Supplementary Information (SI) for CrystEngComm.

Structure, Magnetic Properties and Fluorescence Selectivity of 1D Chain Complexes Based on Pyrazolyl Nitronyl Nitroxide Radical

Jiamin Chu[a], Yi Liu[a], Jing Li[a], Mei Zhu*[a]

[a]*School of Chemistry and Chemical Engineering, Zhejiang Sci-Tech University, Hangzhou 310018, China*

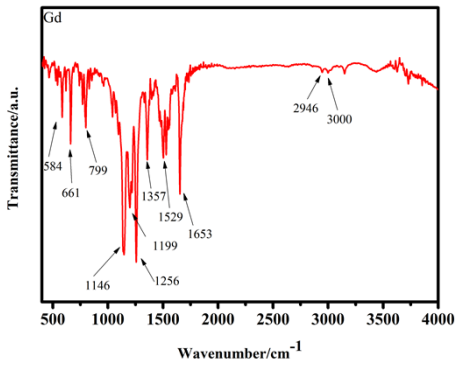

Fig. S1 The IR spectrum of complex **1**.

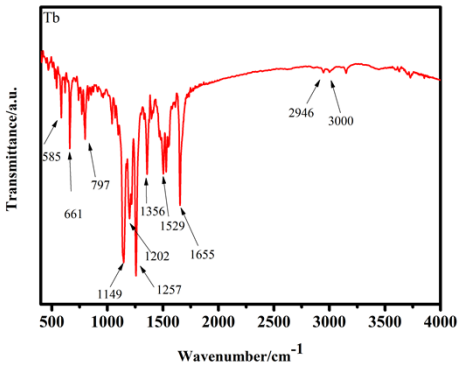

Fig. S2 The IR spectrum of complex **2**.

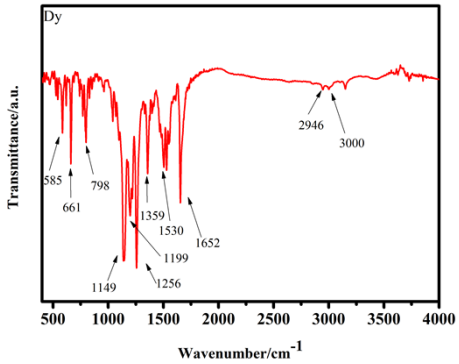

Fig. S3 The IR spectrum of complex **3**.

Table S1 The infrared spectra for complexes **1-3**.

complex	Main IR absorption(cm^{-1})				
Gd	$\nu_{(C-H)}$=2946,3000	$\nu_{(C=O)}$=1653	$\nu_{(N-O)}$=1529	$\nu_{(N-O)}$=1357	$\nu_{(C-N)}$=1257
	$\nu_{(C-O)}$=1199	$\nu_{(N-N)}$=1146	$\nu_{(Benzene\ ring\ fingerprint\ region)}$=799, 661, 584		
Tb	$\nu_{(C-H)}$=2946,3000	$\nu_{(C=O)}$=1655	$\nu_{(N-O)}$=1529	$\nu_{(N-O)}$=1356	$\nu_{(C-N)}$=1256
	$\nu_{(C-O)}$=1202	$\nu_{(N-N)}$=1149	$\nu_{(Benzene\ ring\ fingerprint\ region)}$=797, 661, 585		
Dy	$\nu_{(C-H)}$=2946,3000	$\nu_{(C=O)}$=1652	$\nu_{(N-O)}$=1530	$\nu_{(N-O)}$=1359	$\nu_{(C-N)}$=1256
	$\nu_{(C-O)}$=1199	$\nu_{(N-N)}$=1149	$\nu_{(Benzene\ ring\ fingerprint\ region)}$=798, 661, 585		

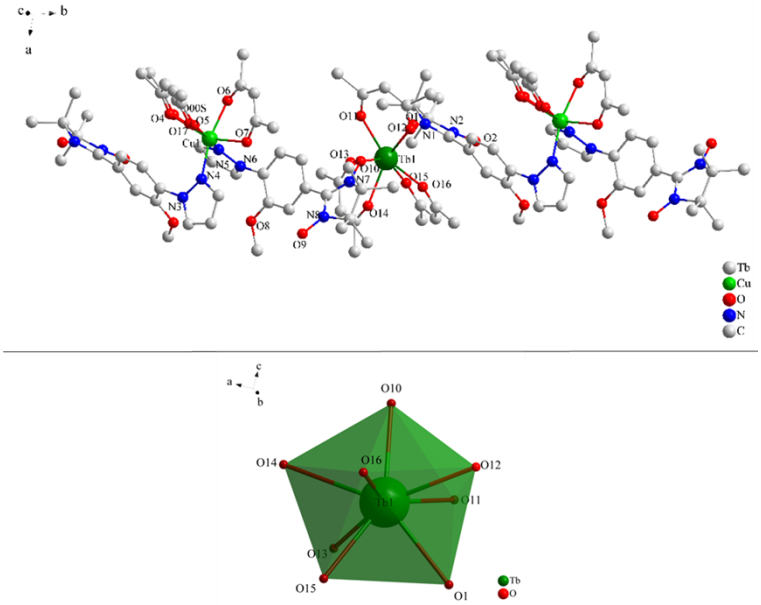

Fig. S4 Crystal structure of complex **2** (top) and coordination polyhedron of Tb (bottom)

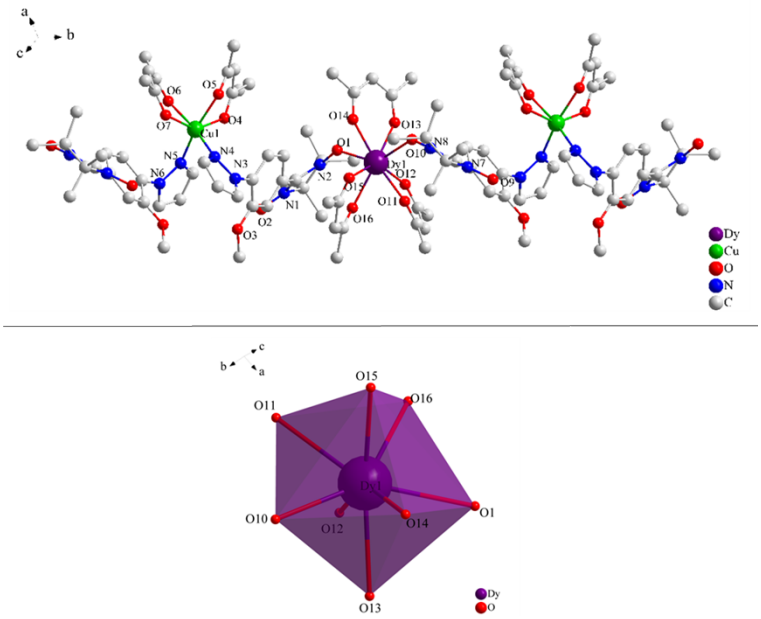

Fig. S5 Crystal structure of complex **3** (top) and coordination polyhedron of Dy (bottom)

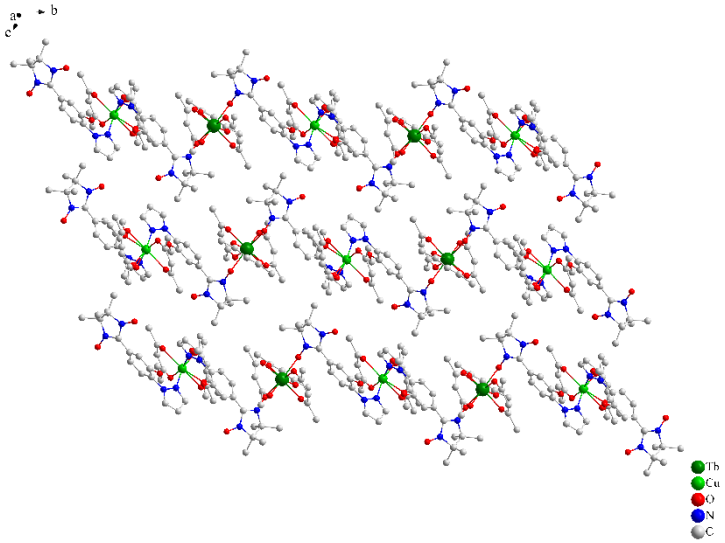

Fig. S6 Crystal packing diagram of complex **2**.

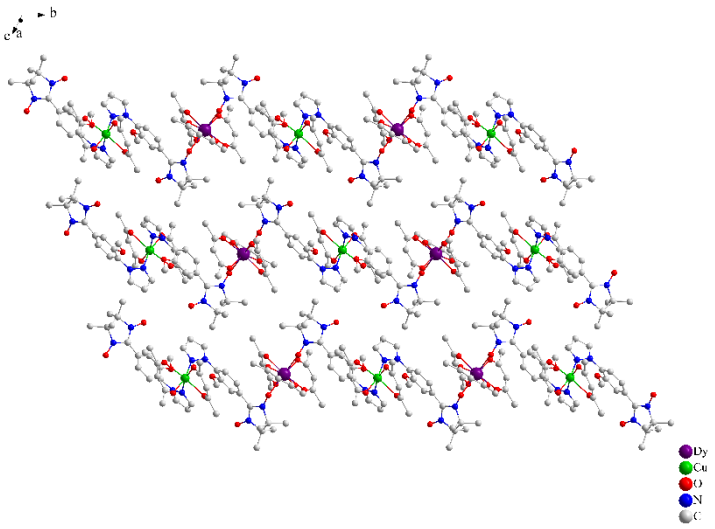

Fig. S7 Crystal packing diagram of complex **3**.

Table S2 Selected bond lengths (Å) and angles (°) for complex **1**.

Bonds			
Gd(1)-O(1)	2.369(5)	Cu(1)-N(5)	2.008(6)
Gd(1)-O(10)	2.330(5)	Cu(1)-O(4)	2.043(5)
Gd(1)-O(11)	2.366(5)	Cu(1)-O(5)	2.297(5)
Gd(1)-O(12)	2.366(5)	Cu(1)-O(6)	2.034(5)
Gd(1)-O(13)	2.416(5)	Cu(1)-O(7)	2.317(5)
Gd(1)-O(14)	2.353(4)	N(2)-O(2)	1.278(8)
Gd(1)-O(15)	2.427(5)	N(8)-O(9)	1.269(9)
Gd(1)-O(16)	2.353(5)	O(1)-N(1)	1.308(7)
Cu(1)-N(4)	2.036(6)	O(10)-N(7)	1.319(8)
Angles			
N(1)-O(1)-Gd(1)	135.1(4)	O(16)-Gd(1)-O(1)	94.57(18)
N(7)-O(10)-Gd(1)	134.9(4)	O(16)-Gd(1)-O(11)	75.40(18)
O(1)-Gd(1)-O(13)	73.42(17)	O(16)-Gd(1)-O(12)	147.45(18)
O(1)-Gd(1)-O(15)	146.11(16)	O(16)-Gd(1)-O(13)	73.65(17)
O(10)-Gd(1)-O(1)	140.01(18)	O(16)-Gd(1)-O(15)	72.15(17)
O(10)-Gd(1)-O(11)	72.77(18)	C(17)-N(4)-Cu(1)	125.6(5)
O(10)-Gd(1)-O(12)	75.71(18)	C(28)-N(5)-Cu(1)	125.4(5)

O(10)-Gd(1)-O(13)	146.25(18)	N(3)-N(4)-Cu(1)	128.4(4)
O(10)-Gd(1)-O(14)	92.45(17)	N(4)-Cu(1)-O(4)	90.4(2)
O(10)-Gd(1)-O(15)	73.87(17)	N(4)-Cu(1)-O(5)	116.0(2)
O(10)-Gd(1)-O(16)	101.66(17)	N(4)-Cu(1)-O(7)	83.8(2)
O(11)-Gd(1)-O(1)	76.46(18)	N(5)-Cu(1)-N(4)	92.8(2)
O(11)-Gd(1)-O(12)	72.86(19)	N(5)-Cu(1)-O(4)	166.1(2)
O(11)-Gd(1)-O(13)	134.33(17)	N(5)-Cu(1)-O(5)	85.1(2)
O(11)-Gd(1)-O(15)	126.78(18)	N(5)-Cu(1)-O(6)	89.5(2)
O(12)-Gd(1)-O(1)	71.21(18)	N(5)-Cu(1)-O(7)	115.2(2)
O(12)-Gd(1)-O(13)	126.01(17)	N(6)-N(5)-Cu(1)	128.7(4)
O(12)-Gd(1)-O(15)	134.63(17)	O(4)-Cu(1)-O(5)	81.4(2)
O(13)-Gd(1)-O(15)	72.93(16)	O(4)-Cu(1)-O(7)	78.6(2)
O(14)-Gd(1)-O(1)	99.88(17)	O(5)-Cu(1)-O(7)	151.9(2)
O(14)-Gd(1)-O(11)	146.93(18)	O(6)-Cu(1)-N(4)	164.3(2)
O(14)-Gd(1)-O(12)	74.88(17)	O(6)-Cu(1)-O(4)	91.0(2)
O(14)-Gd(1)-O(13)	72.56(16)	O(6)-Cu(1)-O(5)	79.6(2)
O(14)-Gd(1)-O(15)	73.65(17)	O(6)-Cu(1)-O(7)	81.2(2)
O(14)-Gd(1)-O(16)	137.41(17)		

Table S3 Selected bond lengths (Å) and angles (°) for complex **2**.

Bonds			
Tb(1)-O(1)	2.370(8)	Cu(1)-O(00S)	2.324(13)
Tb(1)-O(10)	2.320(8)	Cu(1)-O(4)	2.333(15)
Tb(1)-O(11)	2.352(9)	Cu(1)-O(5)	2.052(14)
Tb(1)-O(12)	2.345(8)	Cu(1)-O(6)	2.017(8)
Tb(1)-O(13)	2.348(7)	Cu(1)-O(7)	2.341(8)
Tb(1)-O(14)	2.407(8)	Cu(1)-O(17)	2.051(13)
Tb(1)-O(15)	2.372(8)	N(2)-O(2)	1.291(14)
Tb(1)-O(16)	2.346(7)	N(8)-O(9)	1.282(14)
Cu(1)-N(4)	2.024(10)	O(1)-N(1)	1.283(12)
Cu(1)-N(5)	1.986(10)	O(10)-N(7)	1.314(13)
Angles			

N(1)-O(1)-Tb(1)	135.4(8)	O(16)-Tb(1)-O(15)	73.6(3)
N(7)-O(10)-Tb(1)	134.9(7)	C(17)-N(4)-Cu(1)	125.7(8)
O(1)-Tb(1)-O(14)	147.2(3)	C(28)-N(5)-Cu(1)	124.2(10)
O(1)-Tb(1)-O(15)	73.8(3)	N(3)-N(4)-Cu(1)	128.0(7)
O(10)-Tb(1)-O(1)	138.7(3)	N(4)-Cu(1)-O(00S)	116.5(6)
O(10)-Tb(1)-O(11)	72.7(3)	N(4)-Cu(1)-O(17)	91.1(10)
O(10)-Tb(1)-O(12)	74.8(3)	N(4)-Cu(1)-O(4)	114.6(13)
O(10)-Tb(1)-O(13)	102.3(3)	N(4)-Cu(1)-O(5)	88.8(13)
O(10)-Tb(1)-O(14)	74.1(3)	N(4)-Cu(1)-O(7)	84.1(3)
O(10)-Tb(1)-O(15)	147.2(3)	N(5)-Cu(1)-N(4)	93.4(4)
O(10)-Tb(1)-O(16)	91.9(3)	N(5)-Cu(1)-O(00S)	80.9(6)
O(11)-Tb(1)-O(1)	75.4(3)	N(5)-Cu(1)-O(17)	163.3(10)
O(11)-Tb(1)-O(14)	127.4(3)	N(5)-Cu(1)-O(4)	90.6(8)
O(11)-Tb(1)-O(15)	133.9(3)	N(5)-Cu(1)-O(5)	169.7(13)
O(12)-Tb(1)-O(1)	70.7(3)	N(5)-Cu(1)-O(6)	89.6(4)
O(12)-Tb(1)-O(11)	71.6(3)	N(5)-Cu(1)-O(7)	116.4(3)
O(12)-Tb(1)-O(13)	147.2(3)	N(6)-N(5)-Cu(1)	128.7(7)
O(12)-Tb(1)-O(14)	134.5(3)	O(00S)-Cu(1)-O(7)	153.3(6)
O(12)-Tb(1)-O(15)	126.6(3)	O(17)-Cu(1)-O(00S)	82.7(10)
O(12)-Tb(1)-O(16)	75.1(3)	O(17)-Cu(1)-O(7)	80.0(11)
O(13)-Tb(1)-O(1)	94.8(3)	O(4)-Cu(1)-O(7)	146.9(7)
O(13)-Tb(1)-O(11)	76.3(3)	O(5)-Cu(1)-O(4)	79.4(13)
O(13)-Tb(1)-O(14)	72.3(3)	O(5)-Cu(1)-O(7)	73.8(14)
O(13)-Tb(1)-O(15)	73.0(3)	O(6)-Cu(1)-N(4)	164.9(3)
O(15)-Tb(1)-O(14)	73.5(3)	O(6)-Cu(1)-O(00S)	78.7(10)
O(16)-Tb(1)-O(1)	100.4(3)	O(6)-Cu(1)-O(17)	90.1(12)
O(16)-Tb(1)-O(11)	146.0(3)	O(6)-Cu(1)-O(4)	80.1(12)
O(16)-Tb(1)-O(13)	137.5(3)	O(6)-Cu(1)-O(5)	90.8(15)
O(16)-Tb(1)-O(14)	73.5(2)	O(6)-Cu(1)-O(7)	81.3(3)

Table S4 Selected bond lengths (Å) and angles (°) for complex **3**.

Bonds			
Dy(1)-O(1)	2.345(5)	Cu(1)-N(5)	2.001(7)
Dy(1)-O(10)	2.321(5)	Cu(1)-O(4)	2.307(7)
Dy(1)-O(11)	2.396(5)	Cu(1)-O(5)	2.039(7)
Dy(1)-O(12)	2.345(5)	Cu(1)-O(6)	2.021(6)
Dy(1)-O(13)	2.337(6)	Cu(1)-O(7)	2.314(6)
Dy(1)-O(14)	2.352(5)	N(1)-O(2)	1.272(10)
Dy(1)-O(15)	2.348(5)	N(7)-O(9)	1.277(10)
Dy(1)-O(16)	2.386(5)	O(1)-N(2)	1.294(8)
Cu(1)-N(4)	2.050(7)	O(10)-N(8)	1.311(9)
Angles			
N(2)-O(1)-Dy(1)	135.5(5)	O(14)-Dy(1)-O(16)	126.15(18)
N(8)-O(10)-Dy(1)	134.9(5)	O(15)-Dy(1)-O(11)	73.69(18)
O(1)-Dy(1)-O(11)	146.5(2)	O(15)-Dy(1)-O(14)	74.6(2)
O(1)-Dy(1)-O(12)	94.23(19)	O(15)-Dy(1)-O(16)	72.54(18)
O(1)-Dy(1)-O(14)	71.61(19)	O(16)-Dy(1)-O(11)	73.15(19)
O(1)-Dy(1)-O(15)	100.08(19)	C(17)-N(4)-Cu(1)	125.2(6)
O(1)-Dy(1)-O(16)	73.61(19)	C(28)-N(5)-Cu(1)	126.5(6)
O(10)-Dy(1)-O(1)	139.2(2)	N(3)-N(4)-Cu(1)	128.2(5)
O(10)-Dy(1)-O(11)	73.6(2)	N(4)-Cu(1)-O(4)	115.5(2)
O(10)-Dy(1)-O(12)	101.95(19)	N(4)-Cu(1)-O(7)	84.0(2)
O(10)-Dy(1)-O(13)	73.1(2)	N(5)-Cu(1)-N(4)	93.0(3)
O(10)-Dy(1)-O(14)	75.42(19)	N(5)-Cu(1)-O(4)	84.9(3)
O(10)-Dy(1)-O(15)	92.5(2)	N(5)-Cu(1)-O(5)	165.2(3)
O(10)-Dy(1)-O(16)	146.2(2)	N(5)-Cu(1)-O(6)	90.4(3)
O(12)-Dy(1)-O(11)	72.37(19)	N(5)-Cu(1)-O(7)	116.3(3)
O(12)-Dy(1)-O(14)	147.8(2)	N(6)-N(5)-Cu(1)	128.2(5)
O(12)-Dy(1)-O(15)	137.30(19)	O(4)-Cu(1)-O(7)	151.3(2)
O(12)-Dy(1)-O(16)	73.40(19)	O(5)-Cu(1)-N(4)	90.5(3)
O(13)-Dy(1)-O(1)	76.0(2)	O(5)-Cu(1)-O(4)	80.6(3)

O(13)-Dy(1)-O(11)	126.64(18)	O(5)-Cu(1)-O(7)	78.4(2)
O(13)-Dy(1)-O(12)	75.2(2)	O(6)-Cu(1)-N(4)	164.7(3)
O(13)-Dy(1)-O(14)	73.4(2)	O(6)-Cu(1)-O(4)	79.6(2)
O(13)-Dy(1)-O(15)	147.3(2)	O(6)-Cu(1)-O(5)	90.0(3)
O(13)-Dy(1)-O(16)	133.9(2)	O(6)-Cu(1)-O(7)	81.1(2)
O(14)-Dy(1)-O(11)	134.0(2)		

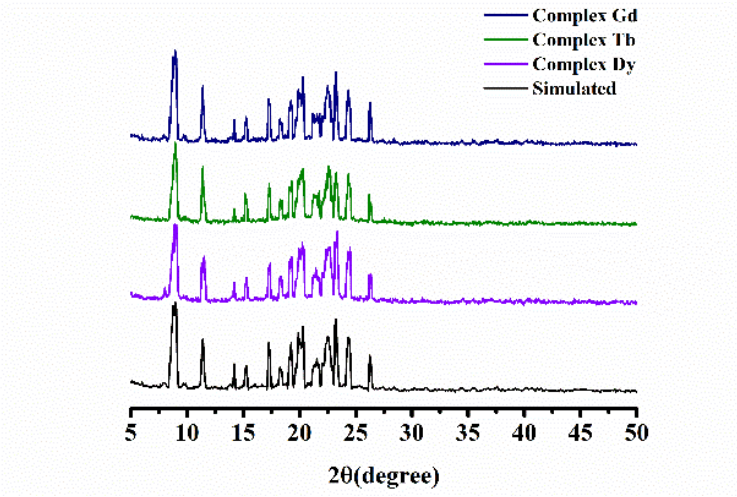

Fig. S8 Powder X-ray diffraction patterns of complexes **1**-**3**.

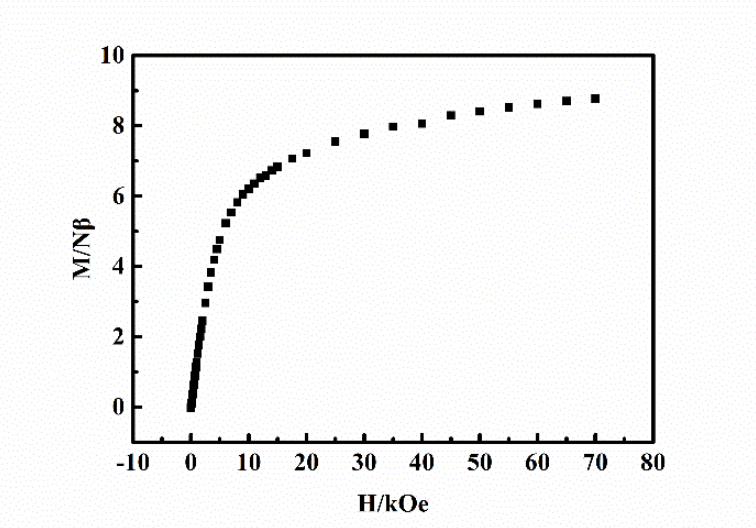

Fig. S9 The *M* vs. *H* plots of complex **2** at 2.0 K

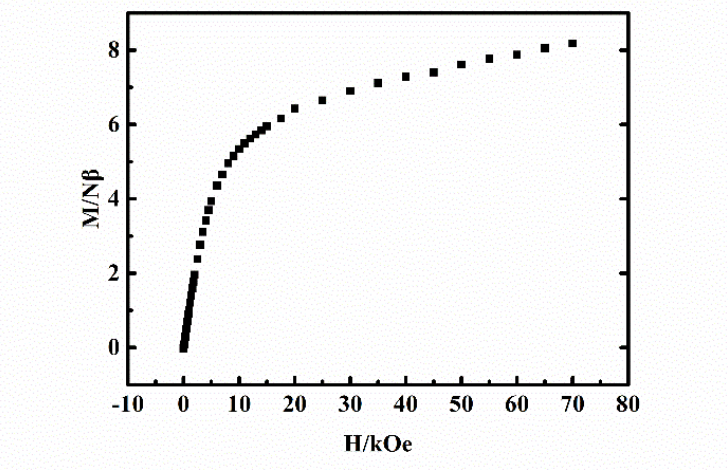

Fig. S10 The *M* vs. *H* plots of complex **3** at 2.0 K

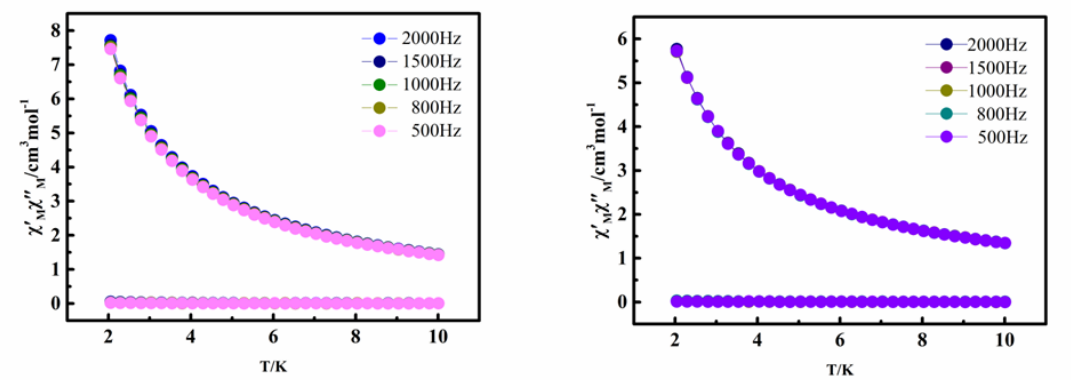

Fig. S11 Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility for complex **2** (left) and **3** (right) in zero dc fields.

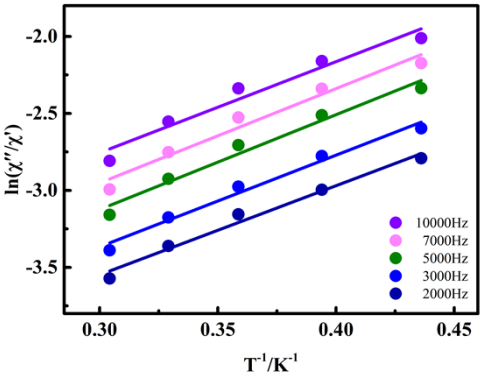

Fig. S12 Extractive ln(χ''/χ') vs 1/T plot for complex **2** (solid-lines: fitting curves).

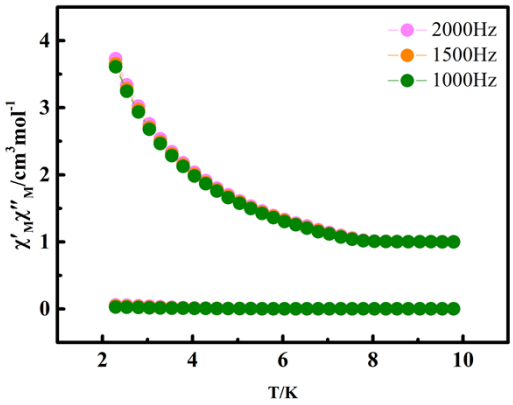

Fig. S13 Temperature-dependent ac signals for **3** at a 3kOe dc field.

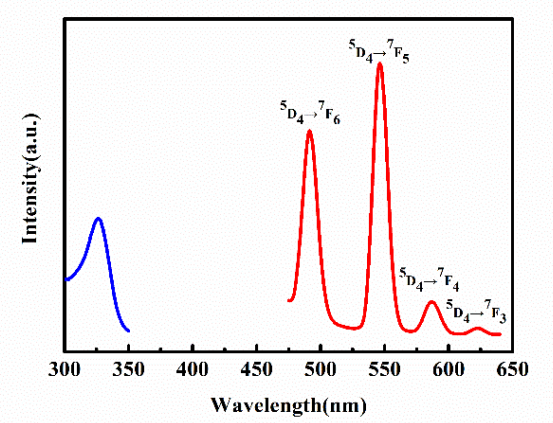

Fig. S14 Excitation (blue) and emission (red) spectra of complex **2** in aqueous solution.

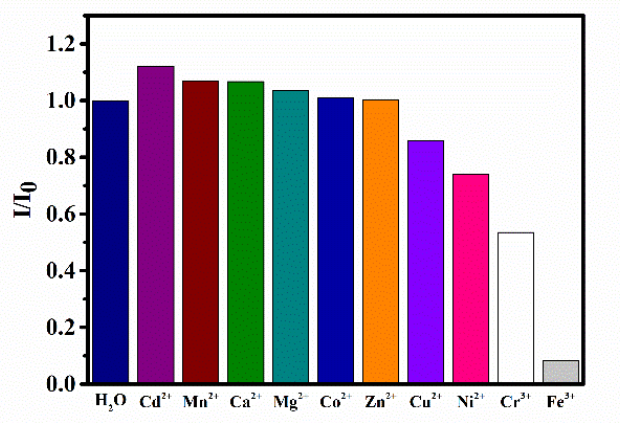

Fig. S15 Luminescence intensity of the transition (546 nm) of complex **2** in different cations suspension system. I and I_0 denote the fluorescence intensity of complex **2** in cation suspension system and water suspension system, respectively.

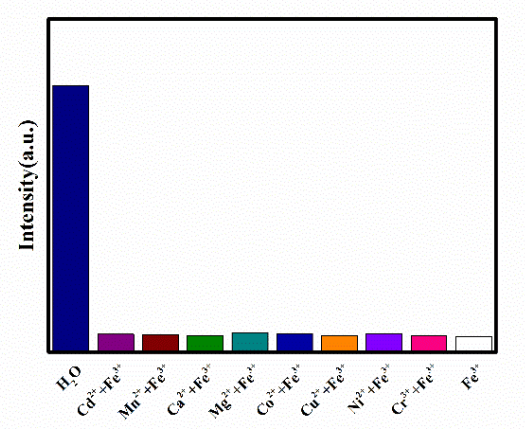

Fig. S16 Comparison of the luminescence intensity of **2** in the presence of mixed cations.

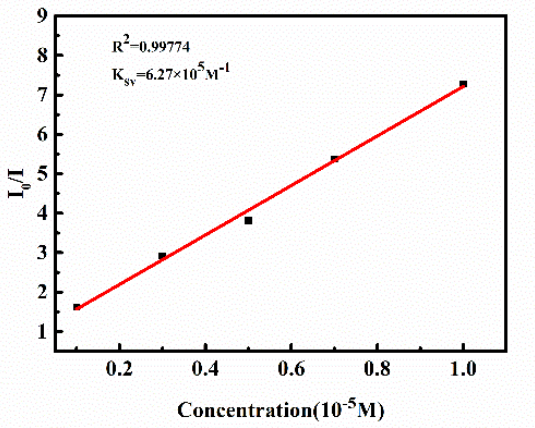

Fig. S17 The Stern-Volmer plot of **2** in the presence of $Cr_2O_7^{2-}$, the red line is linear fitting.

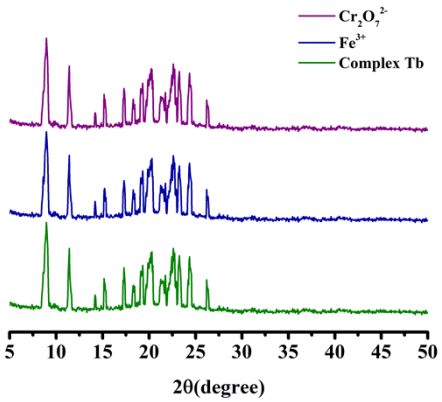

Fig. S18 PXRD patterns of complex **2** after soaking in $Cr_2O_7^{2-}$ and Fe^{3+} ions.

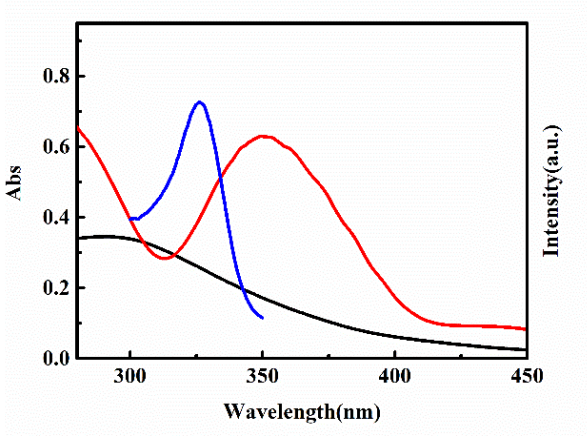

Fig. S19 The UV-vis absorption spectra of $Cr_2O_7^{2-}$ (red) and Fe^{3+} (black), and the excitation spectra of complex **2** (blue).

Table S5 Comparison of $Cr_2O_7^{2-}$ ion detection limits for Complex **2** and some fluorescent materials.

Complexes	$K_{sv}(M^{-1})$	LOD(M)	Ref.
In/Eu-CBDA[a]	1.08×10^4	2.15×10^{-4}	1
$[Eu(L)(HCOO)(H_2O)]_n$[b]	2762.6	1×10^{-5}	2
$[Eu(HL)(H_2O)_2(NO_3)]\cdot NO_3$[c]	7.52×10^4	1.7×10^{-5}	3
$\{[Eu(BCEbpy)(H_2O)_4]\ [Co^{III}(CN)_6]\cdot4H_2O\}_n$[d]	4.31×10^3	9.6×10^{-6}	4
$[Eu_2(phen)_2(bpdc)_3(H_2O)_2]_n\cdot6nH_2O$[e]	5.85×10^4	6.76×10^{-6}	5
$\{[Eu_2L_2(DMF)_4]\}_n$[f]	1.13×10^5	4.01×10^{-6}	6
$[Eu(hfac)_3(NITPh\text{-}DOMe)_2]$[g]	2.339×10^4	1×10^{-7}	7
$[Tb(HL)(H_2O)_2(NO_3)]\cdot NO_3$[c]	4.99×10^4	2.5×10^{-5}	3
$[Tb(L)(HCOO)(H_2O)]_n$[b]	2133.5	2.1×10^{-5}	2
In/Tb-CBDA[a]	1.72×10^4	8.72×10^{-6}	1
$[Tb_2(phen)_2(bpdc)_3(H_2O)_2]_n\cdot6nH_2O$[e]	6.97×10^4	6.73×10^{-6}	5
$\{[Tb_3(bcbp)_3(NO_3)_7]\cdot NO_3\cdot ClO_4\}_n$[h]	1.40×10^4	5.6×10^{-6}	8
$[Tb(Hbptc)(H_2O)_4]\cdot H_2O$[i]	1.27×10^4	2.36×10^{-6}	9
$[Tb(hfac)_3(NIT\text{-}Ph\text{-}3\text{-}COOMe)_2]\cdot0.5C_7H_{16}$[j]	6.13×10^5	1.01×10^{-7}	10
$[Tb(hfac)_3(NITPh\text{-}(OCH_3)_2)_2]$ [k]	2×10^4	1×10^{-7}	11
$[Tb(hfac)_3(NITPh\text{-}Pa)_2][0.5CH_3(CH_2)_5CH_3]$[l]	19860.68	1×10^{-8}	12
$[TbCu(hfac)_5(NIT\text{-}4\text{-}OMe\text{-}3PyzPh)_2]_n$	**6.27×10^5**	**2.92×10^{-7}**	**Our work**

[a] CBDA = 5,5'-(carbonylbis(azanediyl))-diisophthalic acid

[b] H_2L = 5-((2'-cyano-[1,1'-biphenyl]-4-yl)methoxy)isophthalic acid

[c] H_2L = 4-(3,5-dicarboxylphenyl)-2-methylpyridine

[d] BCEbpy = N, N′-bis(carboxymethyl)- 4,4′-bipyridinium dibromide

[e] phen = π-conjugated 1,10-phenanthroline, H_2bpdc = 2,2′ -bipyridine-3,3′ -dicarboxylate

[f] H_3L = 5-(4-carboxybenzyloxy)isophthalic acid

[g] NITPh-DOMe = 2-(3, 4 -dioxylmethylene-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide

[h] $H_2bcbpCl_2$ = 1,1'-bis(4-carboxyphenyl)(4,4'-bipyridinium) dichloride

[i] H_4bptc = 2, 3, 3', 4'-biphenyl tetracarboxylic acid

[j]NITPh-$(OCH_3)_2$=2-(3',4'-dimethoxy-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide

[k]NIT-Ph-3-COOMe=2-(3-(methoxycarbonyl)-phenyl-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide

[l] NITPh-Pa = 2-(3',4'-dioxylmethylene-phenyl)-4,4,5,5-tetramethyl-imidazoline-1-oxyl-3-oxide

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