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Supporting Information

Structural Diversity, Magnetic Properties, or Luminescent Sensing Based Ni(II)/Zn(II) Coordination Polymers of the semirigid ligand of 3,3'-((5-carboxy-1,3-phenylene)bis(oxy))dibenzate

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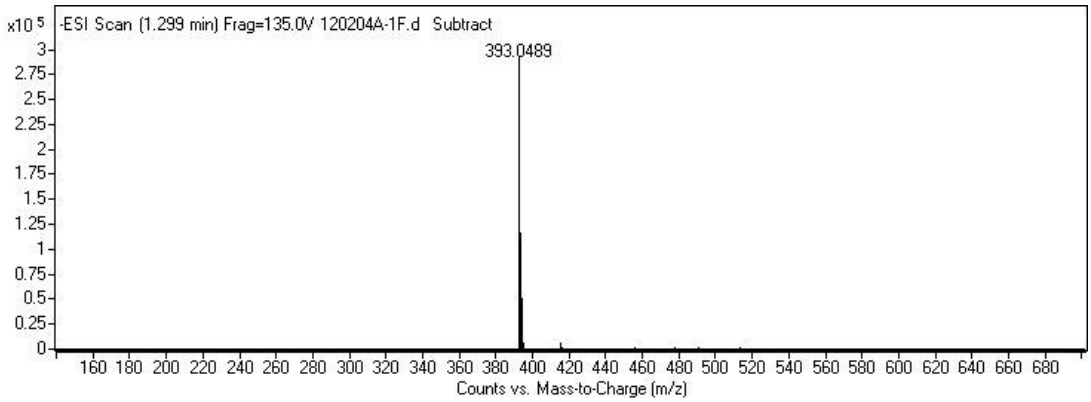


Fig. S1 ESI mass spectra of H_3cpboda ligand

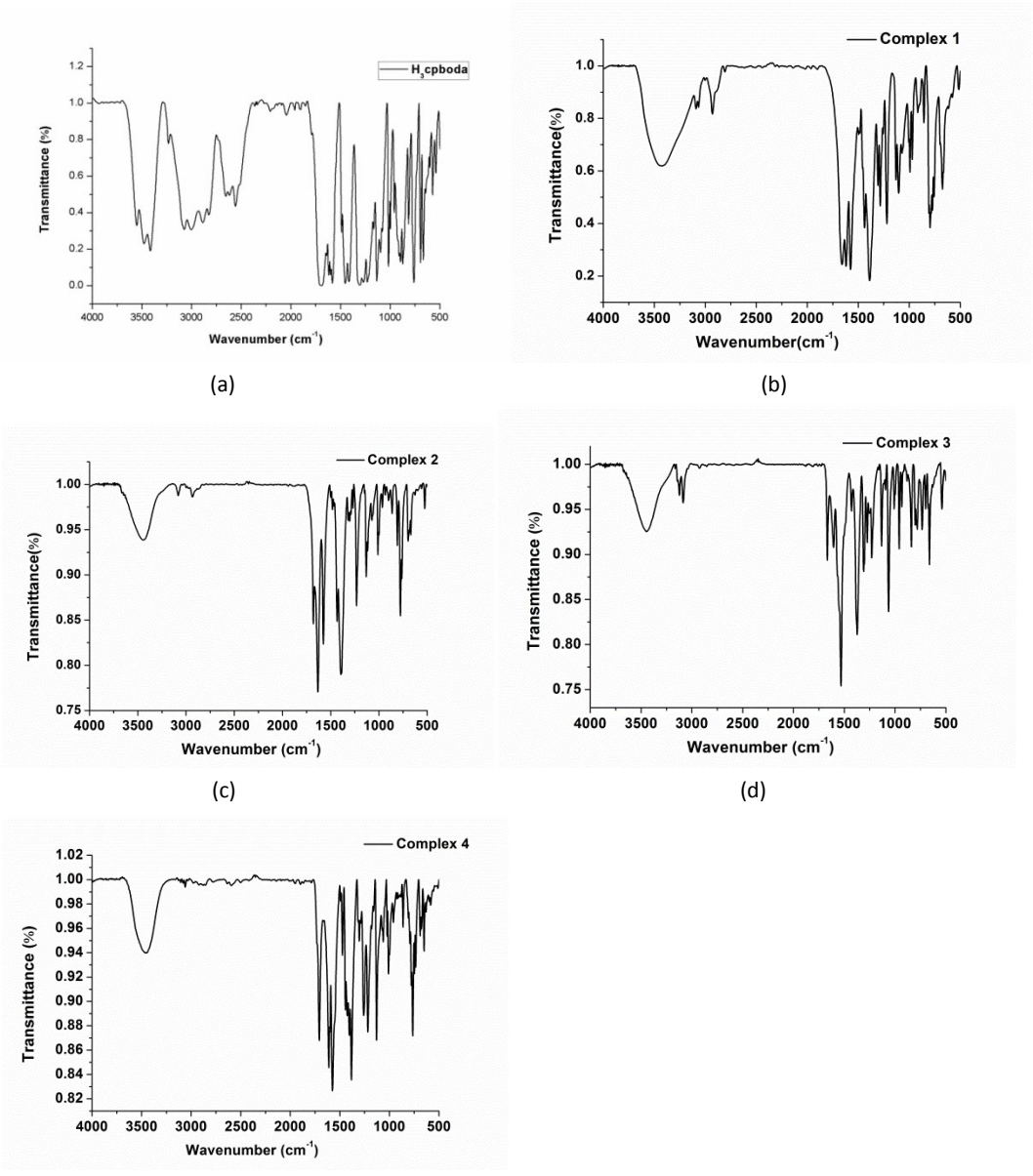


Fig. S2 The IR spectra of H_3cpboda ligand and complexes **1-4**

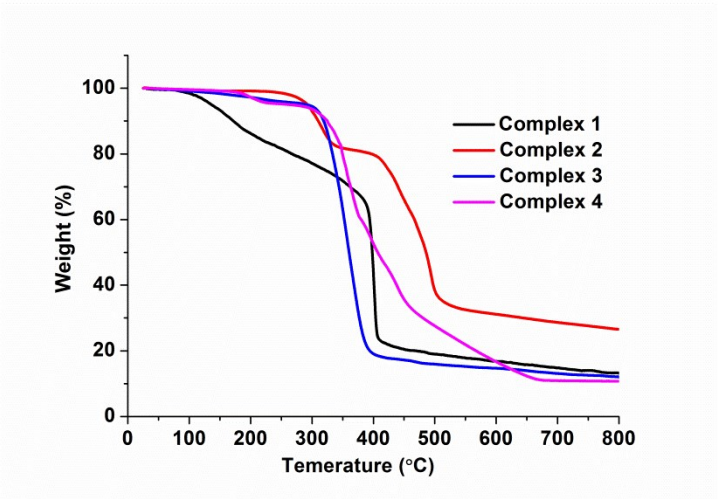


Fig. S3 The thermal curves of complexes **1**-**4**.

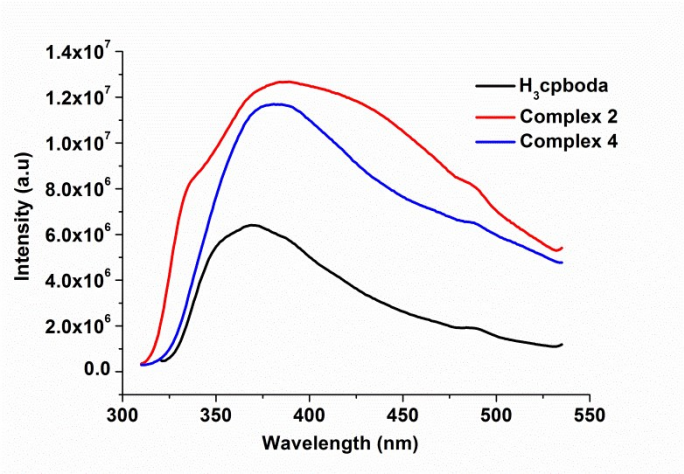


Fig. S4 The solid-state emission spectra of **2** and **4** as well as H_3cpboda at room temperature

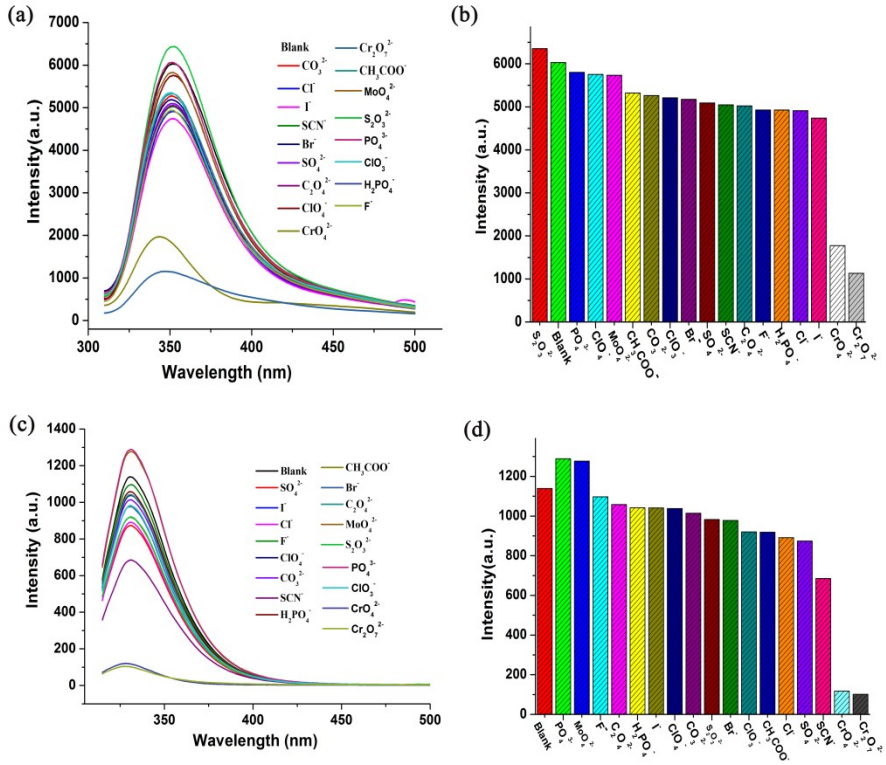
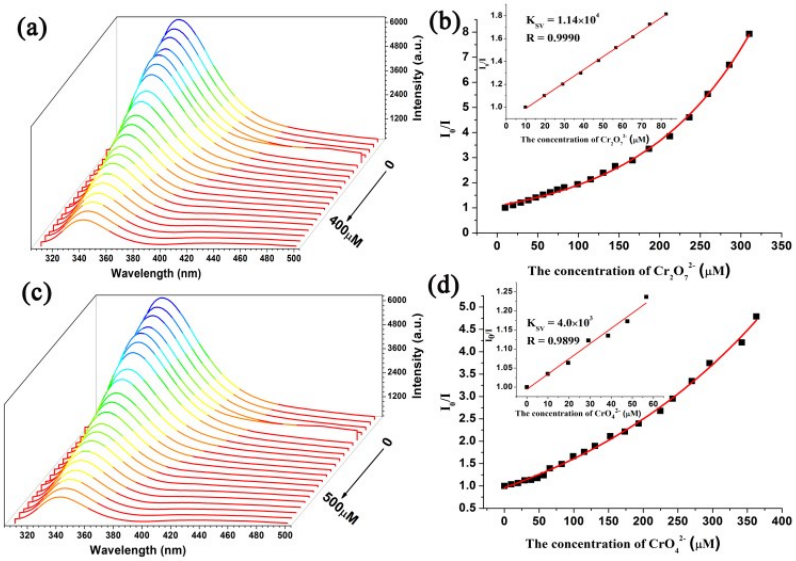


Fig. S5 The luminescence intensities of complexes **2** (a) and (b), **4** (c) and (d), which were dispersed in the aqueous solution of different anions.



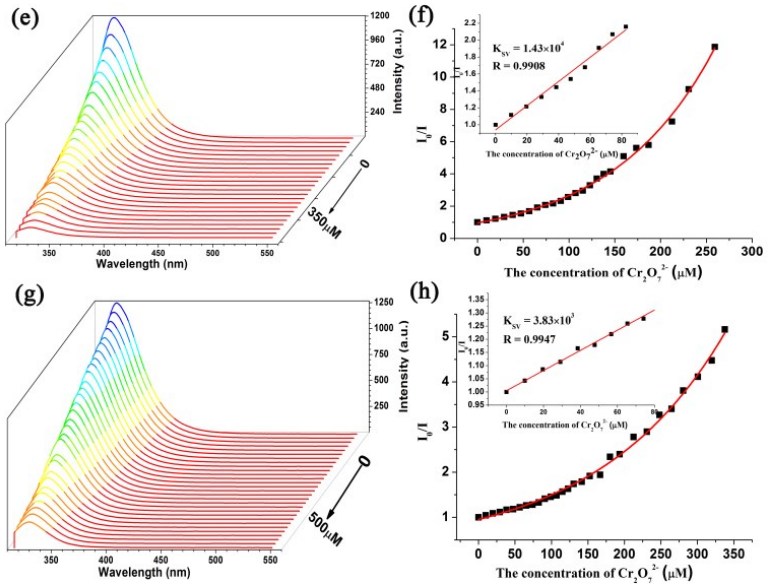
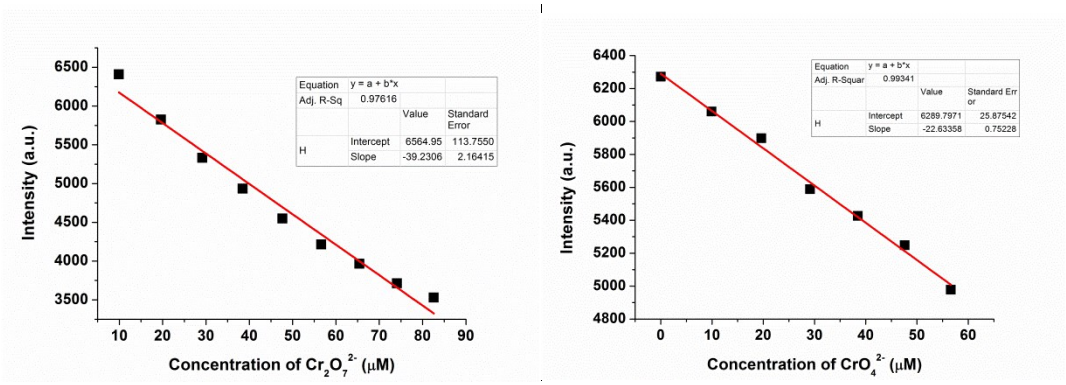
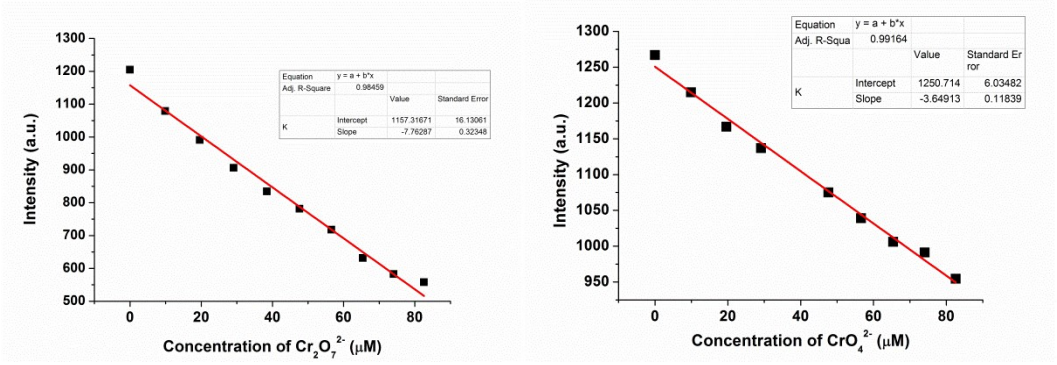


Fig S6 (a) Luminescence responses of **2** (2.00 mg dispersed in 2.00 mL of water) toward different concentrations of $Cr_2O_7^{2-}$ in water, (b) Luminescence responses of **2** toward different concentrations of CrO_4^{2-} in water, (e) Luminescence responses of **4** (2.00 mg dispersed in 2.00 mL of water) toward different concentrations of $Cr_2O_7^{2-}$in water, luminescence responses of **4** toward different concentrations of CrO_4^{2-}in water, (b) Stern–Volmer plot of I_0/I versus $Cr_2O_7^{2-}$ concentration in an aqueous suspension of **2**. (d) Stern–Volmer plot of I_0/I versus CrO_4^{2-} concentration in an aqueous suspension of **2**. (f) Stern–Volmer plot of I_0/I versus $Cr_2O_7^{2}$ concentration in an aqueous suspension of **4**. (h) Stern–Volmer plot of I_0/I versus CrO_4^{2-} concentration in an aqueous suspension of **4.**



(a) (b)



(c) (d)

Fig. S7 Linear region of fluorescence intensity suspensions in water upon incremental addition of $Cr_2O_7^{2-}$ (a) and

CrO_4^{2-} (b) in complex **2**, $Cr_2O_7^{2-}$ (c) and CrO_4^{2-} (d) in complex **4**.

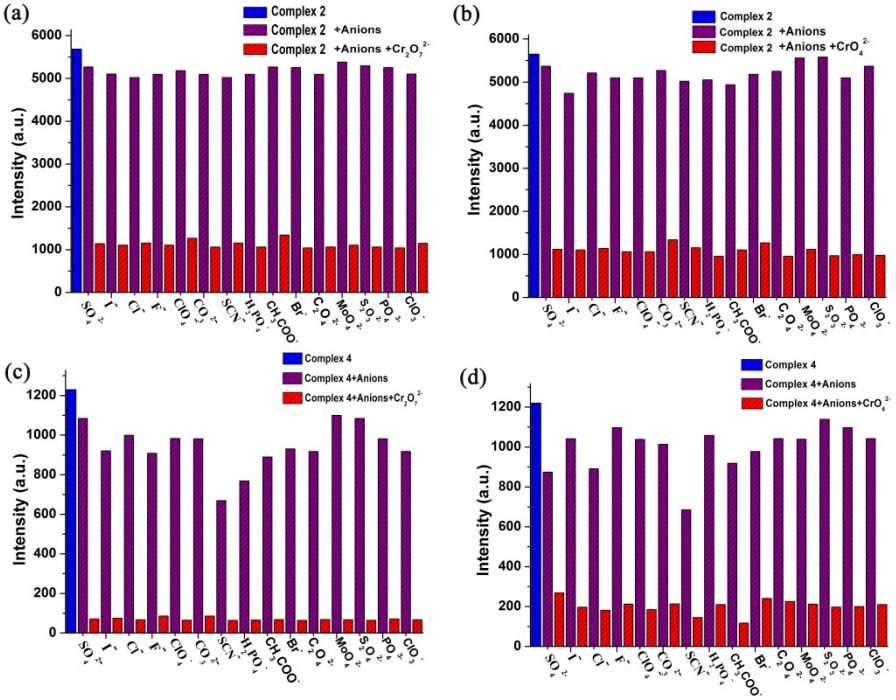


Fig. S8 (a) Interference study of **2** for $Cr_2O_7^{2-}$ anions in the presence of different anions. (b) Interference study of **2** for CrO_4^{2-} anions in the presence of different anions. (c) Interference study of **4** for $Cr_2O_7^{2-}$ anions in the presence of different anions. (d) Interference study of **4** for CrO_4^{2-} anions in the presence of different anions.

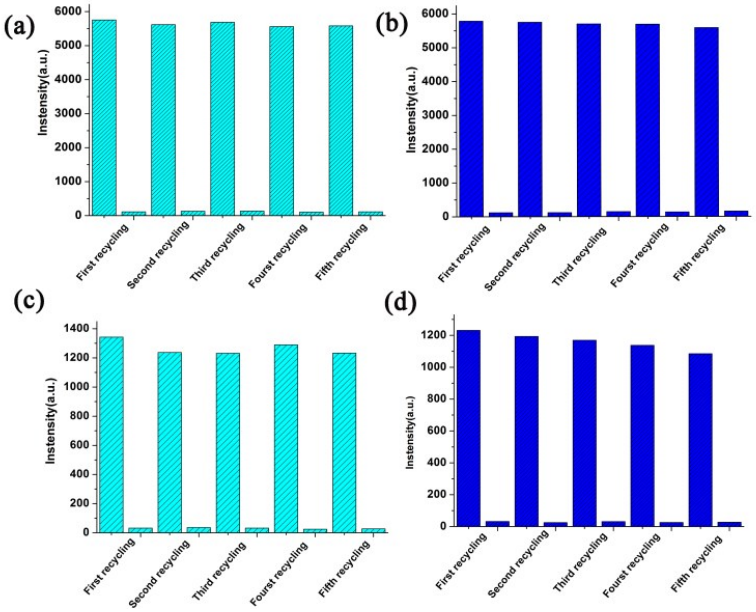
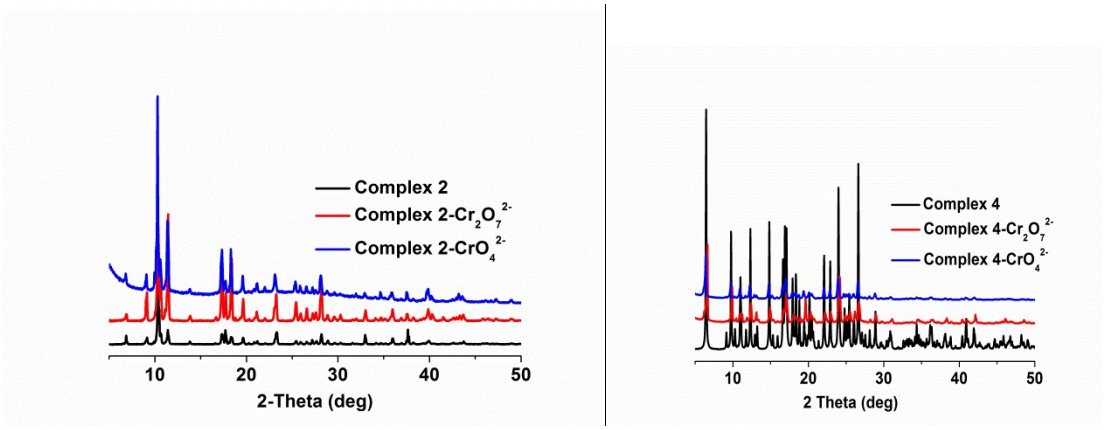


Fig. S9 The luminescence intensity of complexes **2** and **4** for the recognition of $Cr_2O_7^{2-}$ (a) in **2**, (c) in **4**, CrO_4^{2-} (b) in **2**, (d) in **4,** after five recycling processes.



(a) (b)

Fig. S10 The PXRD patterns of simulated complexes **2** and **4** , the PXRD patterns of five cycle tests of **2** and **4** sense $Cr_2O_7^{2-}$ and CrO_4^{2-} anions.

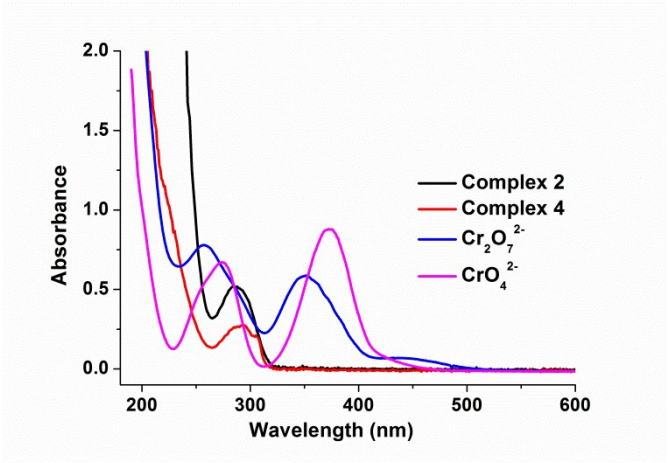


Fig.S11 Liquid UV-vis spectra of complexes **2** and **4**, $Cr_2O_7^{2-}$ and CrO_4^{2-} in the aqueous solution.

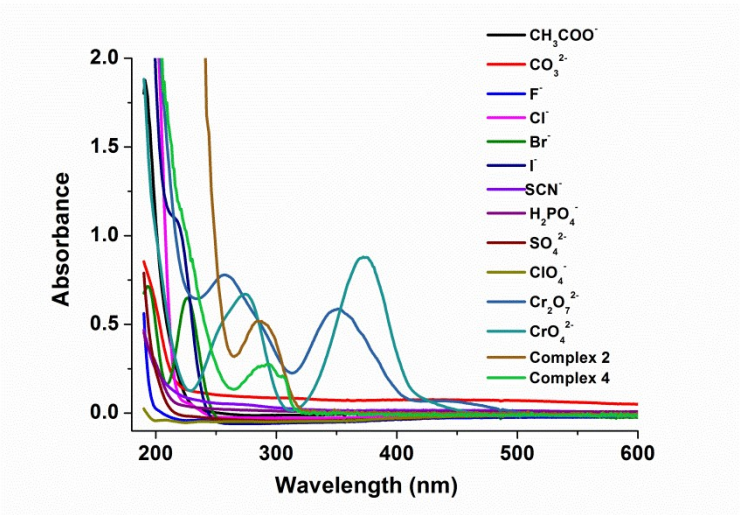


Fig. S12 Liquid UV-vis spectra of complexes **2** , **4** and anions in the aqueous solution

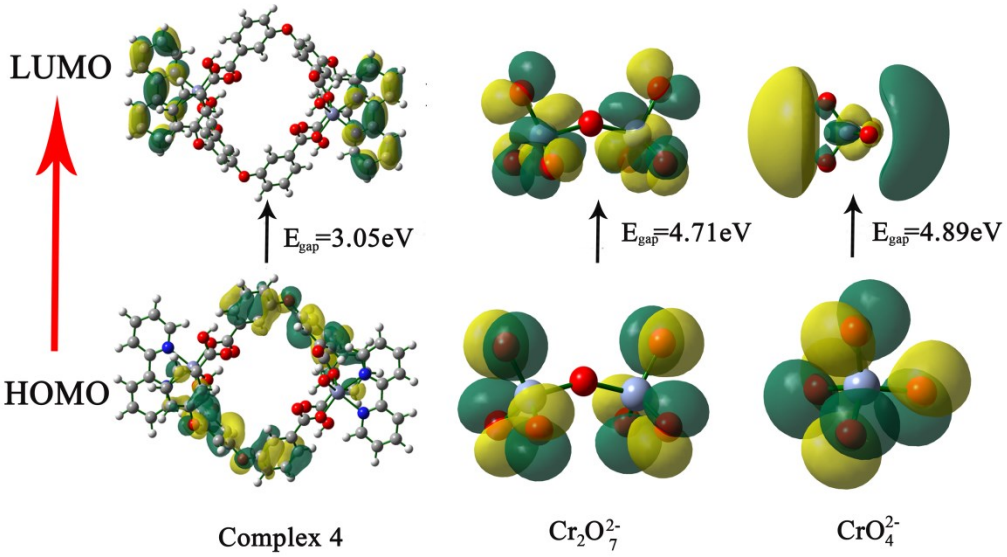


Fig. S13 HOMO and LUMO energies (eV) for the complex 4, $Cr_2O_7^{2-}$ and CrO_4^{2-}.

Table S1 Crystal data and structure refinement for complexes **1 – 4**

	1	2	3	4
CCDC	1955193	1955196	1955195	1955194
Formula	$C_{54}H_{58}N_4Ni_3O_{24}$[+solvent=($C_3H_7NO$)·2(HCOOH)·2($H_2O$)]	$C_{54}H_{58}N_4Zn_3O_{24}$[+solvent=($C_3H_7NO$)·3(HCOOH)·3($H_2O$)]	$C_{105}H_{83}N_{21}Ni_3O_{19}$	$C_{62}H_{44}N_4O_{18}Zn_2$
M_r	1524.35	1608.37	2119.05	1263.75
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
space group	*C*2/*c*	*C*2/*c*		
Temperature(K)	296 (2)	300(2)	296 (2)	300(2)
Size	0.25×0.20×0.15	0.20×0.20×0.10	0.20×0.15×0.10	0.25×0.25×0.20
a (Å)	26.838 (8)	26.833 (3)	13.4660 (6)	10.0734 (3)
b (Å)	16.004 (4)	16.3490 (18)	13.6070 (6)	10.7439 (3)
c (Å)	19.922 (6)	20.321 (2)	13.7158 (6)	13.9706 (4)
α(°)	90	90	97.812 (2)	80.340 (1)
β (°)	128.187 (6)	130.554 (3)	103.166 (2)	79.996 (1)
γ(°)	90	90	94.058 (2)	64.717 (1)
V (Å^3)	6727 (4)	6773.3 (13)	2410.88 (19)	1338.92 (7)
Z	4	4	1	1
D_x/Mg m^{-3}	1.505	1.577	1.460	1.567
μ (mm^{-1})	0.92	1.15	0.66	0.98
R_{int}	0.068	0.038	0.035	0.039
GOF	1.02	1.04	1.00	1.07

F_{000}	3176.0	3336.0	1096.0	648.0
R_1 [$I > 2\sigma(I)$]	0.057	0.076	0.057	0.049
wR_2 [$I > 2\sigma(I)$]	0.154	0.276	0.150	0.104
$\Delta\rho_{max}$ ($eÅ^{-3}$)	0.52	1.65	0.73	0.55
$\Delta\rho_{min}$ ($eÅ^{-3}$)	-0.40	-0.185	-0.93	-0.66

Table S2 Comparison of various CPs sensors for the detection of Cr(VI).

	CPs-based fluorescent Materials	Analyte	Quenching constant (K_{SV}, M^{-1})	Detection Limits (LOD, μM)	Media	Ref.
1	$\{[Zn_2(TPOM)(NH_2\text{-}BDC)_2]\cdot 4H_2O\}_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	7.59×10^3, 4.45×10^3	3.9/4.8	DMF	***S1***
	$[Zn(btz)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	4.23×10^3, 3.19×10^3	2/10	water	
2	$[Zn(ttz)H_2O]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.19×10^3, 2.35×10^3	2/20	water	***S2***
3	$[Zn_2(TPOM)(NH_2\text{-}BDC)_2]\cdot 4H_2O$	($Cr_2O_7^{2-}$/CrO_4^{2-})	7.59×10^3, 4.45×10^3	3.9/4.8	DMF	***S3***
4	$Eu(CBIP)(HCOO)(H_2O)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.76×10^3, 1.54×10^3	1.0/1.2	water	***S4***
	$[Cd(\mu_3\text{-Hcpboda})(1,4\text{-bib})]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.62×10^4, 7.61×10^3	2.29/3.91	water	
5	$\{[Cd_3(\mu_4\text{-cpboda})_2(\mu_{1,1}\text{-}OH_2)_2(phen)_2]\cdot 2DMF\cdot 1.5H_2O\}_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.38×10^4, 1.43×10^4	4.27/4.4	water	***S5***
6	$[Cd(4\text{-tkpvb})(5\text{-tert-BIPA})]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.5×10^4, 4.78×10^4	0.12/0.08	water	***S6***
7	$[Zn(\mu_3\text{-Hcpota})(phen)]_n\cdot nH_2O$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1×10^4, 3.51×10^3	3.62/8.06	water	***S7***
	$[Zn(IPA)(L)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.37×10^3, 1.0×10^3	12.0/18.3	water	
8	$[Cd(IPA)(L)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.91×10^3, 1.20×10^3	2.26/2.52	water	***S8***
	$\{[Zn_3(\mu_4\text{-cpboda})_2(\mu_2\text{-}H_2O)_2(DMF)_2(H_2O)_2]\cdot 3DMF\cdot 4HCOOH\}_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.14×10^4, 4.0×10^3	1.73/3.12	water	
9						**This work**
	$[Zn(Hcpboda)(2,2bipy)(H_2O)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.40×10^4, 3.83×10^3	3.04/5.33	water	

Tables S3. Selected bond lengths [Å] and angles [°] for complexes 1-4.

Complex 1

Ni1—O6	2.023 (3)	Ni2—O5	2.025 (3)
Ni1—O6^{i}	2.023 (3)	Ni2—O1	2.029 (4)
Ni1—O2	2.033 (3)	Ni2—O10	2.053 (4)
Ni1—O2^{i}	2.033 (3)	Ni2—O11	2.046 (3)
Ni1—O9	2.095 (3)	Ni2—O9	2.072 (3)
Ni1—O9^{i}	2.095 (3)	Ni2—O7	2.079 (3)
O6—Ni1—O6^{i}	180.0	O2—Ni1—O9^{i}	88.45 (13)
O6—Ni1—O2	90.98 (13)	O2^{i}—Ni1—O9^{i}	91.55 (13)

O6^{i}—Ni1—O2	89.02 (13)	O9—Ni1—O9^{i}	180.0
O6—Ni1—O2^{i}	89.02 (13)	O5—Ni2—O1	94.51 (15)
O6^{i}—Ni1—O2^{i}	90.98 (13)	O5—Ni2—O10	89.34 (17)
O2—Ni1—O2^{i}	180.00 (9)	O1—Ni2—O10	173.23 (15)
O6—Ni1—O9	95.04 (13)	O5—Ni2—O11	85.40 (13)
O6^{i}—Ni1—O9	84.96 (13)	O1—Ni2—O11	88.44 (13)
O2—Ni1—O9	91.55 (13)	O10—Ni2—O11	86.32 (15)
O2^{i}—Ni1—O9	88.45 (13)	O5—Ni2—O9	91.38 (13)
O6—Ni1—O9^{i}	84.96 (13)	O1—Ni2—O9	94.71 (13)
O6^{i}—Ni1—O9^{i}	95.04 (13)	O10—Ni2—O9	90.76 (14)
O11—Ni2—O7	91.65 (13)	O11—Ni2—O9	175.67 (12)
O9—Ni2—O7	91.57 (12)	O5—Ni2—O7	177.05 (13)
O10—Ni2—O7	90.63 (16)	O1—Ni2—O7	85.24 (14)
Ni2—O9—Ni1	113.16 (14)		

Complex 2

Zn1—O6	2.1305 (16)	Zn2—O1	2.134 (2)
Zn1—O6^{i}	2.1306 (16)	Zn2—O11	2.1535 (19)
Zn1—O2	2.1467 (17)	Zn2—O5	2.1680 (18)
Zn1—O2^{i}	2.1468 (17)	Zn2—O7	2.192 (2)
Zn1—O9^{i}	2.2627 (17)	Zn2—O10	2.182 (2)
Zn1—O9	2.2628 (17)	Zn2—O9	2.2514 (15)
O6—Zn1—O6^{i}	180.0	O1—Zn2—O11	88.15 (8)
O6—Zn1—O2	91.34 (8)	O1—Zn2—O5	94.55 (8)
O6^{i}—Zn1—O2	88.66 (8)	O11—Zn2—O5	87.46 (8)
O6—Zn1—O2^{i}	88.66 (8)	O1—Zn2—O7	84.73 (10)
O6^{i}—Zn1—O2^{i}	91.34 (8)	O11—Zn2—O7	94.20 (8)
O2—Zn1—O2^{i}	180.00 (5)	O5—Zn2—O7	178.16 (8)
O6—Zn1—O9^{i}	87.54 (7)	O1—Zn2—O10	170.10 (9)
O6^{i}—Zn1—O9^{i}	92.46 (7)	O11—Zn2—O10	87.06 (8)
O2—Zn1—O9^{i}	89.49 (7)	O5—Zn2—O10	93.89 (8)
O2^{i}—Zn1—O9^{i}	90.51 (7)	O7—Zn2—O10	86.99 (9)
O6—Zn1—O9	92.46 (7)	O1—Zn2—O9	94.12 (7)

O6^{i}—Zn1—O9	87.54 (6)	O11—Zn2—O9	177.20 (7)
O2—Zn1—O9	90.51 (7)	O5—Zn2—O9	90.72 (7)
O2^{i}—Zn1—O9	89.49 (7)	O7—Zn2—O9	87.65 (7)
O9^{i}—Zn1—O9	180.0	O10—Zn2—O9	90.95 (7)

Complex 3

Ni1—N4i	2.0809 (18)	Ni2—N9	2.0399 (17)
Ni1—N8ii	2.0987 (16)	Ni2—N9^{iv}	2.0399 (17)
Ni1—O9iii	2.1045 (15)	Ni2—O7	2.0902 (15)
Ni1—N1	2.1047 (17)	Ni2—O7^{iv}	2.0903 (15)
Ni1—N5	2.1054 (16)	Ni2—O5	2.0974 (15)
Ni1—O1	2.1431 (15)	Ni2—O5^{iv}	2.0974 (15)
N4^{i}—Ni1—N8^{ii}	90.62 (7)	N4^{i}—Ni1—O1	86.64 (7)
N4^{i}—Ni1—O9^{iii}	98.92 (7)	N8^{ii}—Ni1—O1	87.25 (6)
N8^{ii}—Ni1—O9^{iii}	94.57 (6)	O9^{iii}—Ni1—O1	174.12 (6)
N4^{i}—Ni1—N1	175.34 (7)	N1—Ni1—O1	88.80 (7)
N8^{ii}—Ni1—N1	88.21 (7)	N5—Ni1—O1	93.18 (6)
O9^{iii}—Ni1—N1	85.67 (7)	N9—Ni2—N9^{iv}	180.0
N4^{i}—Ni1—N5	87.48 (7)	N9—Ni2—O7	87.72 (7)
N8^{ii}—Ni1—N5	178.03 (7)	N9^{iv}—Ni2—O7	92.27 (7)
O9^{iii}—Ni1—N5	85.18 (7)	N9—Ni2—O7^{iv}	92.27 (7)
N1—Ni1—N5	93.73 (7)	N9^{iv}—Ni2—O7^{iv}	87.73 (7)
O7—Ni2—O7^{iv}	180.0	N9—Ni2—O5^{iv}	91.57 (7)
N9—Ni2—O5	88.43 (7)	N9^{iv}—Ni2—O5^{iv}	88.44 (7)
N9^{iv}—Ni2—O5	91.57 (7)	O7—Ni2—O5^{iv}	89.41 (6)
O7—Ni2—O5	90.60 (6)	O7^{iv}—Ni2—O5^{iv}	90.60 (6)
O7^{iv}—Ni2—O5	89.40 (6)	O5—Ni2—O5^{iv}	180.0

Complex 4

Zn1—O7^{i}	1.994 (2)	Zn1—N2	2.115 (2)
Zn1—O9	2.039 (2)	Zn1—N1	2.159 (2)
Zn1—O3	2.050 (2)		
O7^{i}—Zn1—O9	94.23 (9)	O3—Zn1—N2	104.52 (9)

O7^{i}—Zn1—O3	95.15 (10)	O7^{i}—Zn1—N1	170.31 (10)
O9—Zn1—O3	139.75 (9)	O9—Zn1—N1	86.21 (9)
O7^{i}—Zn1—N2	94.41 (10)	O3—Zn1—N1	90.70 (9)
O9—Zn1—N2	113.65 (9)	N2—Zn1—N1	76.61 (10)

Symmetry codes: for complex 1: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*, *z*-1/2; (iii) *x*, -*y*, *z*+1/2. For complex 2: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*, *z*-1/2; (iii) *x*, -*y*, *z*+1/2. For complex **3**: (i) *x*, *y*+1, *z*; (ii) *x*, *y*, *z*-1; (iii) -*x*+1, -*y*+1, -*z*; (iv) -*x*, -*y*, -*z*-1; (v) -*x*-1, -*y*, -*z*-1; (vi) -*x*, -*y*+1, -*z*+1; (vii) *x*, *y*-1, *z*; (viii) *x*, *y*, *z*+1. For complex 4: (i) -*x*+2, -*y*, -*z*+1.

Tables S4. Hydrogen bonds in crystal packing [Å, °] of complexes **1**, **2** and **4**.

Complex 1

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O10—H10*B*···O12	0.82	2.17	2.923 (11)	154
O10—H10*A*···O10^{ii}	0.82	2.56	3.062 (14)	121
O9—H9*B*···O12	0.82	2.04	2.691 (11)	136
O9—H9*B*···O2^{i}	0.82	2.40	2.891 (8)	120
O9—H9*A*···O8	0.82	1.78	2.518 (8)	148

Complex 3

O7—H7*A*···O6	0.82	1.86	2.586 (2)	148
O7—H7*B*···O2^{i}	0.94	1.87	2.806 (2)	173

Complex 4

O6—H6···O4^{i}	0.82	1.83	2.643 (3)	173
O9—H9*A*···O4^{ii}	0.82	2.07	2.799 (2)	148
O9—H9*B*···O8^{iii}	0.82	1.83	2.645 (2)	171

Symmetry codes: For complex 1 (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) -*x*, *y*, -*z*+1/2; For complex 2: (i) *x*, *y*, *z*-1; For complex 4: (i) *x*, *y*+1, *z*; (ii) -*x*+1, -*y*, -*z*+1; (iii) *x*-1, *y*, *z*.

Table S5 LOD calculations for $Cr_2O_7^{2-}$ and CrO_4^{2-}

		Complex **2**		Complex **4**	
	Blank	$Cr_2O_7^{2-}$	CrO_4^{2-}	$Cr_2O_7^{2-}$	CrO_4^{2-}
Fluorescence Intensity	1	6493	6495	1243	1274
	2	6473	6467	1226	1261
	3	6433	6429	1245	1277

	4	6467	6464	1227	1262
	5	6437	6437	1237	1265
Standard deviation (σ)		22.64	23.53	7.88	6.49
Slope (m)		39.23μM	22.63 μM	7.76μM	3.65 μM
Detection limit (3σ/m)		1.73μM (0.508ppm)	3.12μM (0.605ppm)	3.04 μM (0.890ppm)	5.33μM (1.03ppm)

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