-mail: ypchen007@sina.com

Contents

1. IR spectra of complexes 1-2 and related ligands

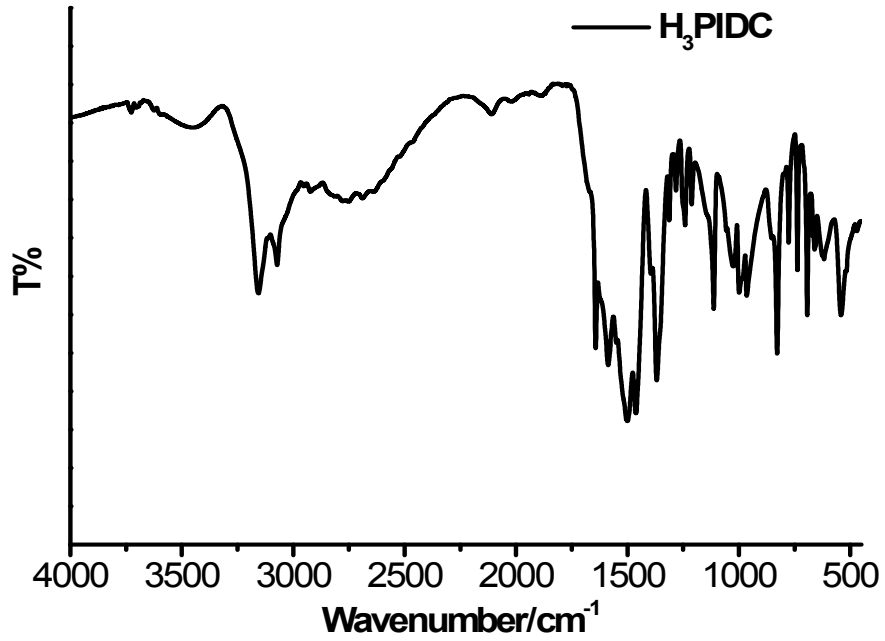

Fig. S1 IR spectrum of H_3PIDC ligand

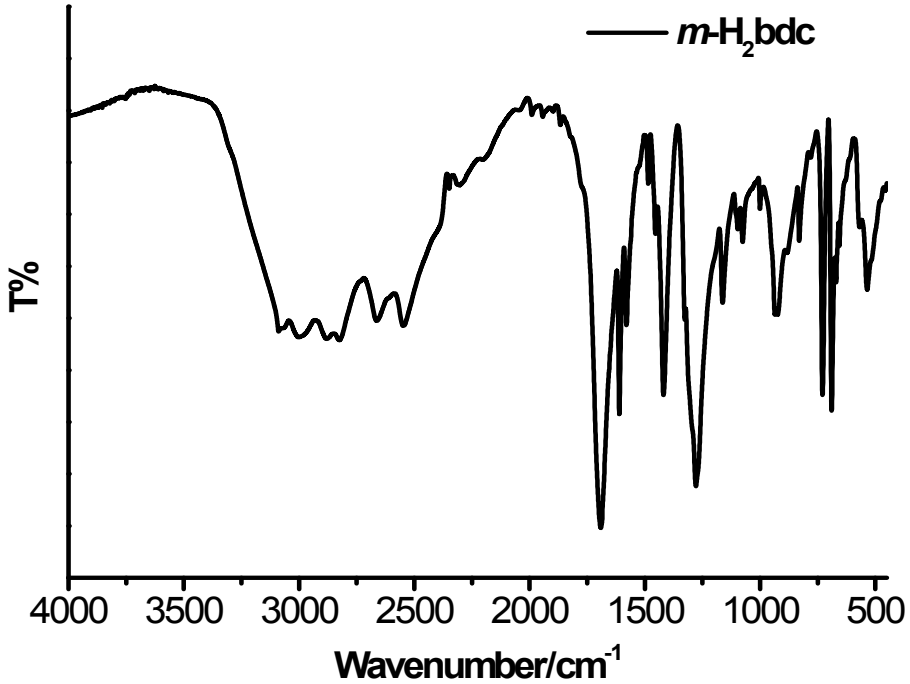

Fig. S2 IR spectrum of *m*-H_2bdc ligand

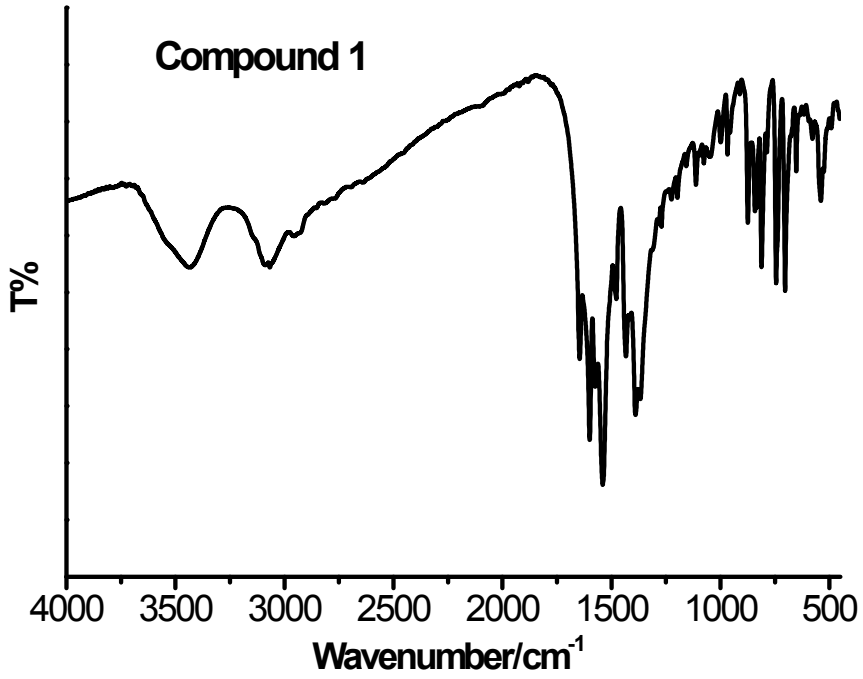

Fig. S3 IR spectra of Compound **1**

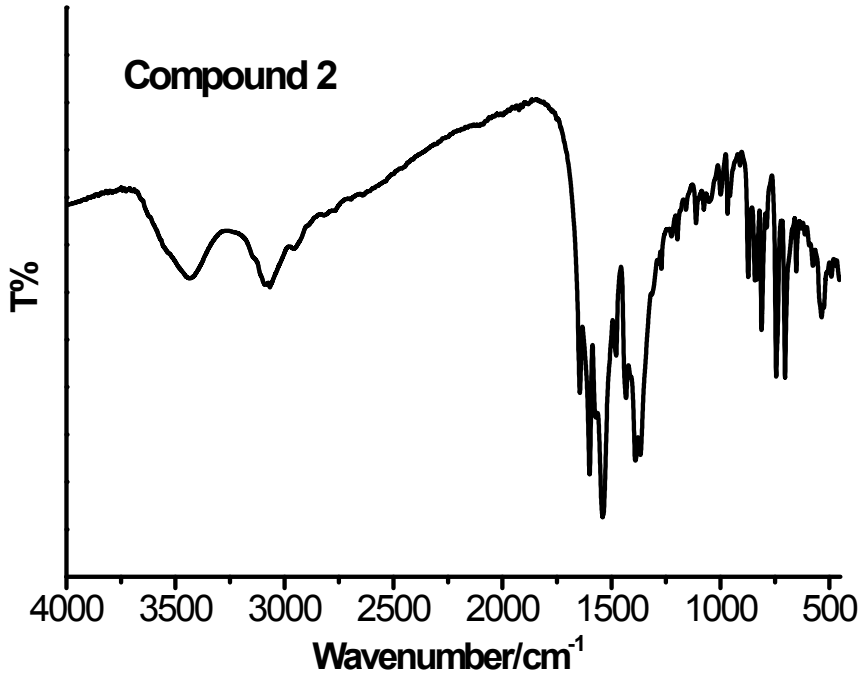

Fig. S4 IR spectra of Compound **2**

2. Selected bond lengths (Å) and angles (deg) for compound 2

Table S1 Select Bond lengths [Å] and angles [°] for **2**

Bond	Dist[Å]	Bond	Dist[Å]
Tb(1)-O(7)#1	2.277(3)	Tb(1)-O(5)	2.378(3)
Tb(1)-O(8)#2	2.317(3)	Tb(1)-O(4)	2.432(3)
Tb(1)-O(2)	2.336(3)	Tb(1)-O(3)#3	2.479(3)
Tb(1)-O(6)#3	2.373(3)	Tb(1)-O(4)#3	2.577(3)

Bond	Angles(°)	Bond	Angles(°)
O(7)#1-Tb(1)-O(8)#2	155.15(13)	O(5)-Tb(1)-O(4)	70.96(12)
O(7)#1-Tb(1)-O(2)	90.91(13)	O(7)#1-Tb(1)-O(3)#3	69.63(12)
O(8)#2-Tb(1)-O(2)	85.29(12)	O(8)#2-Tb(1)-O(3)#3	125.75(12)
O(7)#1-Tb(1)-O(6)#3	87.32(12)	O(2)-Tb(1)-O(3)#3	141.79(12)
O(8)#2-Tb(1)-O(6)#3	114.69(13)	O(6)#3-Tb(1)-O(3)#3	73.79(13)
O(2)-Tb(1)-O(6)#3	72.71(13)	O(5)-Tb(1)-O(3)#3	72.98(12)
O(7)#1-Tb(1)-O(5)	89.20(12)	O(4)-Tb(1)-O(3)#3	127.84(11)
O(8)#2-Tb(1)-O(5)	78.92(12)	O(7)#1-Tb(1)-O(4)#3	120.22(11)
O(2)-Tb(1)-O(5)	141.55(13)	O(8)#2-Tb(1)-O(4)#3	79.66(11)
O(6)#3-Tb(1)-O(5)	145.64(13)	O(2)-Tb(1)-O(4)#3	130.48(13)
O(7)#1-Tb(1)-O(4)	73.44(11)	O(6)#3-Tb(1)-O(4)#3	71.60(11)
O(8)#2-Tb(1)-O(4)	82.03(12)	O(5)-Tb(1)-O(4)#3	80.87(12)
O(2)-Tb(1)-O(4)	72.27(12)	O(4)-Tb(1)-O(4)#3	148.83(3)
O(6)#3-Tb(1)-O(4)	139.44(12)	O(3)#3-Tb(1)-O(4)#3	51.01(11)

3. H-Bonds of compound 2 and hydrogen bonds in compound 2

Table. S2 H-Bonds of compound **2**

Donor	H....Acceptor	D - H (Å)	H...A(Å)	D...A(Å)	D - H…A(°)
N2	H2 O1	0.86	1.92	2.772(8)	169
C3	H3 O1	0.93	2.33	3.113(10)	141

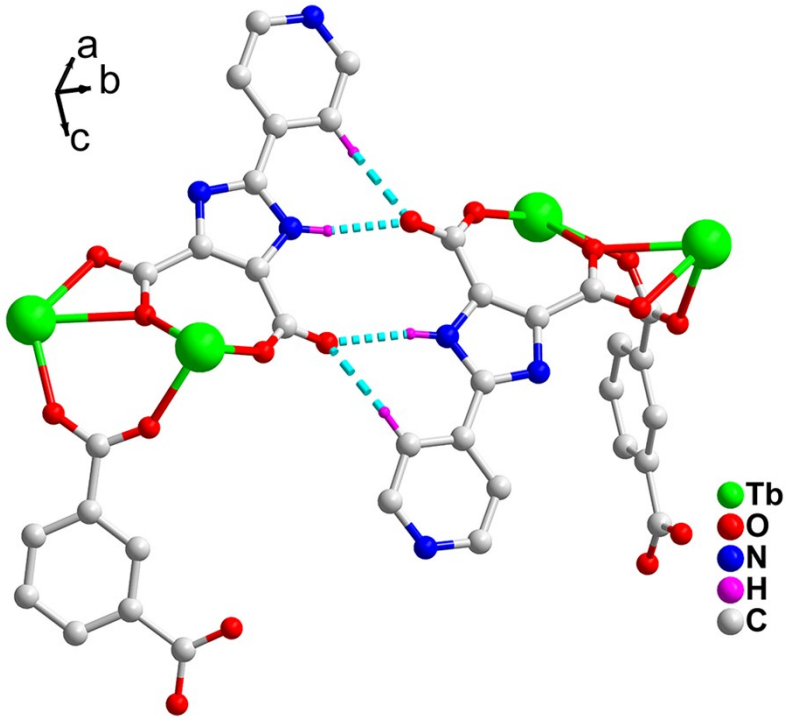

Fig. S5 C-H…O hydrogen bonds between pyridyl groups and carboxylate groups, and N-H…O hydrogen bonds between imidazole groups and carboxylate groups in compound **2.**

4. Powder X-ray diffraction patterns of compounds 1 and 2

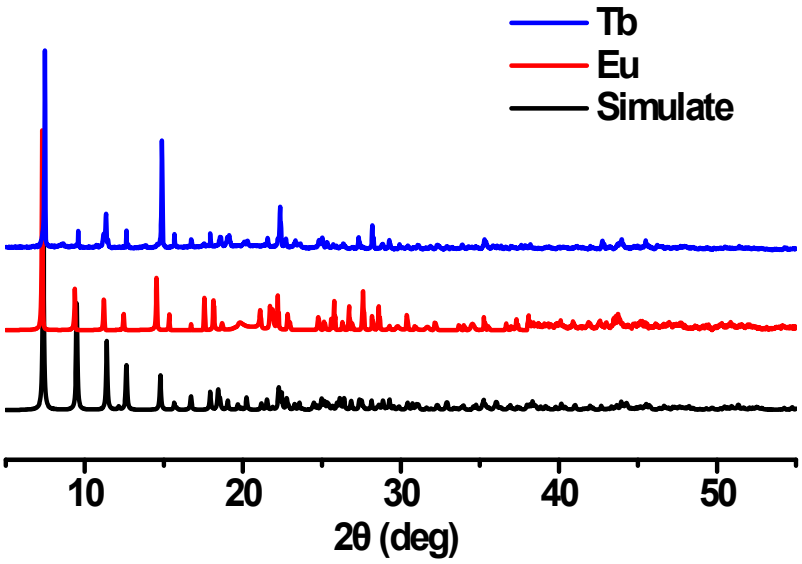

Fig. S6 Powder XRD patterns of **1** (Eu) and **2** (Tb)

5. The TGA diagrams of compounds 1 and 2

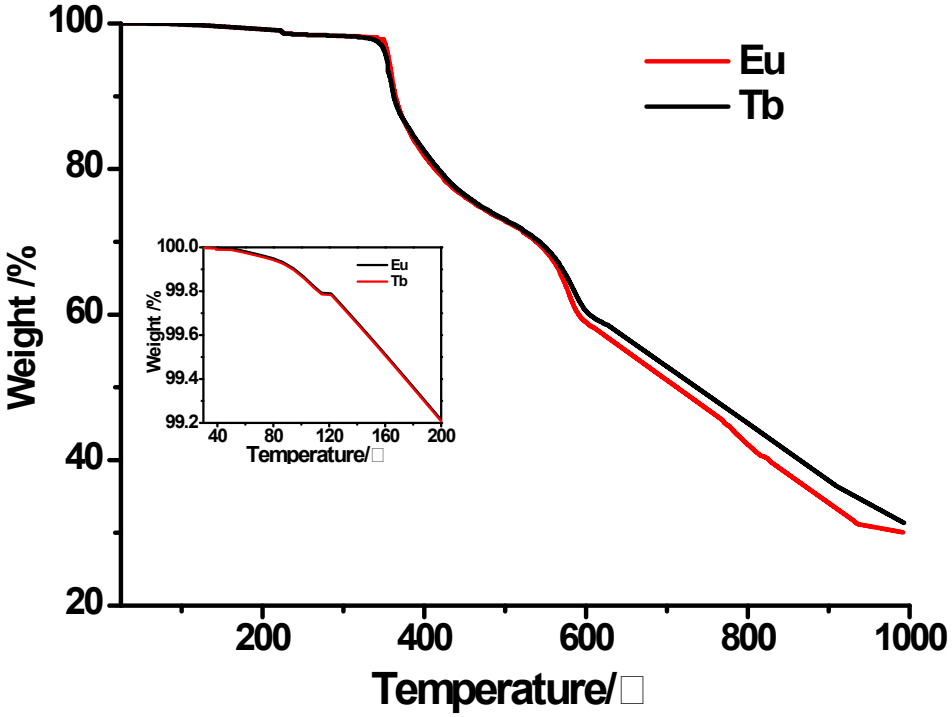

Fig. S7 The TGA diagrams of compounds **1** and **2**

6. Solid-state photoluminescent spectra of 1-2 and related ligands

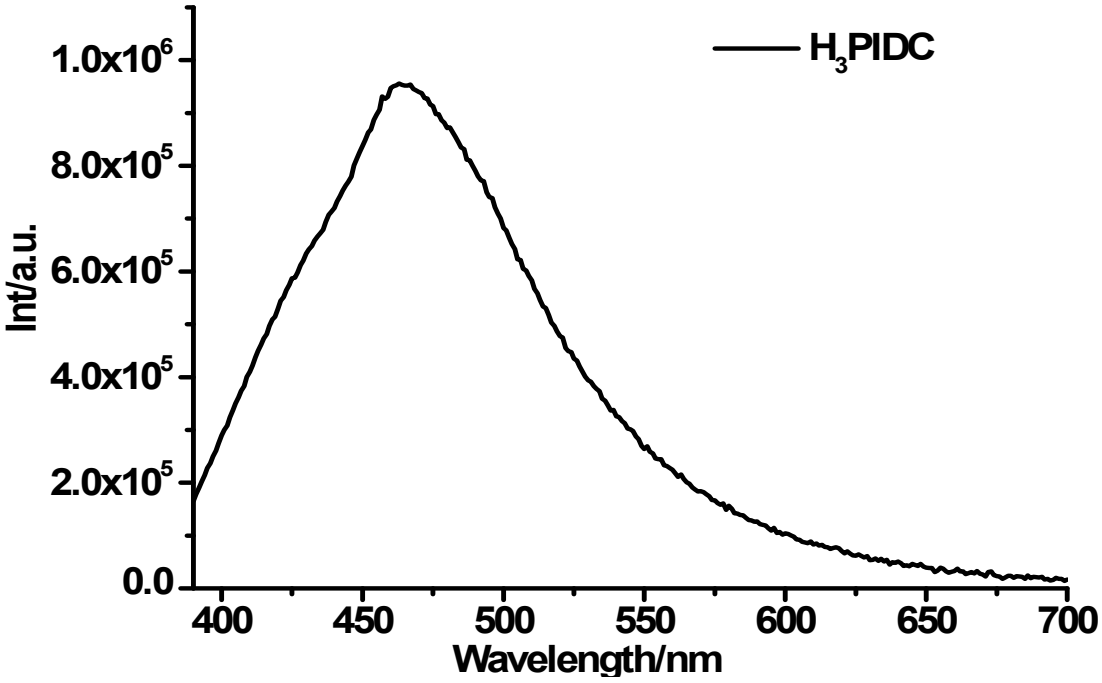

Fig. S8 Photoluminescent sprctra of H_3PIDC ligand (λ_{ex}=364nm)

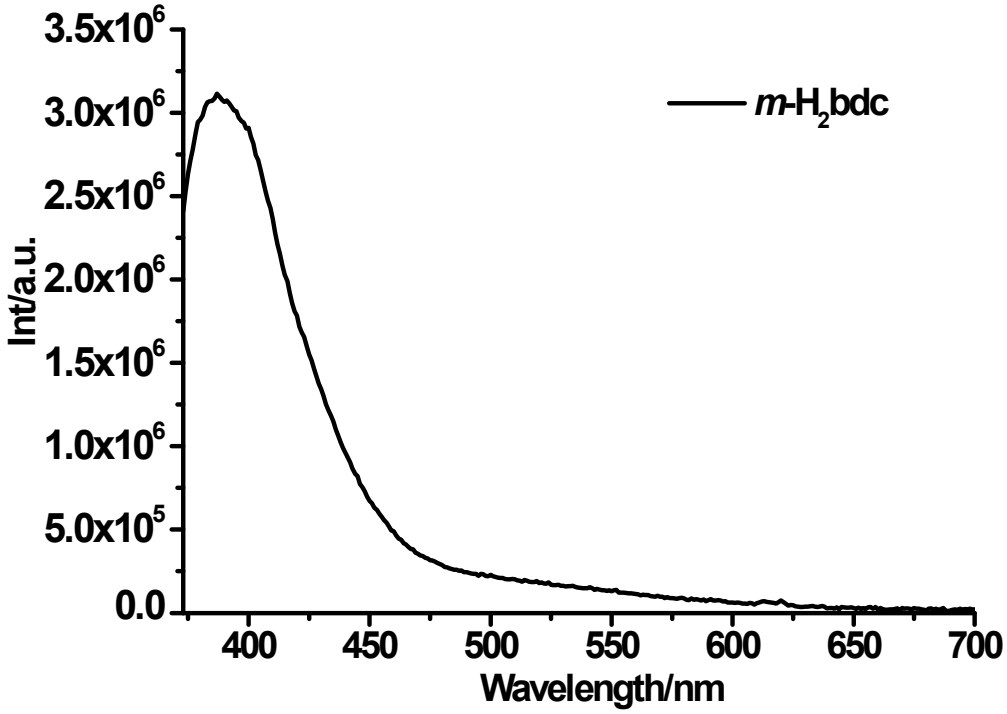

Fig. S9 Photoluminescent sprctra of H_2bdc ligand (λ_{ex}=354nm)

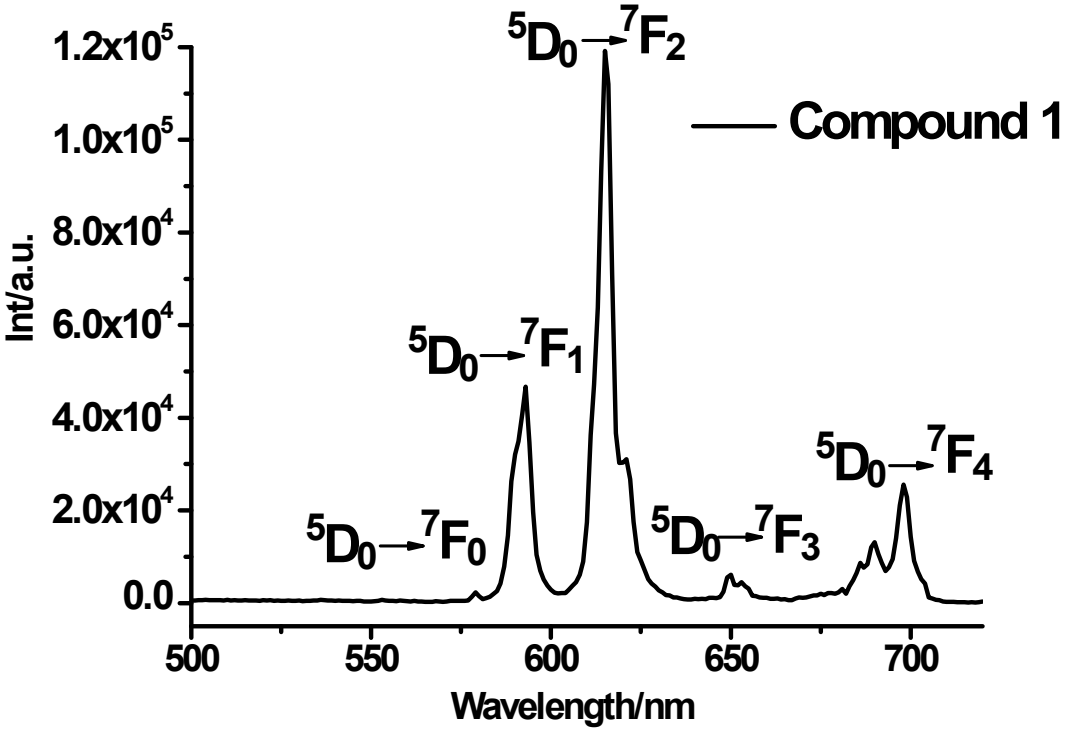

Fig. S10 Emission spectra of **1** (excitation at 370 nm) in the solid state at room temperature.

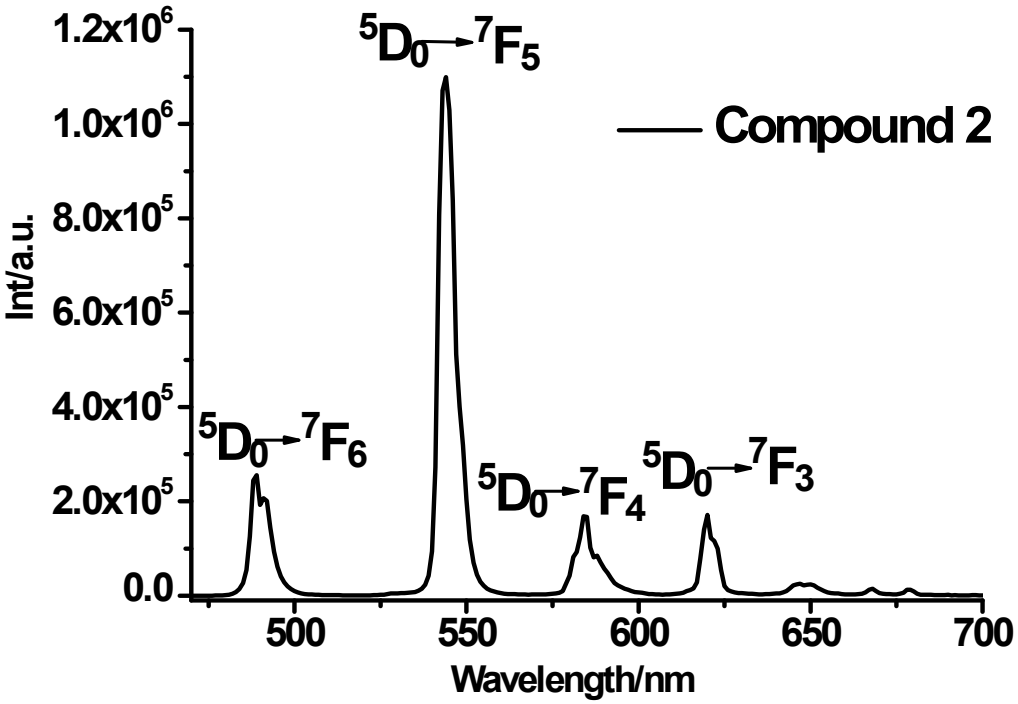

Fig. S11 Emission spectra of **2** (excitation at 370 nm) in the solid state at room temperature.

7. Powder X-ray diffraction patterns of compounds 1 and 2 after immersed in Cr^{2+} and $Cr_2O_7^{2-}$aqueous solutions

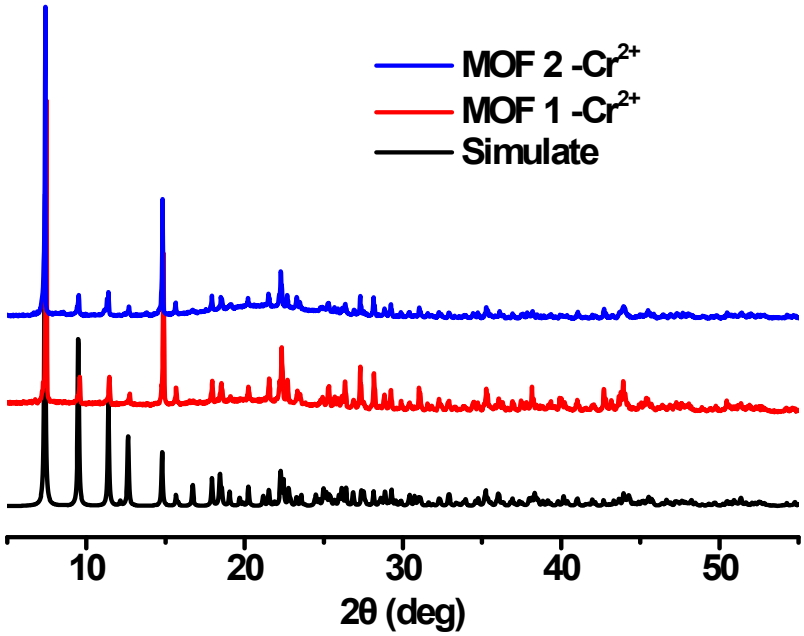

Fig. S12 The PXRD of compounds **1** and **2** after immersed in Cr^{2+}aqueous solutions for 3 hours

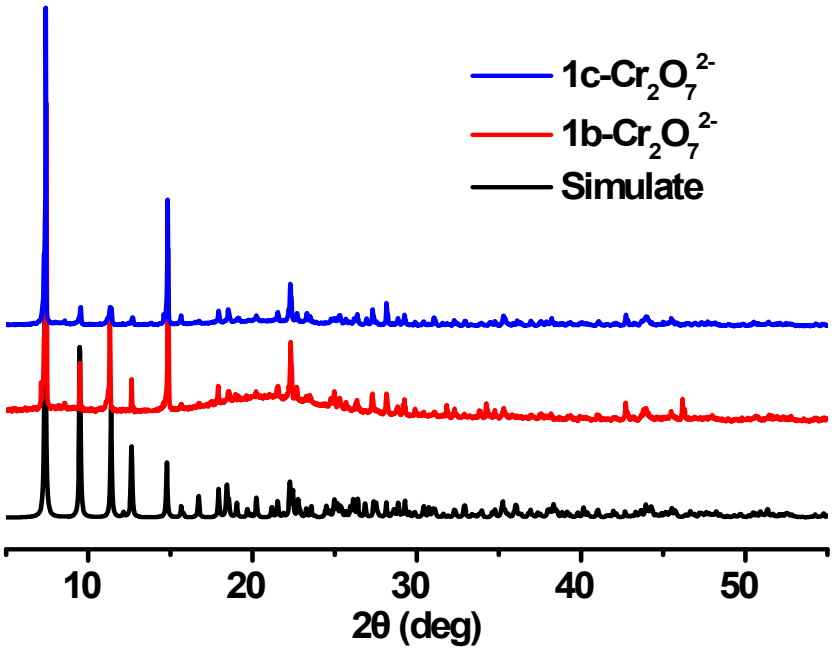

Fig. S13 The PXRD of compounds **1** and **2** after immersed in $Cr_2O_7^{2-}$ aqueous solutions for 3 hours

8. Solid-state excitation spectrum spectra of 1 and 2

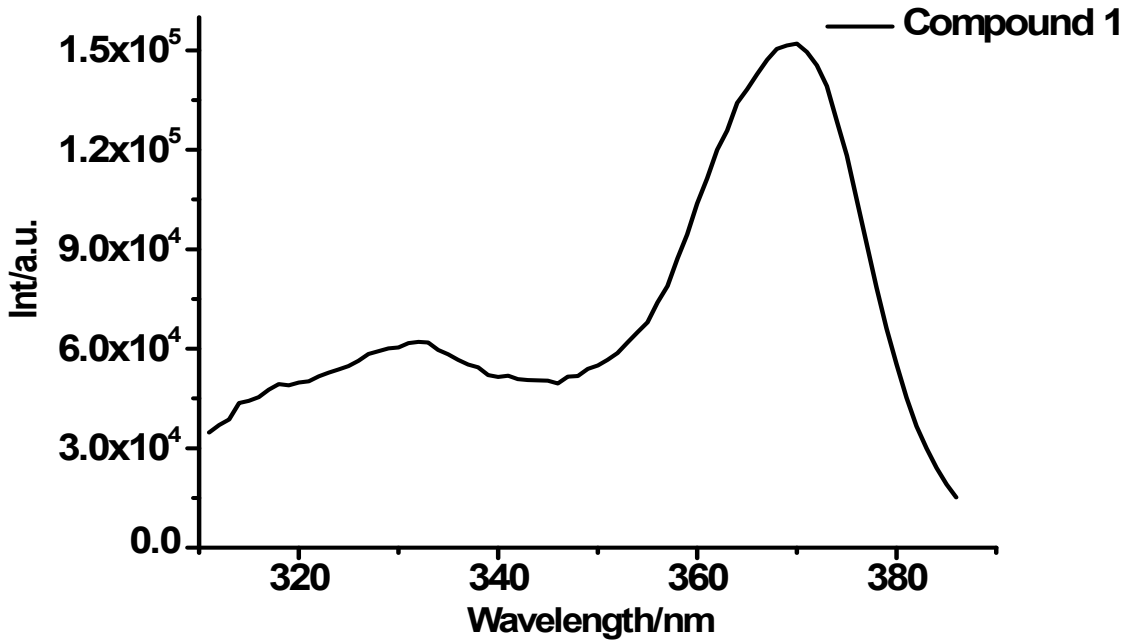

Fig. S14 Solid-state excitation spectra of **1** (λ_{em}=612nm)

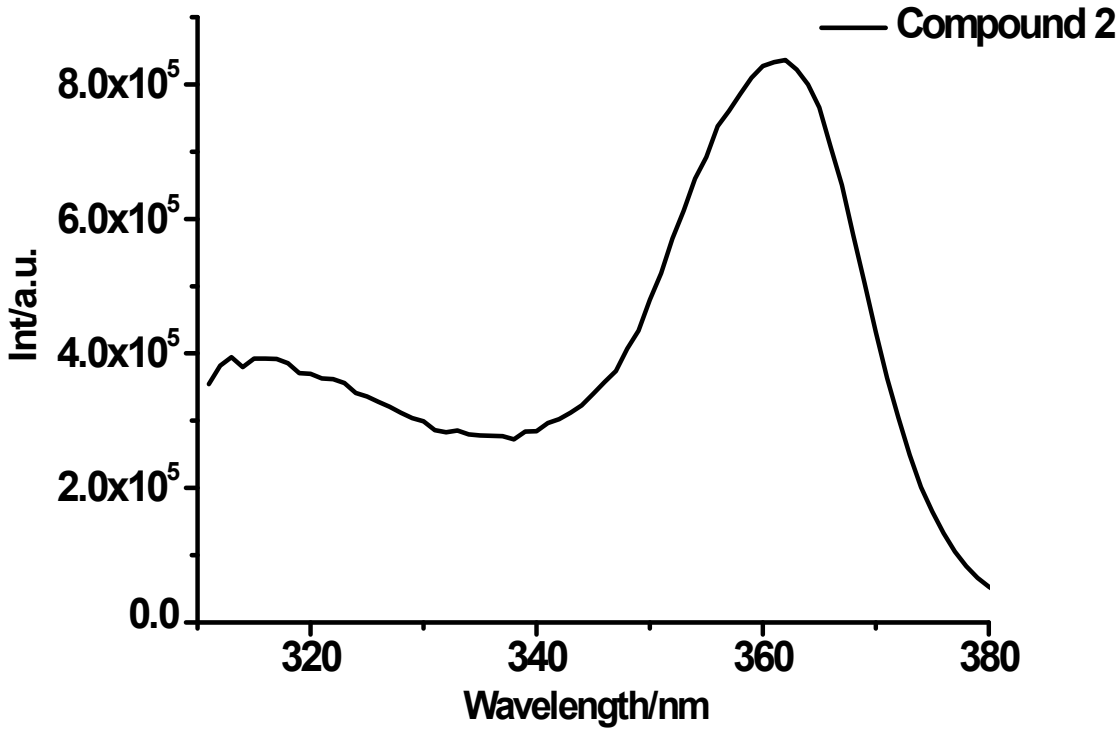

Fig. S15 Solid-state excitation spectra of **2** (λ_{em}=543nm)

9. The UV-Vis spectra of $CrCl_2$ and $K_2Cr_2O_7$ aqueous solutions

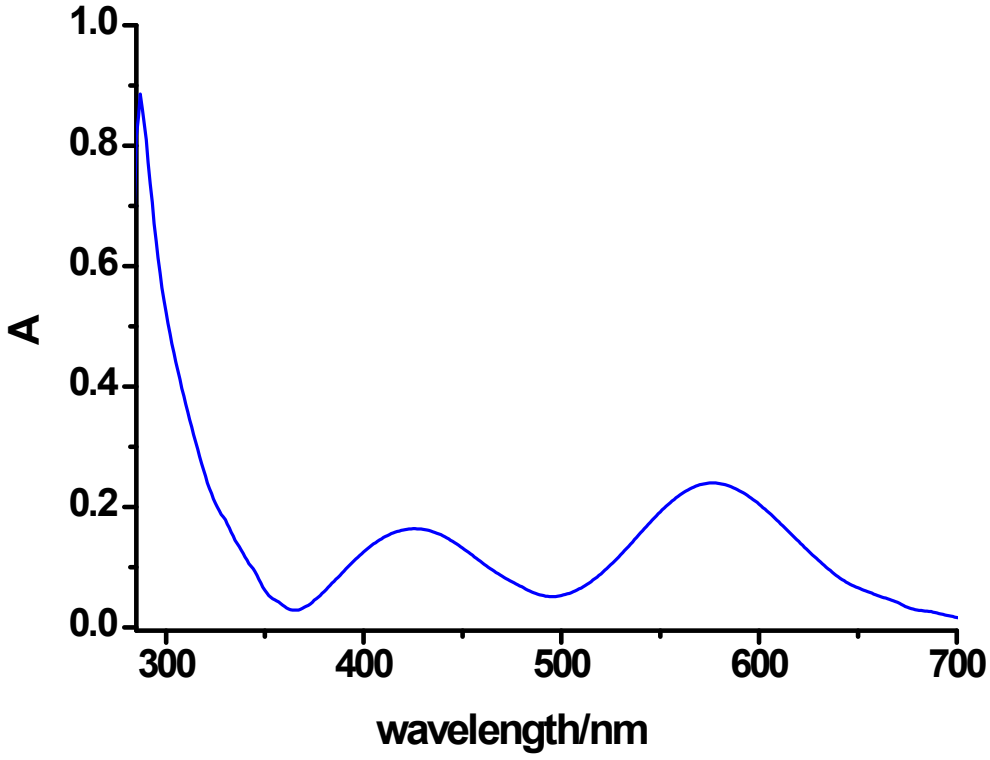

Fig. S16 The UV-Vis spectra of aqueous solution containing Cr^{2+}

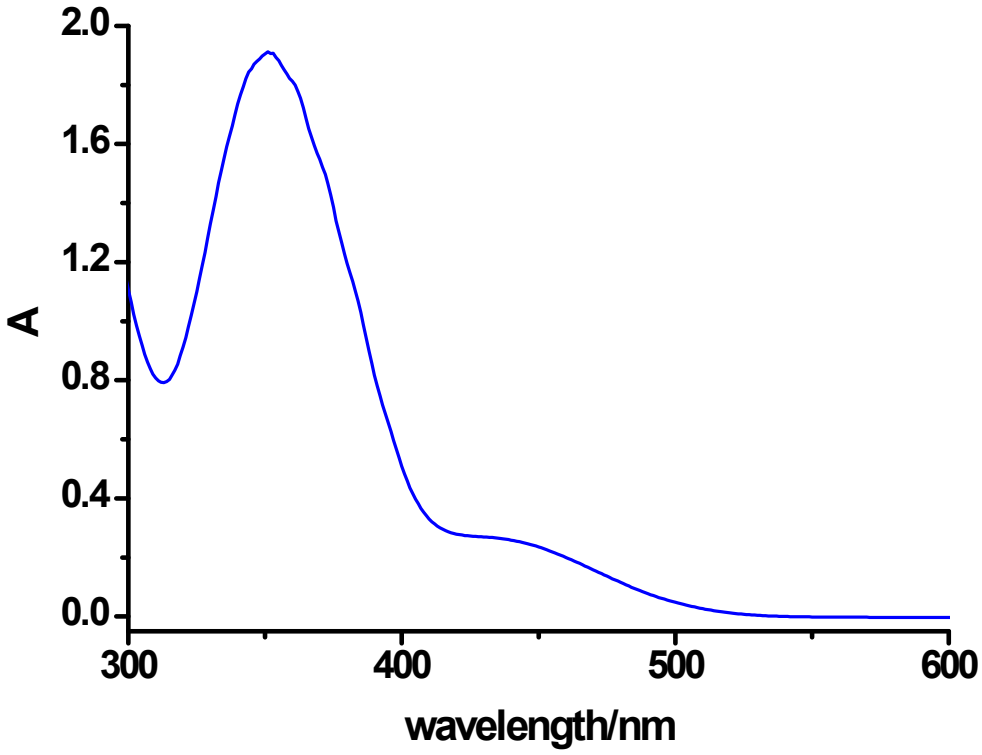

Fig. S17 The UV-Vis spectra of aqueous solution containing $Cr_2O_7^{2-}$

10. The 3D framework view along *b* direction and the shortest distance of N atoms

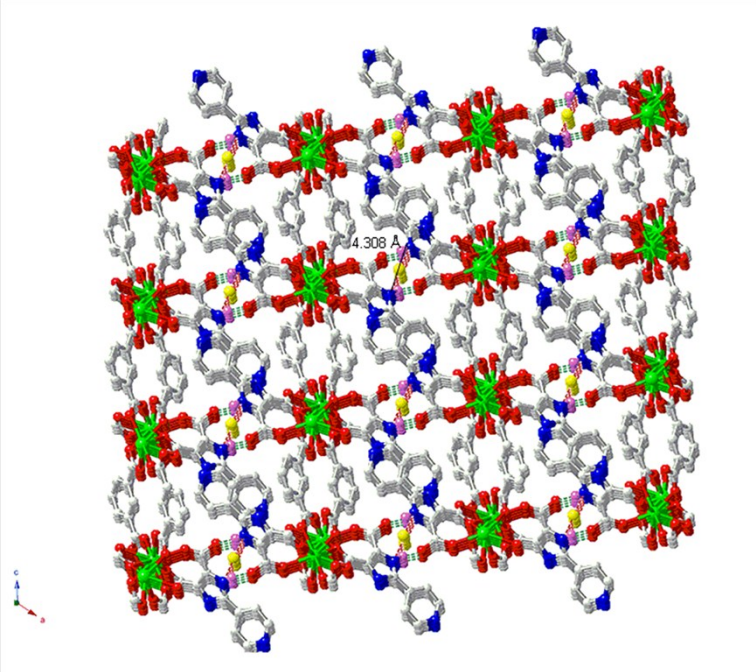

Fig.S18 The 3D framework view along *b* direction and the shortest distance of N atoms. Color code: Tb, green; O, red; N, blue; C, grey; H, pink; Dummy

11. Cr-N bond lengths (Å)

Table. S3 Cr-N bond length

Complex	Bond length [Å]	Complex	Bond length [Å]
$C_{44}H_{29}CrF_{24}N_2O_{16}Tb_2 \cdot 0.5(CH_2Cl_2) \cdot H_2O$	2. 095	$C_{64}H_{88}Cr_3N_6P_3 \cdot 0.5(C_7H_8) \cdot$	2. 062
$C_{22}H_{24}CrF_{24}N_5O_{22}^{+} \cdot 0.5(C_4H_8O_2) \cdot 2(ClO_4^{-})$	2. 052	$C_{56}H_{80}CrN_2O_4$	1. 949
$C_{23}H_{42}Cr_2N_{40}$	1. 865	$C_{19}H_{46}CrN_9O_{12}$	2. 061
$C_{19}H_{17}ClCrN_4O_2^{+} \cdot 0.5(C_4H_8O_2) \cdot 0.5(C_2H_3N) \cdot BF_4$-	2. 088	$C_{16}H_{24}CrF_6N_4^{+} \cdot CF_3O_3S^{-} \cdot C_2H_3N$	2. 071
$C_{42}H_{40}Cr_2N_8\ C_6H_6$	1. 965	$C_{13}H_{22}CrN_4O_3^{+} \cdot ClO_4^{-} \cdot H_2O$	2. 050