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Supporting Information for the Manuscript

Exploring the Syntheses, Structures, Topologies, Luminescence Sensing and Magnetism of Zn(II) and Mn(II) Coordination Polymers Based on a Semirigid Tricarboxylate Ligand

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Tables S1. Selected bond lengths [Å] and angles [°] for complexes 1-4.

Complex **1**

Mn(1)-O(1)	2.0986(16)	O(1)-Mn(1)-O(2)#1	109.34(8)
Mn(1)-O(2)#1	2.1313(18)	O(1)-Mn(1)-O(3)#2	99.05(8)
Mn(1)-O(3)#2	2.1572(17)	O(2)#1-Mn(1)-O(3)#2	89.30(8)
Mn(1)-O(8)	2.251(3)	O(1)-Mn(1)-O(8)	88.54(9)
Mn(1)-N(1)	2.292(2)	O(2)#1-Mn(1)-O(8)	161.89(9)
Mn(1)-N(2)	2.304(2)	O(3)#2-Mn(1)-O(8)	90.69(9)
O(1)-Mn(1)-O(2)#1	109.34(8)	N(2)-Mn(1)-O(2)#2	149.29(7)
O(1)-Mn(1)-O(3)#2	99.05(8)	N(1)-Mn(1)-O(2)#2	85.68(8)
O(2)#1-Mn(1)-O(3)#2	89.30(8)	O(4)-Mn(1)-C(15)#2	130.38(8)
O(1)-Mn(1)-O(8)	88.54(9)	O(5)#1-Mn(1)-C(15)#2	100.66(9)
O(2)#1-Mn(1)-O(8)	161.89(9)	O(3)#2-Mn(1)-C(15)#2	29.32(8)
O(3)#2-Mn(1)-O(8)	90.69(9)	N(2)-Mn(1)-C(15)#2	125.81(8)
O(1)-Mn(1)-N(1)	156.43(9)	N(1)-Mn(1)-C(15)#2	87.36(8)
O(2)#1-Mn(1)-N(1)	89.54(10)	O(2)#2-Mn(1)-C(15)#2	28.90(8)

Complex **2**

Mn(1)-O(8)	2.139(3)	O(8)-Mn(1)-N(7)	87.65(14)
Mn(1)-O(10)#1	2.175(4)	O(10)#1-Mn(1)-N(7)	95.09(14)
Mn(1)-O(1)	2.212(4)	O(1)-Mn(1)-N(7)	86.88(14)
Mn(1)-N(3)	2.214(4)	N(3)-Mn(1)-N(7)	172.79(17)
Mn(1)-O(15)	2.218(3)	O(15)-Mn(1)-N(7)	91.12(14)
Mn(1)-N(7)	2.252(4)	O(12)#1-Mn(2)-O(9)	96.82(13)
Mn(2)-O(12)#1	2.168(3)	O(12)#1-Mn(2)-O(3)#2	83.34(13)
Mn(2)-O(9)	2.172(4)	O(9)-Mn(2)-O(3)#2	179.17(13)
Mn(2)-O(3)#2	2.175(3)	O(12)#1-Mn(2)-O(2)#3	170.34(14)
Mn(2)-O(2)#3	2.193(4)	O(9)-Mn(2)-O(2)#3	91.00(13)
Mn(2)-N(5)	2.272(4)	O(3)#2-Mn(2)-O(2)#3	88.75(14)
Mn(2)-N(2)	2.279(4)	O(12)#1-Mn(2)-N(5)	99.31(14)
O(8)-Mn(1)-O(10)#1	95.95(14)	O(9)-Mn(2)-N(5)	88.28(14)
O(8)-Mn(1)-O(1)	90.59(14)	O(3)#2-Mn(2)-N(5)	92.49(14)
O(10)#1-Mn(1)-O(1)	173.24(13)	O(2)#3-Mn(2)-N(5)	86.53(14)
O(8)-Mn(1)-N(3)	96.93(15)	O(12)#1-Mn(2)-N(2)	85.76(15)
O(10)#1-Mn(1)-N(3)	89.99(15)	O(9)-Mn(2)-N(2)	87.17(15)
O(1)-Mn(1)-N(3)	87.50(15)	O(3)#2-Mn(2)-N(2)	92.04(15)
O(8)-Mn(1)-O(15)	175.01(14)	O(2)#3-Mn(2)-N(2)	89.00(15)
O(10)#1-Mn(1)-O(15)	79.33(13)	N(5)-Mn(2)-N(2)	173.56(16)
O(1)-Mn(1)-O(15)	94.18(13)	N(3)-Mn(1)-O(15)	84.78(15)

Complex **3**

Zn(1)-O(1)	1.978(2)	O(1)-Zn(1)-O(4)#1	111.54(11)
Zn(1)-O(4)#1	2.012(2)	O(1)-Zn(1)-O(2)#2	112.52(10)
Zn(1)-O(2)#2	2.058(2)	O(4)#1-Zn(1)-O(2)#2	84.71(10)
Zn(1)-N(2)	2.149(3)	O(1)-Zn(1)-N(2)	100.04(11)
Zn(1)-N(1)	2.156(3)	O(4)#1-Zn(1)-N(2)	100.97(11)
O(4)#1-Zn(1)-N(1)	154.18(11)	O(2)#2-Zn(1)-N(2)	142.31(11)
O(2)#2-Zn(1)-N(1)	82.38(10)	O(1)-Zn(1)-N(1)	94.07(10)
N(2)-Zn(1)-N(1)	76.71(11)		

Complex **4**

Zn(1)-O(1)	2.057(4)	N(2)-Zn(1)-O(1)#1	90.46(17)
Zn(1)-N(2)	2.089(5)	O(5)-Zn(1)-O(1)#1	170.19(18)
Zn(1)-O(5)	2.109(4)	O(1)-Zn(1)-O(8)	154.98(18)
Zn(1)-O(7)	2.146(5)	N(2)-Zn(1)-O(8)	96.8(2)
Zn(1)-O(1)#1	2.175(4)	O(5)-Zn(1)-O(8)	92.8(2)
Zn(1)-O(8)	2.235(6)	O(7)-Zn(1)-O(8)	59.9(2)
Zn(1)-C(15)	2.537(7)	O(1)#1-Zn(1)-O(8)	96.38(18)
Zn(2)-O(4)	1.956(4)	O(1)-Zn(1)-C(15)	125.4(2)
Zn(2)-O(1)	1.961(4)	N(2)-Zn(1)-C(15)	126.2(2)
Zn(2)-O(3)#2	1.994(5)	O(5)-Zn(1)-C(15)	97.7(2)
Zn(2)-N(1)#3	2.018(5)	O(7)-Zn(1)-C(15)	30.3(2)
O(1)-Zn(1)-N(2)	107.91(19)	O(1)#1-Zn(1)-C(15)	91.94(18)
O(1)-Zn(1)-O(5)	92.97(18)	O(8)-Zn(1)-C(15)	29.6(2)
N(2)-Zn(1)-O(5)	85.15(19)	O(4)-Zn(2)-O(1)	108.86(18)
O(1)-Zn(1)-O(7)	95.15(19)	O(4)-Zn(2)-O(3)#2	122.3(2)
N(2)-Zn(1)-O(7)	156.3(2)	O(1)-Zn(2)-O(3)#2	99.78(18)
O(5)-Zn(1)-O(7)	99.5(2)	O(4)-Zn(2)-N(1)#3	100.4(2)
O(1)-Zn(1)-O(1)#1	80.03(17)	O(1)-Zn(2)-N(1)#3	127.04(19)
N(2)-Zn(1)-O(1)#1	90.46(17)	O(3)#2-Zn(2)-N(1)#3	100.4(2)
O(5)-Zn(1)-O(1)#1	170.18(18)		

Symmetry codes: for complex **1**: #1 -x+1, -y, -z+1; #2 -x+1, -y, -z; for complex **2**: #1 x, y-1, z; #2 x-1, y-1 , z; #3 x-1, y, z; for complex **3**: #1 x, -y+1/2, z-1/2; #2 -x+1, -y, -z; for complex **4**: #1 -x+1, -y+1, -z+1; #2 -x, y-1/2, -z+1/2; #3 x, y, z-1.

Tables S2. Hydrogen bonds in crystal packing [Å, °] of complexes 1-3.

	D-H···A	*d*(D-H)	*d*(H...A)	*d*(D...A)	<(DHA)	Symmetry code
1	O(8)-H(8A)···O(5)	0.84	2.39	3.008(7)	131.4	x, -y+1/2, z-1/2
	O(8)-H(8B)···O(3)	0.83	1.88	2.661(6)	156.6	-x, y-1/2, -z+1/2
	O(6)-H(6)···O(8)	0.84	1.67	2.506(6)	175.2	
2	O(15)-H(15B)···O(11)	0.82	2.31	3.121(5)	168.6	x, y-1, z
	O(15)-H(15A)···O(3)	0.82	1.86	2.651(5)	162.8	x, y-1, z
	O(13)-H(13)···O(4)	0.82	1.79	2.612(5)	176.0	-x+2, -y+3, -z+1
	O(7)-H(7A)···O(6)	0.82	1.84	2.648(6)	168.1	-x+1, -y+2, -z
3	O(6)-H(6A)···O(3)	0.82	1.92	2.705(4)	159.3	x+1, y, z
	O(8)-H(8A)···O(5)	0.82	2.41	3.091(7)	141.5	x, -y+1/2, z+1/2
	O(8)-H(8B)···O(3)	0.82	1.97	2.778(8)	169.3	

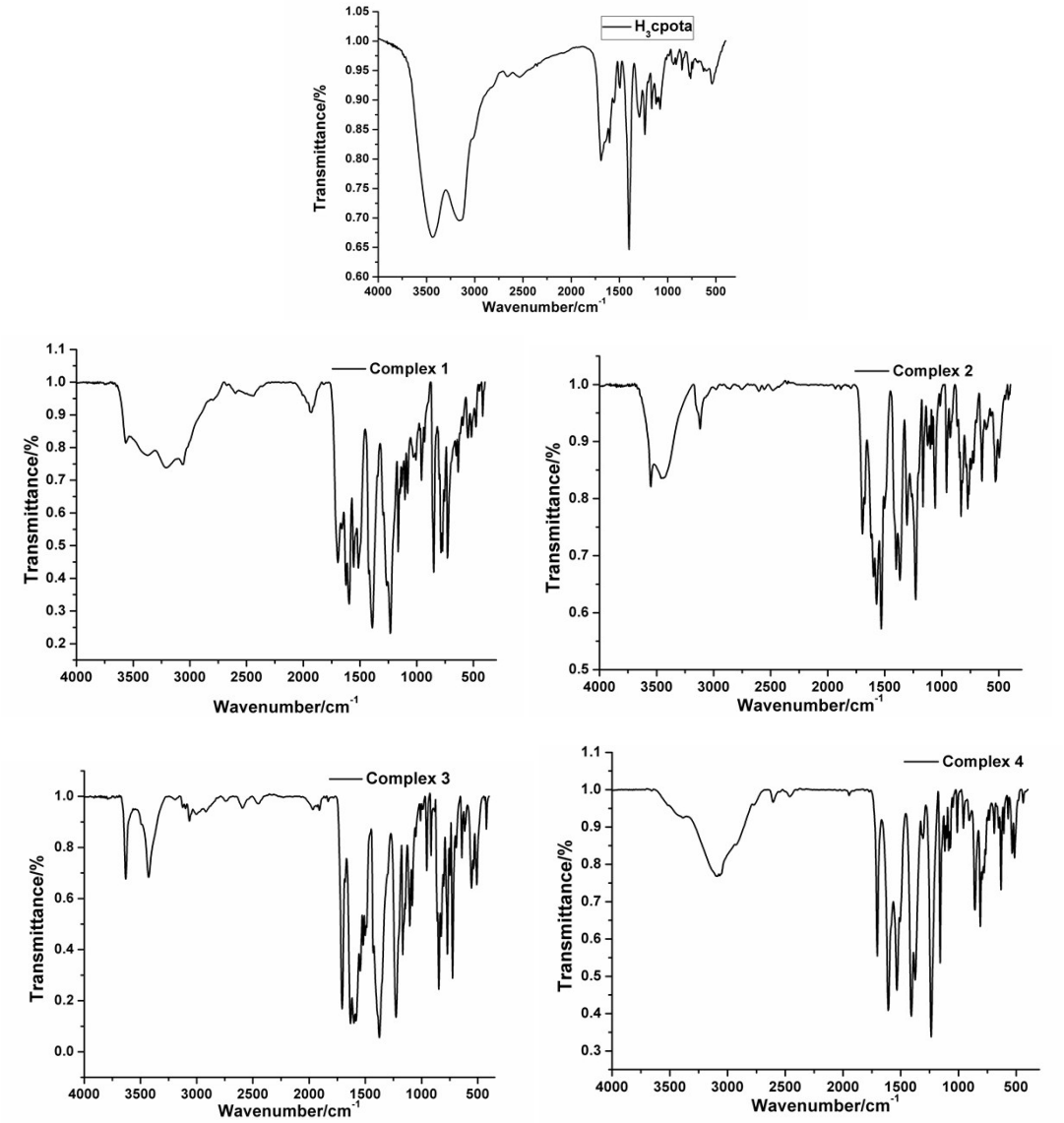

Fig. S1 The IR spectra of H_3cpota ligand and complexes **1**-**4**.

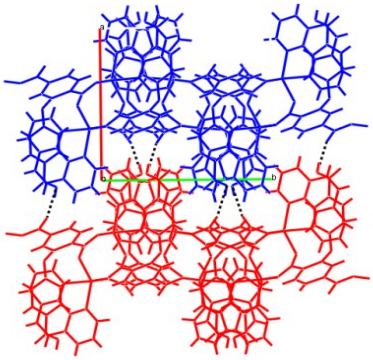

Fig. S2 3D supramolecular architecture of **3** viewed along the *ab* plane. (Blank dotted lines present the H-bonds).

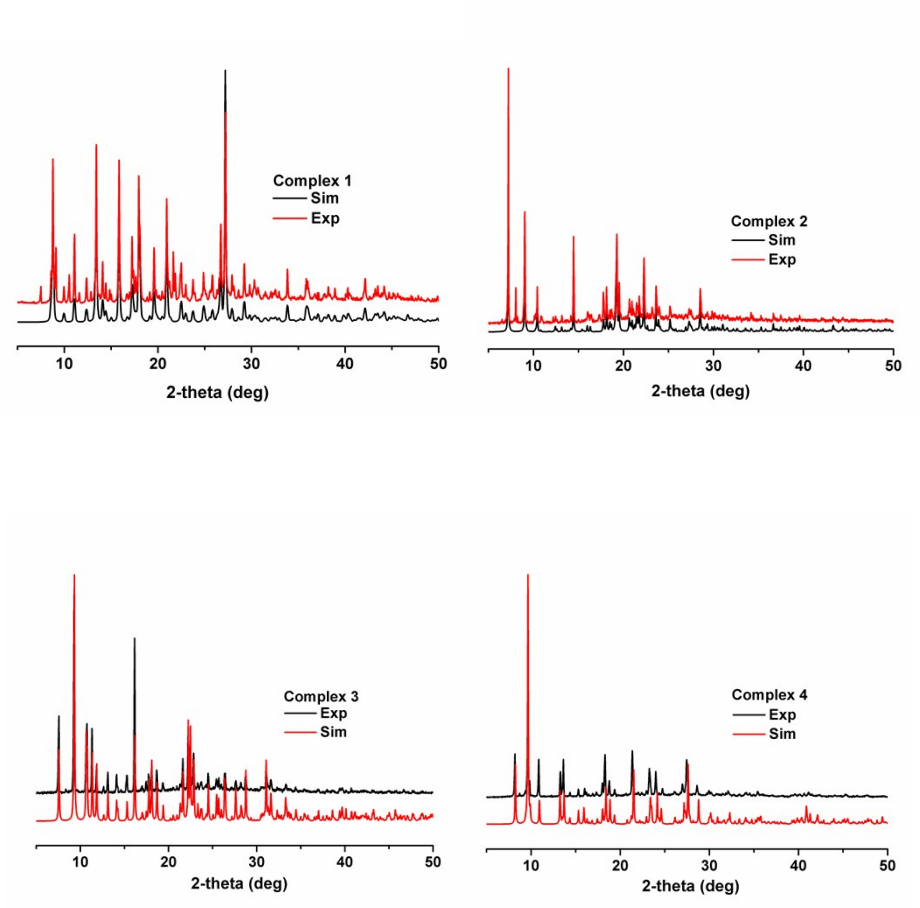

Fig. S3 PXRD patterns of complexes **1**–**4** at room temperature. Blank patterns correspond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

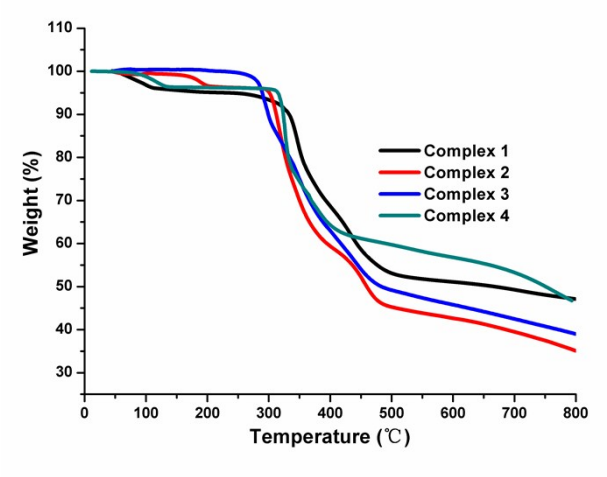

Fig. S4 The thermal curves of complexes **1**-**4**.

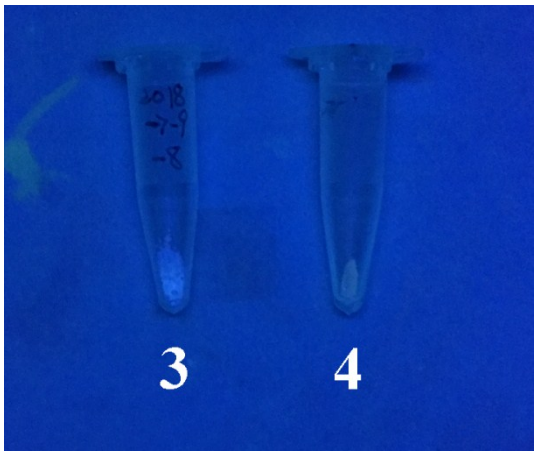

Fig. S5 Digital photograph for the fluorescence of complexes **3** and **4** under 365nm UV radiation.

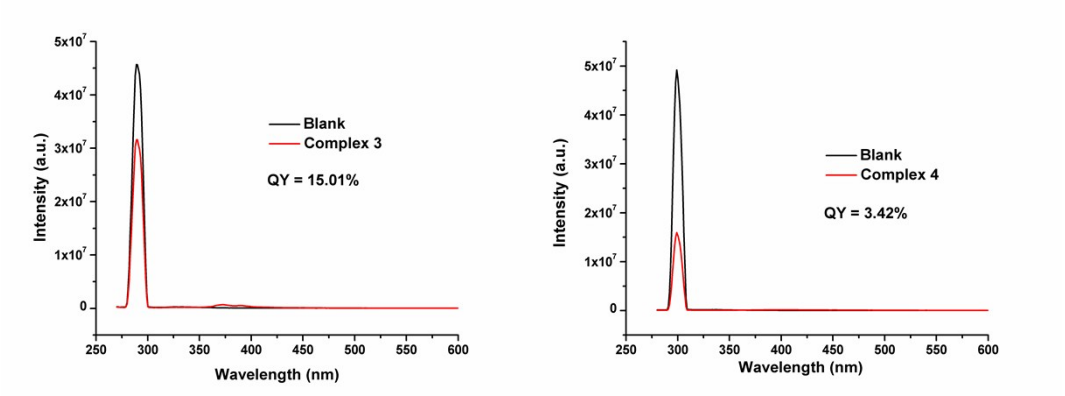

Fig. S6 The luminescent quantum yields of complexes **3** and **4**.

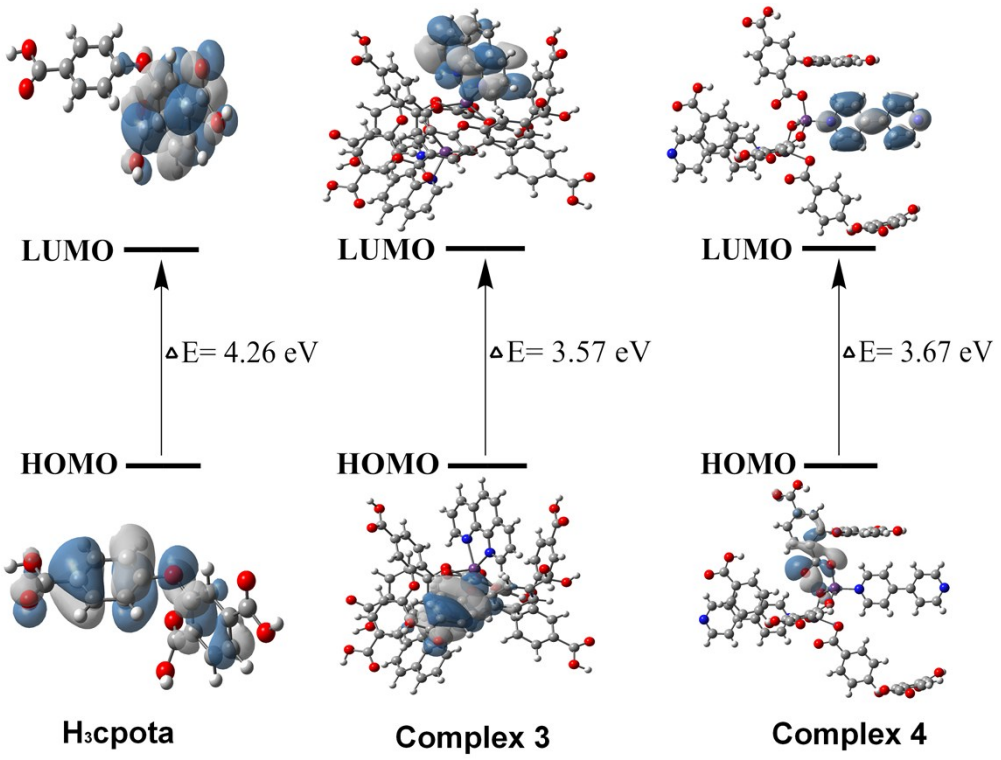

Fig. S7 The frontier MOs of H_3cpota ligand and complexes **3** and **4**.

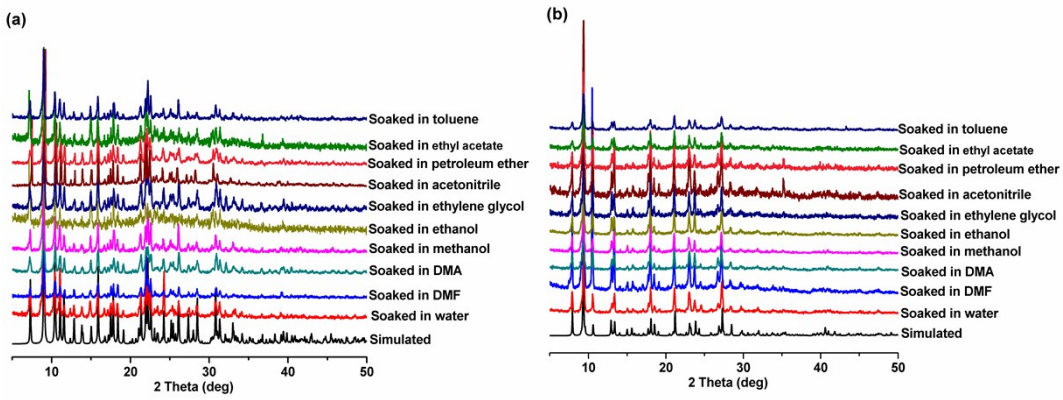

Fig. S8 PXRD patterns of **3** (a) and **4** (b) in different solvent.

Table S3. ICP experiments of **3** and **4** after immersing in aqueous solution

Sample	Concentration of Zn(II) ions (ug/mL)
Blank sample (H_2O)	0.0562
Sample 1	0.5230
Sample 2	0.2796

(The Sample 1 was the aqueous solution after 10 mg samples of **3** immersed for one week, The Sample 2 was the aqueous solution after 10 mg samples of **4** immersed for one week.)

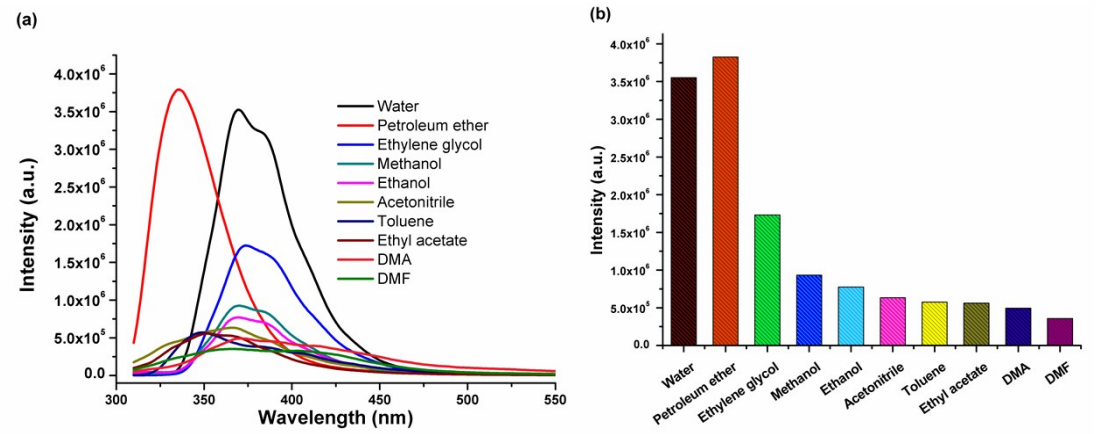

Fig. S9 (a) The emission spectra of complex **3** in different solvents. (b) The emission intensity of complex **3** in different solvents.

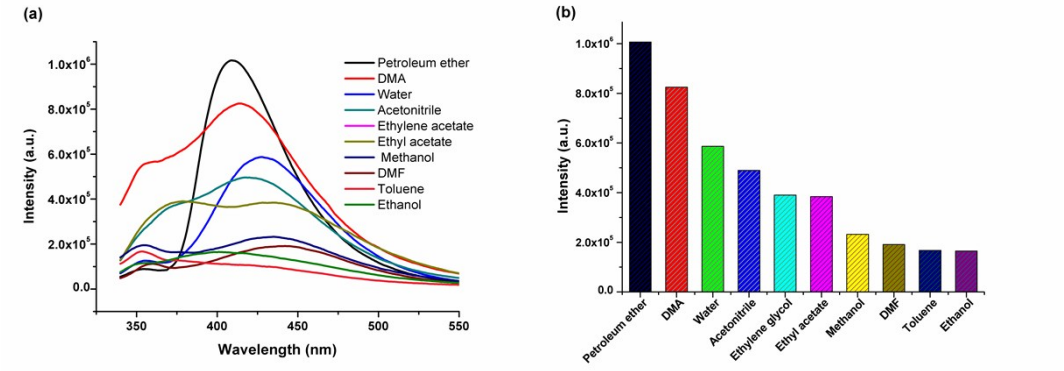

Fig. S10 (a) The emission spectra of complex **4** in different solvents. (b) The emission intensity of complex **4** in different solvents.

Section S1: Calculation of detection limit for $Cr_2O_7^{2-}$ and CrO_4^{2-}.

Detection limit (LOD = $3\sigma/m$) was calculated as early reports,[S1] where the σ equal to $100 \times (I_{SE}/I_0)$, I_{SE} is the standard error of the luminescence intensity measurement, as determined by the baseline measurement of blank samples monitored at 370 nm, and I_0 *is* the measured luminescence intensity of **3** in deionized water. The slope(m) was obtained from the linear fit of the concentration-dependent luminescence intensity curve in the low concentration region. In a typical experiment to determine limit of detection, incremental amount of 0.001 M aqueous $Cr_2O_7^{2-}$ /CrO_4^{2-} solution in the volume ranging 0.0 μL to 100 μL was added to the water suspension (2 mg complex **3** dispersed in 2 ml water) of complex **3**. The slope should be the correlation between the chromium concentration and $(I_0 - I)/I_0$%. I is the fluorescence intensity thus observed for each incremental addition of aqueous $Cr_2O_7^{2-}$/CrO_4^{2-} solution. Slop of the curve thus drawn was found to be $Cr_2O_7^{2-}$ = 0.685 (R_2 = 0.996); CrO_4^{2-} = 0.275 (R_2 = 0.995) for complex **3** (Fig. S11).

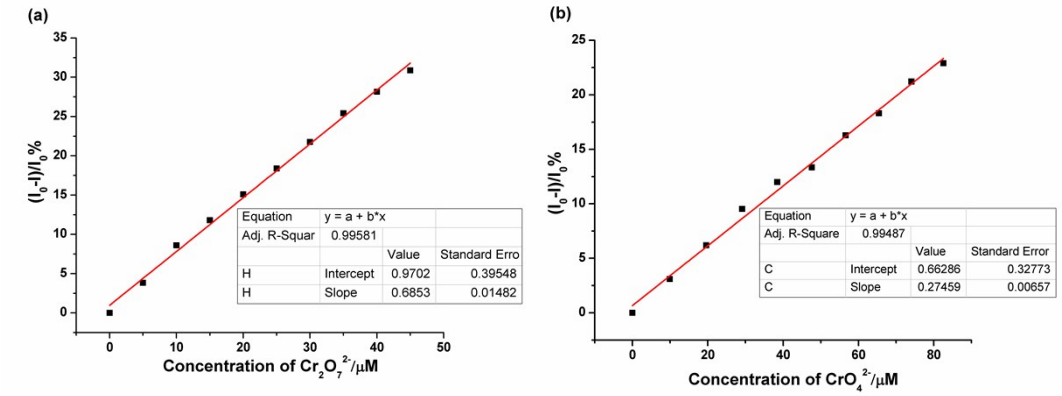

Fig. S11 Linear region of fluorescence intensity (λ_{ex} = 290 nm) of complex **3** suspensions in water upon incremental addition of $Cr_2O_7^{2-}$/CrO_4^{2-}solutions.

Table S4 LOD calculations for $Cr_2O_7^{2-}$ and CrO_4^{2-}

Complex **3**	Blank	$Cr_2O_7^{2-}$	CrO_4^{2-}
Fluorescence Intensity Complex **3**	1	3196720	3543720
	2	3245180	3536540
	3	3235170	3556430
	4	3232670	3549820
	5	3187530	3554690
I_{SE}		25590.32	26361.41
I_0		3088490	3553320
Standard deviation (σ)		0.829	0.742
Slope (m)		0.685	0.276
Detection limit (3σ/m)		3.62 μM	8.06 μM

Table S5. Comparison of various CPs sensors for the detection of Cr(VI).

	CPs[a]	Analyte(CrO_4^{2-} /$Cr_2O_7^{2-}$)	K_{sv}[1]	LOD(μM)	Media	Ref
1	$[Zn(btz)]_n$	CrO_4^{2-}	3.19×10^3	10	H_2O	S2
		$Cr_2O_7^{2-}$	4.23×10^3	2		
	$[Zn(ttz)H_2O]_n$	CrO_4^{2-}	2.35×10^3	20	H_2O	
		$Cr_2O_7^{2-}$	2.19×10^3	2		
2	$[Zn(IPA)(L)]_n$	CrO_4^{2-}	1.00×10^3	18.33	H_2O	S3
		$Cr_2O_7^{2-}$	1.37×10^3	12.02		
	$[Cd(IPA)(L)]_n$	CrO_4^{2-}	1.30×10^3	2.52		
		$Cr_2O_7^{2-}$	2.91×10^3	2.26		
3	$\{[Cd(4\text{-}BMPD)(BPDC)]\cdot 2H_2O\}_n$	$Cr_2O_7^{2-}$	6.4×10^3	37.6	H_2O	S4
	$\{[Cd(4\text{-}BMPD)(SDBA)(H_2O)]\cdot 0.5H_2O\}_n$	$Cr_2O_7^{2-}$	4.97×10^3	48.6		
4	$[Eu_2(tpbpc)_4\cdot CO_3\cdot H_2O]\cdot DMF\cdot solvent$	CrO_4^{2-}	4.85×10^3	0.33	H_2O	S5

		$Cr_2O_7^{2-}$	1.04×10^4	1.07		
5	$Eu(CBIP)(HCOO)(H_2O)]_n$	CrO_4^{2-}	1.54×10^3	1.2	H_2O	S6
		$Cr_2O_7^{2-}$	2.76×10^3	1.0		
	$Tb(CBIP)(HCOO)(H_2O)]_n$	CrO_4^{2-}	130×10^3	1.8	H_2O	
		$Cr_2O_7^{2-}$	2.13×10^3	2.1		
6	$[Cd(4\text{-tkpvb})(5\text{-tert-BIPA})]_n$	CrO_4^{2-}	4.68×104	0.08	H_2O	S7
		$Cr_2O_7^{2-}$	2.50×104	0.12		
7	$[Zn(\mu_3\text{-Hcpota})(phen)]_n \cdot nH_2O$	CrO_4^{2-}	3.51×10^3	8.06	H_2O	This work
		$Cr_2O_7^{2-}$	1.00×10^4	3.62		

([a]Abbreviations of involved ligands in compounds: H_2btz = 1,5-bis(5-tetrazolo)-3-oxapentane; H_3ttz = 1,2,3-tris-[2-(5-tetrazolo)-ethoxy]propane; L = 3-pyridylcarbox-aldehyde nicotinoylhydrazone; H_2IPA = isophthalic acid; 4-BMPD = 4,4′-(2,5-bis-(methylthio)-1,4-phenylene)dipyridine; H_2BPDC = 4,4′-biphenyldicarboxylic acid, H_2SDBA = 4,4′-sulfonyldibenzoic acid; Htpbpc = 4′-[4,2′;6′,4″]-terpyridin-4′-yl-biphenyl-4-carboxylic acid; H_2CBIP = 5-((2′-cyano-[1,1′-biphenyl]-4-yl)methoxy)isophthalic acid; 4-tkpvb = 1,2,4,5-tetrakis(4-pyridylvinyl)benzene; 5-tert-H2BIPA = 5-tert-butyl-isophthalic acid.) ([1] K_{sv} = quenching constant, M^{-1}).

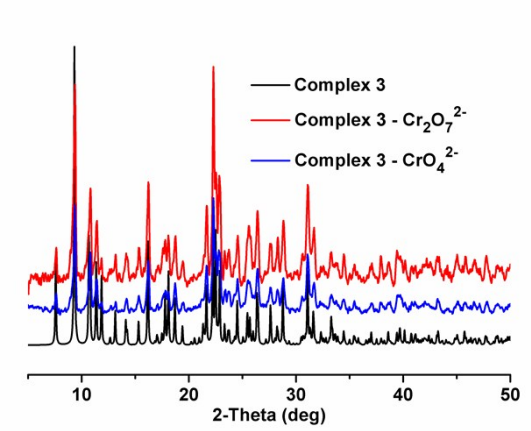

Fig. S12 The PXRD patterns of simulated complex **3** and the PXRD patterns of **3** for the recognition of $Cr_2O_7^{2-}$ and CrO_4^{2-} after five recycling processes.

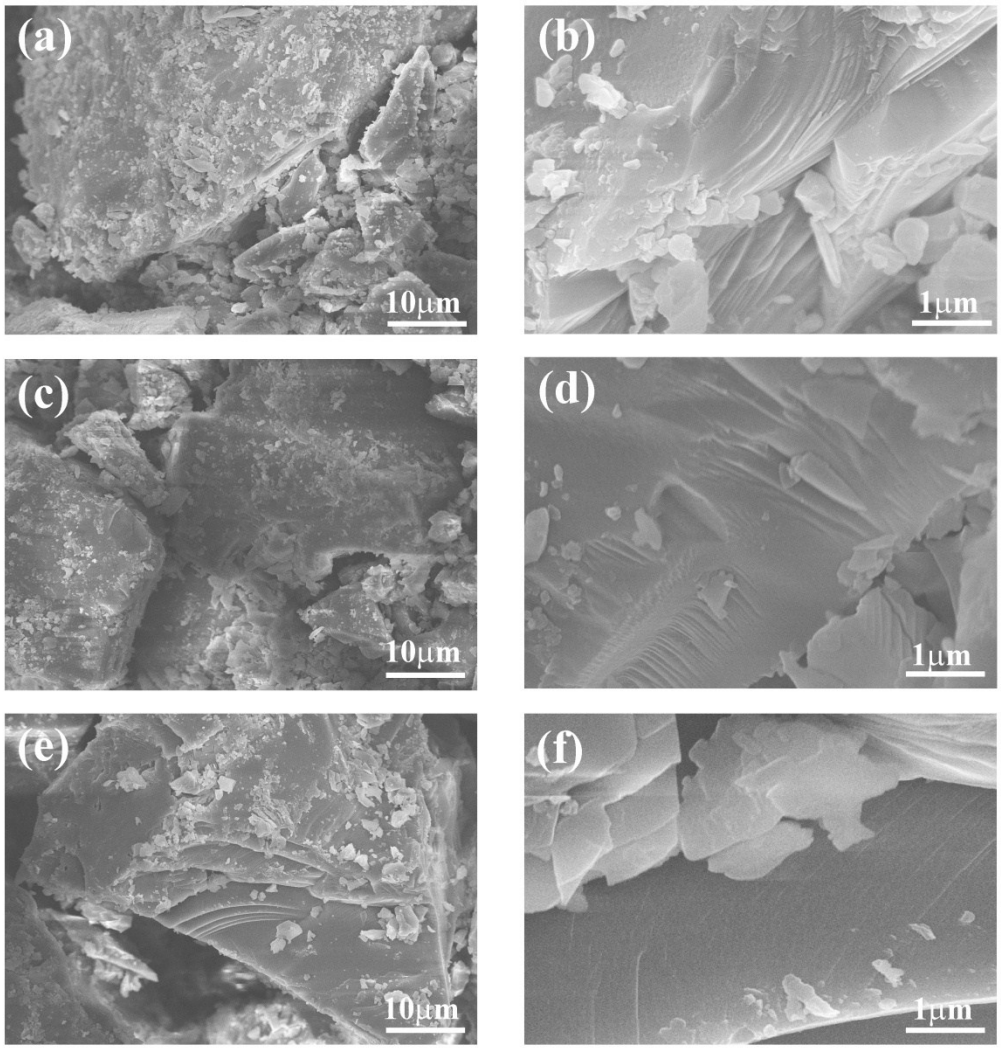

Fig. S13 The SEM images of the (a-b) pure phase **3**, (c-d) **3** after $Cr_2O_7^{2-}$ detection experiment, and (e-f) **3** after CrO_4^{2-} detection experiment, with the bars of 10 μm and 1 μm, respectively.

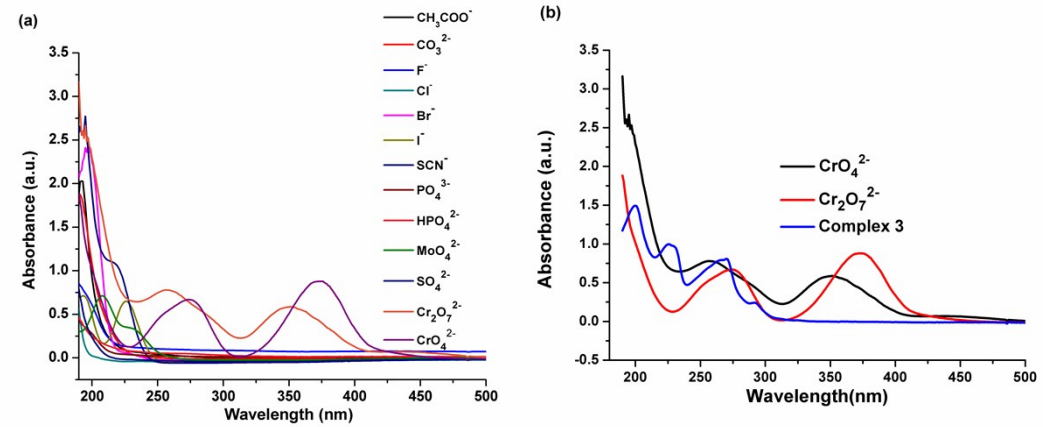

Fig. S14 Liquid UV-vis spectra of various different anions and complex **3** in the aqueous solution.

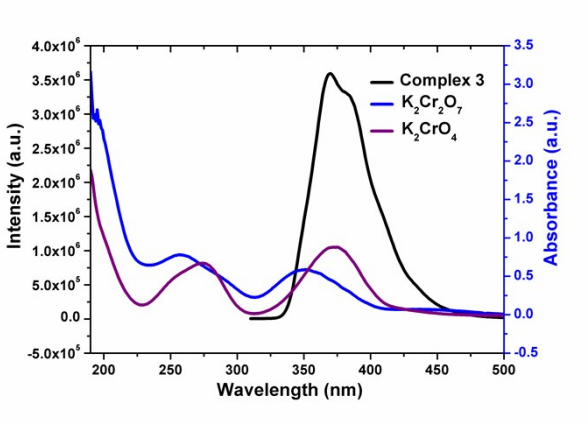

Fig. S15 Liquid UV-vis spectra of $Cr_2O_7^{2-}$ and CrO_4^{2-} anions and emission spectra of complex **3** in the aqueous solution.

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