Supporting Information

Structural diversity, magnetic property, or luminescence sensing of Co(II) and Cd(II) coordination polymers derived from designed 3,3'-((5-carboxy-1,3-phenylene)bis(oxy))dibenzoic acid

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Tables S1. Selected bond lengths [Å] and angles [°] for complexes 1-5.

Complex 1

Co1—O4	2.050 (3)	Co2—O1^{i}	2.030 (2)
Co1—O2	2.054 (2)	Co2—O1	2.030 (2)
Co1—O5	2.090 (2)	Co2—O3^{i}	2.067 (3)
Co1—N1	2.125 (3)	Co2—O3	2.067 (2)
Co1—N2	2.133 (3)	Co2—O9^{i}	2.199 (2)
Co1—O9	2.188 (2)	Co2—O9	2.199 (2)
O4—Co1—O2	94.67 (10)	O5—Co1—N2	91.06 (10)
O4—Co1—O5	86.31 (10)	N1—Co1—N2	76.16 (11)
O2—Co1—O5	177.53 (10)	O4—Co1—O9	89.54 (9)
O4—Co1—N1	91.46 (11)	O2—Co1—O9	88.78 (9)
O2—Co1—N1	88.05 (10)	O5—Co1—O9	88.96 (8)
O5—Co1—N1	94.20 (10)	N1—Co1—O9	176.74 (10)
O4—Co1—N2	167.14 (10)	N2—Co1—O9	103.01 (10)
O2—Co1—N2	88.47 (10)	O1^{i}—Co2—O1	180.0
O1^{i}—Co2—O3^{i}	89.47 (11)	O3^{i}—Co2—O9^{i}	95.83 (9)
O1—Co2—O3^{i}	90.53 (11)	O3—Co2—O9^{i}	84.17 (9)
O1^{i}—Co2—O3	90.53 (11)	O1^{i}—Co2—O9	87.97 (9)
O1—Co2—O3	89.47 (11)	O1—Co2—O9	92.03 (9)
O3^{i}—Co2—O3	180.0	O3^{i}—Co2—O9	84.17 (9)

O1^{i}—Co2—O9^{i}	92.03 (9)	O3—Co2—O9	95.83 (9)
O1—Co2—O9^{i}	87.97 (9)	O9^{i}—Co2—O9	180.0
C7—O1—Co2	138.3 (2)		

Complex 2

Co1—O5^{i}	2.009 (2)	Co2—N3	2.076 (3)
Co1—O5	2.009 (2)	Co2—N2^{ii}	2.100 (3)
Co1—O9^{i}	2.134 (2)	Co2—O2^{iii}	2.128 (2)
Co1—O9	2.134 (2)	Co2—O1^{iii}	2.165 (3)
Co1—N1	2.189 (3)	Co2—O8	2.332 (3)
Co1—N1^{i}	2.189 (3)	Co2—C7^{iii}	2.479 (4)
Co2—O7	2.036 (2)	O9—Co1—N1	87.68 (9)
O5^{i}—Co1—O5	180.0	O5^{i}—Co1—N1^{i}	89.94 (10)
O5^{i}—Co1—O9^{i}	90.93 (10)	O5—Co1—N1^{i}	90.06 (10)
O5—Co1—O9^{i}	89.06 (10)	O9^{i}—Co1—N1^{i}	87.68 (9)
O5^{i}—Co1—O9	89.07 (10)	O9—Co1—N1^{i}	92.32 (9)
O5—Co1—O9	90.94 (10)	N1—Co1—N1^{i}	180.00 (9)
O9^{i}—Co1—O9	180.0	O7—Co2—N3	94.41 (12)
O5^{i}—Co1—N1	90.06 (10)	O7—Co2—N2^{ii}	101.69 (11)
O5—Co1—N1	89.94 (10)	N3—Co2—N2^{ii}	98.02 (12)
O9^{i}—Co1—N1	92.32 (9)	O9—Co1—N1	87.68 (9)
O7—Co2—O2^{iii}	156.54 (11)	O7—Co2—O8	59.47 (11)
N3—Co2—O2^{iii}	94.96 (11)	N3—Co2—O8	151.37 (11)
N2^{ii}—Co2—O2^{iii}	98.23 (10)	N2^{ii}—Co2—O8	98.69 (11)
O7—Co2—O1^{iii}	97.93 (10)	O2^{iii}—Co2—O8	105.43 (10)
N3—Co2—O1^{iii}	88.90 (12)	O1^{iii}—Co2—O8	83.91 (11)
N2^{ii}—Co2—O1^{iii}	158.58 (10)	O7—Co2—C7^{iii}	127.69 (11)
O2^{iii}—Co2—O1^{iii}	60.84 (9)	N3—Co2—C7^{iii}	90.26 (13)
N2^{ii}—Co2—C7^{iii}	129.16 (11)	O1^{iii}—Co2—C7^{iii}	30.01 (10)
O2^{iii}—Co2—C7^{iii}	30.93 (10)	O8—Co2—C7^{iii}	96.95 (12)

Complex 3

Co1—O6^{ii}	2.049 (4)	Co1—N5	2.145 (6)
Co1—O5	2.084 (5)	Co1—N1	2.142 (5)
Co1—N4^{iii}	2.122 (5)	Co1—O9	2.284 (5)

C33—N4—C32	105.2 (6)	N3—C33—H33	123.7
C33—N4—Co1^{i}	127.5 (5)	C31—C32—N4	110.0 (7)
C32—N4—Co1^{i}	127.4 (5)	C31—C32—H32	125.0
N4—C33—N3	112.6 (6)	N4—C32—H32	125.0
N4—C33—H33	123.7	O6^{ii}—Co1—O5	107.94 (18)
O6^{ii}—Co1—N4^{iii}	89.6 (2)	O5—Co1—N1	87.53 (19)
O5—Co1—N4^{iii}	92.3 (2)	N4^{iii}—Co1—N1	179.2 (2)
O6^{ii}—Co1—N5	165.18 (19)	N5—Co1—N1	87.7 (2)
O5—Co1—N5	86.5 (2)	O6^{ii}—Co1—O9	83.77 (18)
N4^{iii}—Co1—N5	93.1 (2)	O5—Co1—O9	168.20 (18)
O6^{ii}—Co1—N1	89.66 (19)	O5—Co1—N1	87.53 (19)
N4^{iii}—Co1—O9	89.1 (2)	N1—Co1—O9	91.2 (2)
N5—Co1—O9	81.7 (2)		

Complex 4

Cd1—O2	2.2923 (11)	Cd1—N4^{ii}	2.3548 (13)
Cd1—N1	2.3079 (12)	Cd1—O4^{iii}	2.3947 (12)
Cd1—O4^{i}	2.3195 (11)	Cd1—O1	2.5770 (13)
O2—Cd1—N1	95.32 (5)	N4^{ii}—Cd1—O4^{iii}	83.95 (5)
O2—Cd1—O4^{i}	125.50 (4)	O2—Cd1—O1	53.25 (4)
N1—Cd1—O4^{i}	106.50 (4)	N1—Cd1—O1	80.44 (5)
O2—Cd1—N4^{ii}	82.43 (5)	O4^{i}—Cd1—O1	173.02 (4)
N1—Cd1—N4^{ii}	171.63 (4)	N4^{ii}—Cd1—O1	91.83 (5)
O4^{i}—Cd1—N4^{ii}	81.21 (5)	O4^{iii}—Cd1—O1	103.40 (4)
O2—Cd1—O4^{iii}	152.31 (4)	O4^{i}—Cd1—O4^{iii}	75.62 (4)
N1—Cd1—O4^{iii}	94.69 (4)		

Complex 5

Cd1—O4	2.235 (2)	Cd2—O1^{i}	2.218 (2)
Cd1—O2	2.239 (2)	Cd2—O1	2.218 (2)
Cd1—O5	2.284 (2)	Cd2—O3	2.252 (3)
Cd1—N1	2.328 (3)	Cd2—O3^{i}	2.252 (3)
Cd1—O9	2.343 (2)	Cd2—O9	2.396 (2)
Cd1—N2	2.345 (3)	Cd2—O9^{i}	2.396 (2)
O4—Cd1—O2	91.48 (10)	N1—Cd1—O9	169.19 (9)

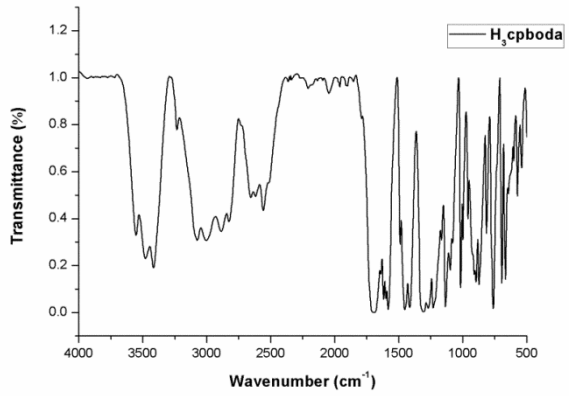
O4—Cd1—O5	82.98 (11)	O4—Cd1—N2	162.59 (10)
O2—Cd1—O5	172.70 (9)	O2—Cd1—N2	94.98 (9)
O4—Cd1—N1	92.07 (10)	O5—Cd1—N2	91.68 (10)
O2—Cd1—N1	90.44 (10)	N1—Cd1—N2	71.77 (10)
O5—Cd1—N1	94.50 (9)	O9—Cd1—N2	97.80 (9)
O4—Cd1—O9	97.93 (9)	$O1^{i}$—Cd2—O1	180.0
O2—Cd1—O9	93.39 (9)	$O1^{i}$—Cd2—O3	89.05 (11)
O5—Cd1—O9	82.71 (8)	O1—Cd2—O3	90.95 (11)
O1—Cd2—$O3^{i}$	89.05 (11)	O3—Cd2—O9	100.03 (9)
O3—Cd2—$O3^{i}$	180.0	$O3^{i}$—Cd2—O9	79.97 (9)
$O1^{i}$—Cd2—O9	85.56 (9)	$O1^{i}$—Cd2—$O9^{i}$	94.44 (9)
O1—Cd2—O9	94.44 (9)	O1—Cd2—$O9^{i}$	85.56 (9)
$O3^{i}$—Cd2—$O9^{i}$	100.03 (9)	O9—Cd2—$O9^{i}$	180.00 (4)

Symmetry codes: for complex1: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*+1, *z*-1/2; (iii) *x*, -*y*+1, *z*+1/2. for complex 2: (i) -*x*+2, -*y*, -*z*; (ii) -*x*+1, *y*+1/2, -*z*+3/2; (iii) -*x*+1, *y*-1/2, -*z*+3/2; (iv) -*x*+1, -*y*, -*z*+3. for complex 3: (i) *x*, *y*-1, *z*; (ii) -*x*+1, -*y*+1, -*z*+1; (iii) *x*, *y*+1, *z*; (iv) -*x*, -*y*, -*z*. for complex 4: (i) *x*+1, *y*+1, *z*+1; (ii) *x*+1, *y*, *z*+1; (iii) -*x*+1, -*y*, -*z*+2; (iv) *x*-1, *y*, *z*-1; (v) *x*-1, *y*-1, *z*-1. for complex 5: (i) -*x*+1/2, -*y*+1/2, -*z*+1; (ii) *x*, -*y*+1, *z*-1/2; (iii) *x*, -*y*+1, *z*+1/2.

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

Complex1	*D*—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
	C6—H6···$O6^{i}$	0.93	2.70	3.584 (4)	160
Complex4	O7—H7*A*···$O1^{i}$	0.82	1.80	2.6102 (17)	171
Complex5	O9—H9*A*···O6	0.84	1.74	2.511 (3)	152

Symmetry codes: for complex1: (i) -*x*+1/2, -*y*+1/2, -*z*+1. for complex 4: (i) *x*+1, *y*, *z*.



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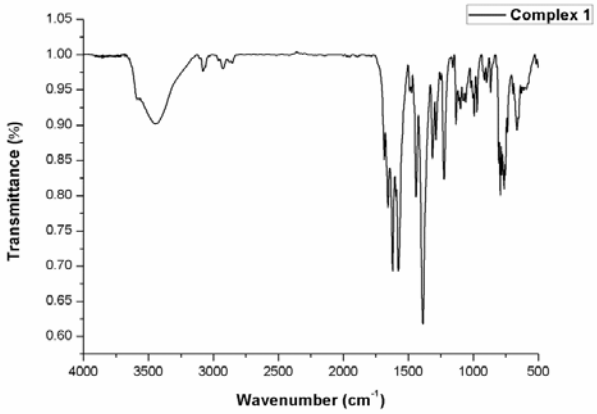

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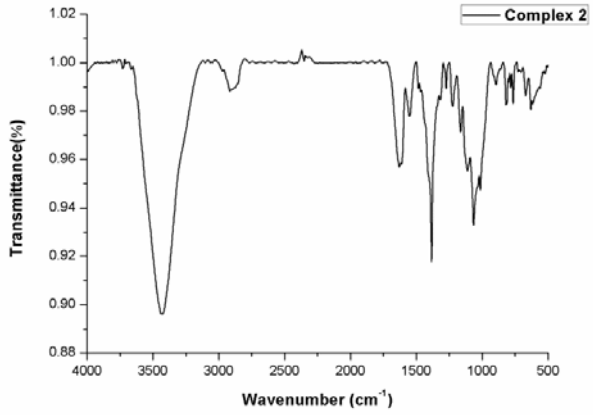

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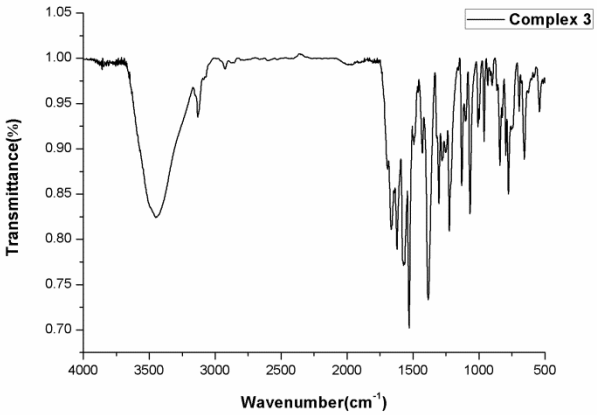

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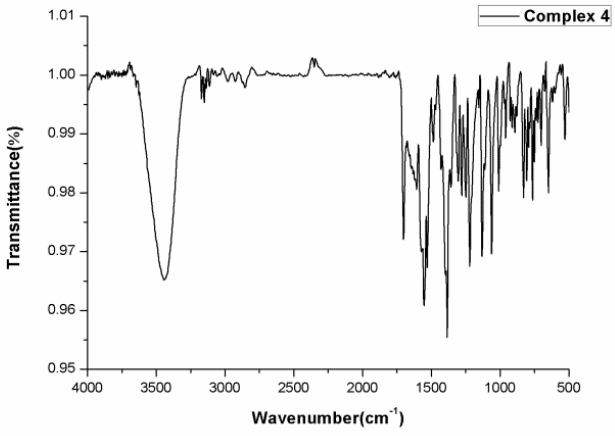
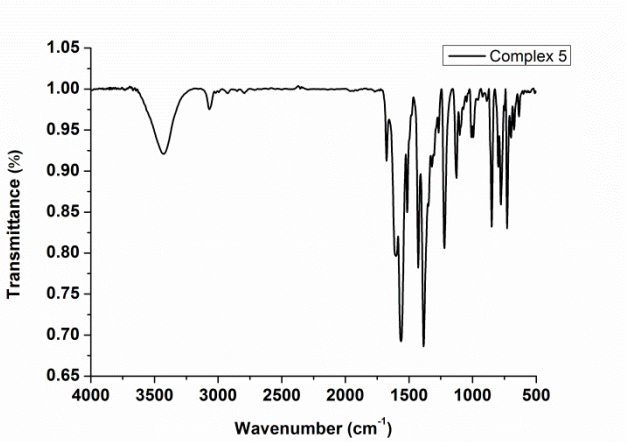
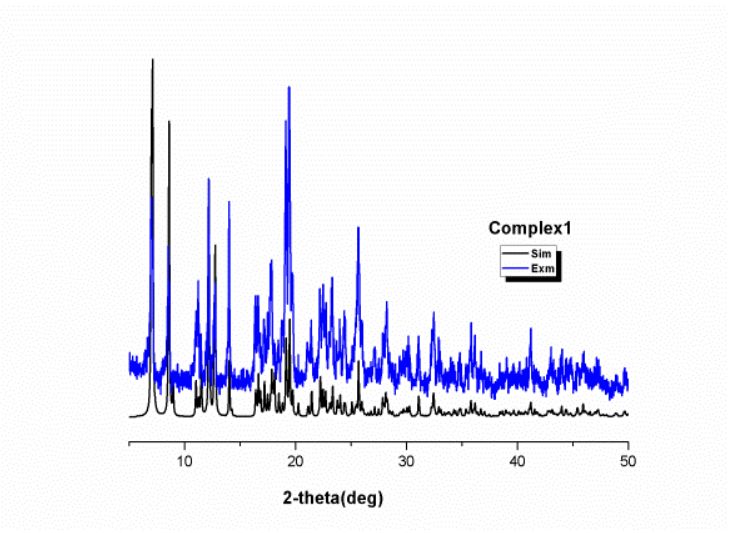


(e)

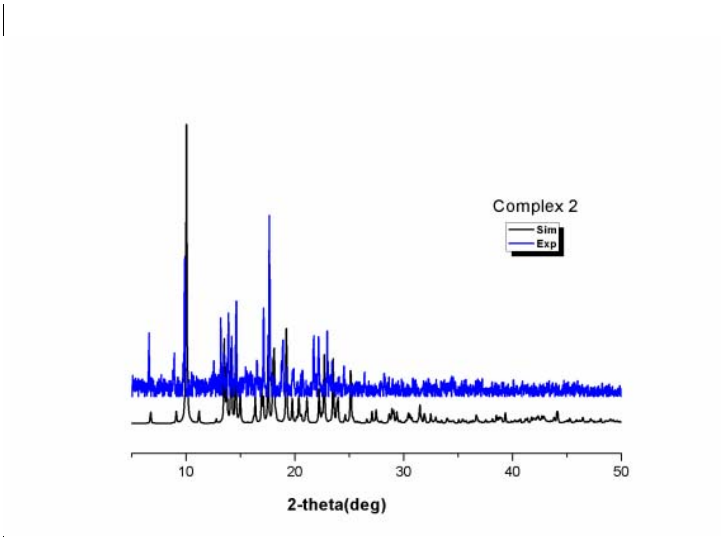


(f)

Fig. S1 The IR spectra of H_3cpboda ligand and complexes **1-5.**



(a)



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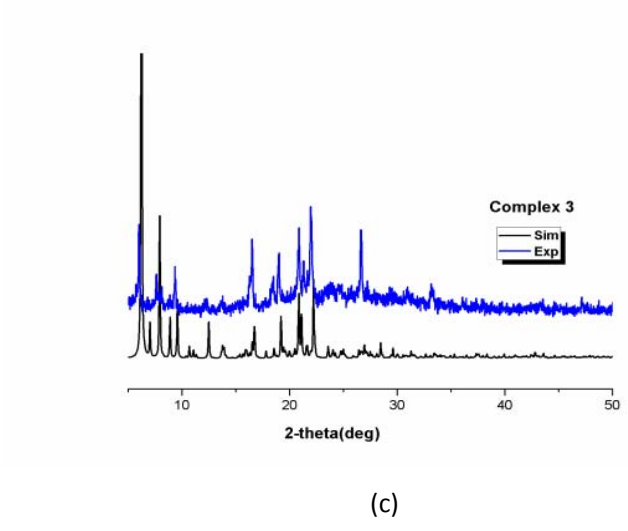

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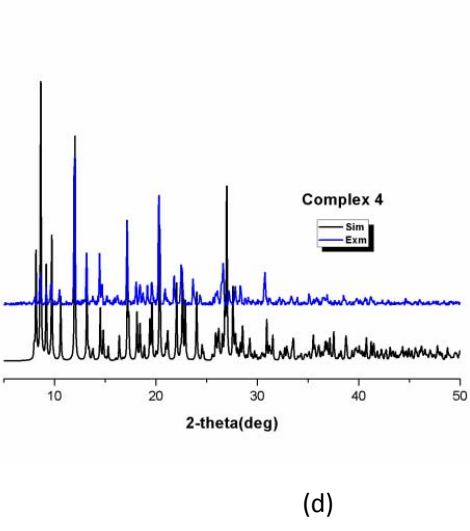

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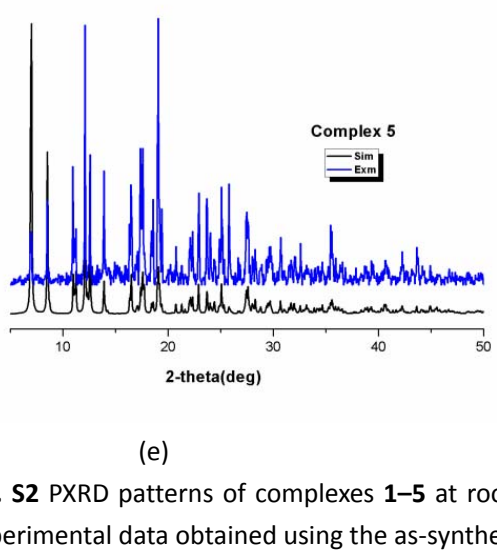


(e)

Fig. S2 PXRD patterns of complexes **1–5** at room temperature. Blue patterns correspond to the experimental data obtained using the as-synthesized bulk samples. Black patterns were simulated from the single crystal X-ray data.

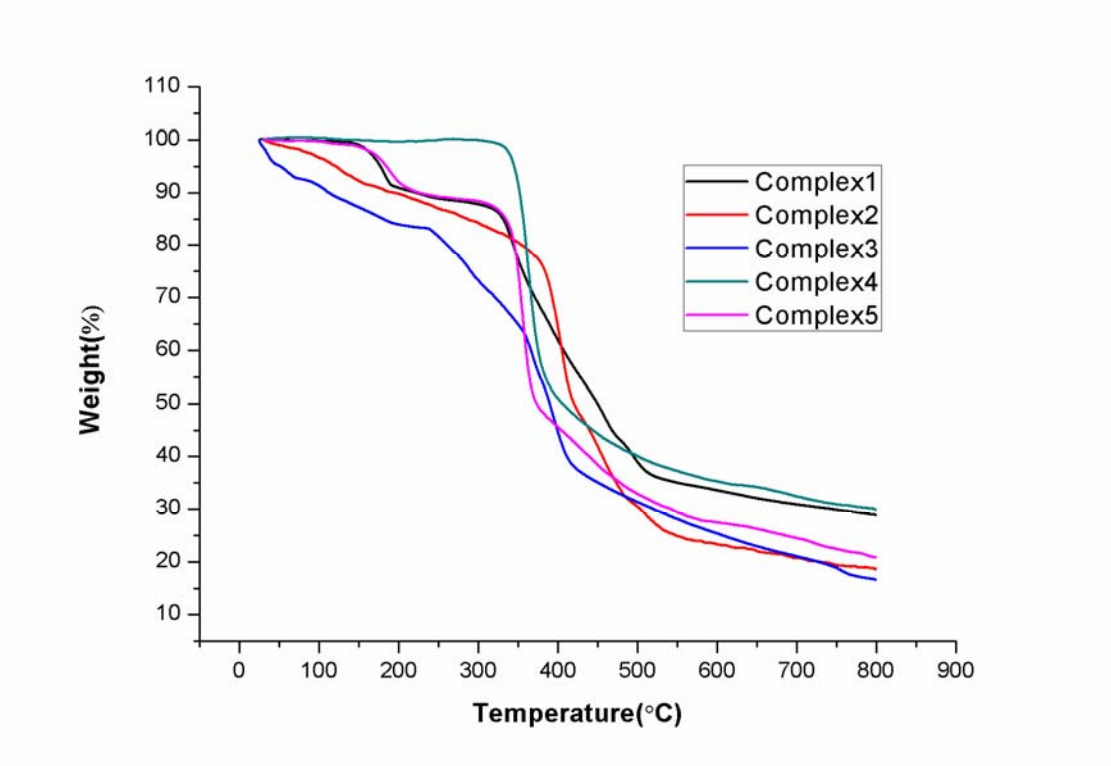


Fig. S3 The thermal curves of complexes **1**-**5**.

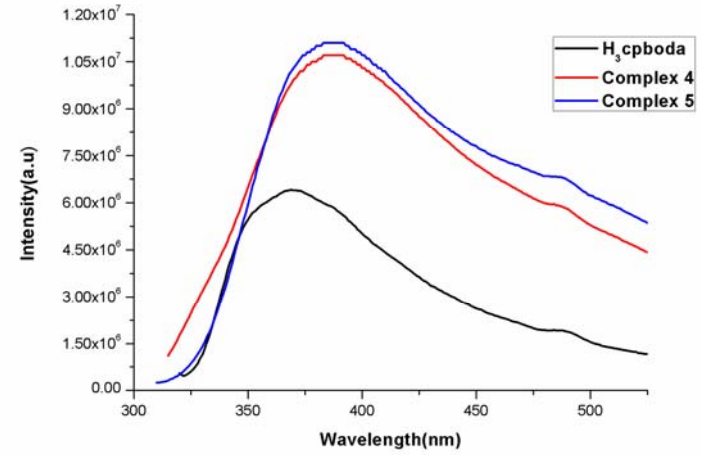


Fig. S4 The solid-state emission spectra of **4** and **5** as well as H_3cpboda at room temperature

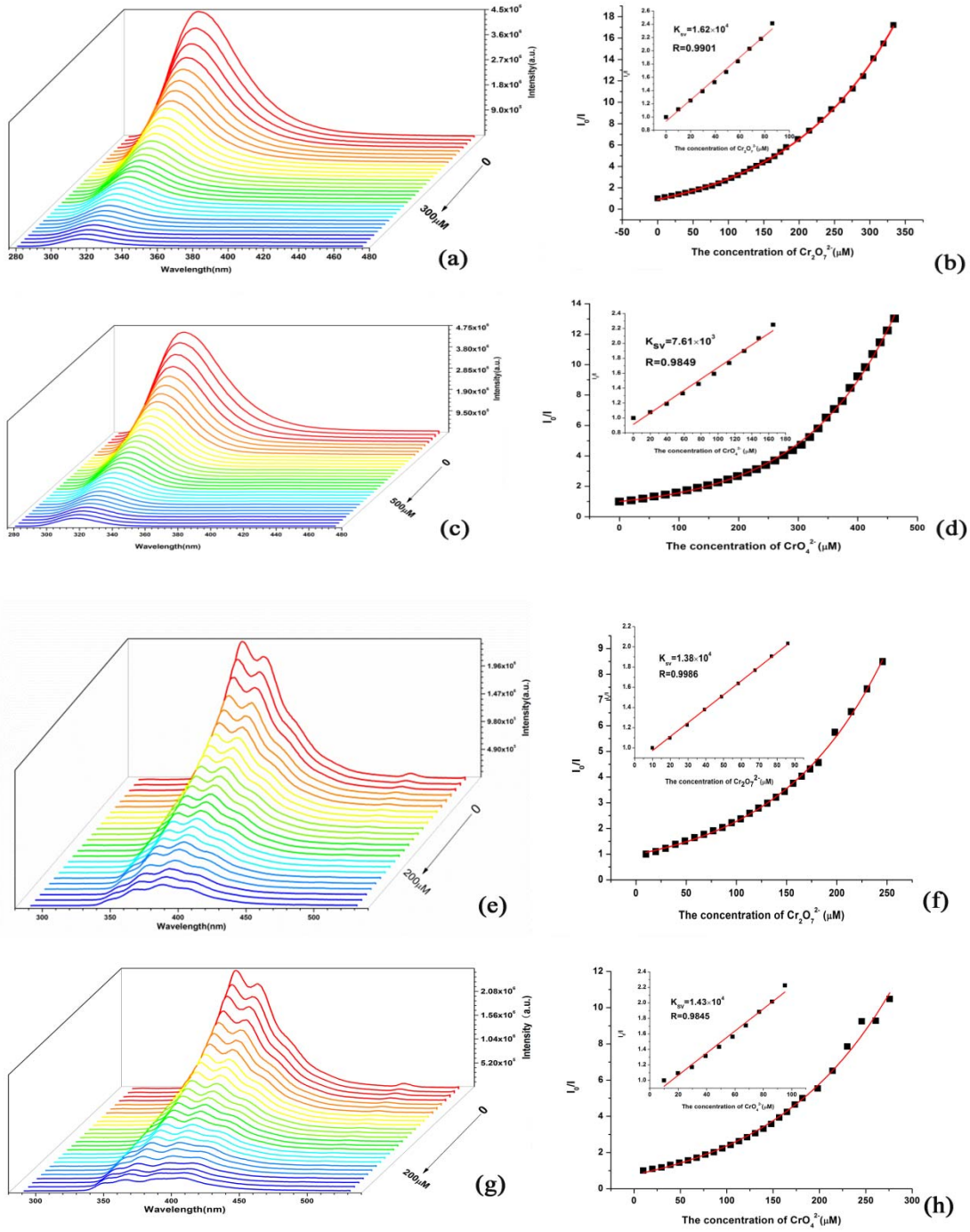


Fig S5 (a) Luminescence responses of **4** (2.00 mg dispersed in 2.00 mL of water) toward different concentrations of $Cr_2O_7^{2-}$ in water, (b) Luminescence responses of **4** toward different concentrations of CrO_4^{2-} in water, (e) Luminescence responses of **5** (2.00 mg dispersed in 2.00 mL of water) toward different concentrations of $Cr_2O_7^{2-}$in water, Luminescence responses of **5** 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 **4**. (d) Stern–Volmer plot of I_0/I versus CrO_4^{2-} concentration in an aqueous suspension of **4**. (f) Stern–Volmer plot of I_0/I versus $Cr_2O_7^{2}$ concentration in an aqueous suspension of **5**. (h) Stern–Volmer plot of I_0/I versus CrO_4^{2-} concentration in an aqueous suspension of **5**.

Section S1: Calculation of Detection Limit for $Cr_2O_7^{2-}$ and CrO_4^{2-}

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 50 µL was added to the water suspension (2 mg complexes **4** and **5** dispersed in 2 ml water, respectively). Fluorescence intensity thus observed for each incremental addition of aqueous $Cr_2O_7^{2-}$/CrO_4^{2-} solution was plotted against the respective increasing concentration of $Cr_2O_7^{2-}$/CrO_4^{2-}. Slop of the curve thus drawn was found to be $Cr_2O_7^{2-}$ =2.97 x 10^4 (R_2 = 0.980) and CrO_4^{2-} = 2.09 x 10^4 (R_2 = 0.991) for complex **4**, $Cr_2O_7^{2-}$ =2.15 x 10^4 (R_2 = 0.979) and CrO_4^{2-} = 1.81 x 10^4 (R_2 = 0.993) for complex **5**. Standard deviation (σ) in the LOD determination for complexes **4** and **5** were calculated from five blank measurements for each LCP. Detection limit (LOD = 3σ/m) was calculated as per an earlier report,[S1,S2] while the findings were tabulated ahead:

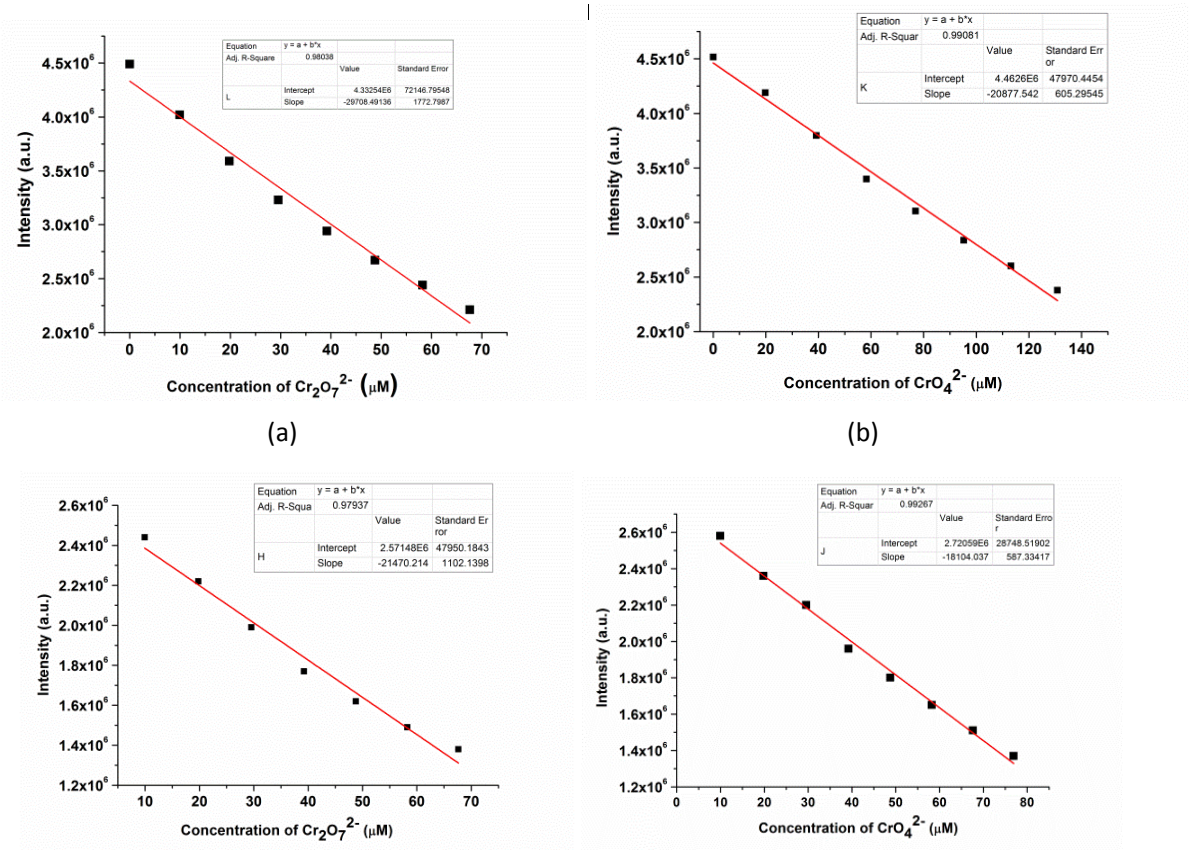


Fig. S6 Linear region of fluorescence intensity suspensions in water upon incremental addition of $Cr_2O_7^{2-}$ (a) and CrO_4^{2-} (b) in complex **4**, $Cr_2O_7^{2-}$ (c) and CrO_4^{2-} (d) in complex **5**.

Table S3 LOD calculations for $Cr_2O_7^{2-}$ and CrO_4^{2-}

		Complex **4**		Complex **5**	
	Blank	$Cr_2O_7^{2-}$	CrO_4^{2-}	$Cr_2O_7^{2-}$	CrO_4^{2-}
Fluorescence Intensity	1	4265900	4339520	2087310	2145350
	2	4258610	4338770	2092910	2170480
	3	4258440	4280000	2054720	2193360
	4	4308690	4311180	2126600	2128070
	5	4293060	4329560	2128070	2180680
Standard deviation (σ)		22737.83	27210.39	30559.27	26552.59
Slope (m)		29708.49 µM	20877.54 µM	21470.21 µM	18104.04 µM
Detection limit (3σ/m)		2.29 Mm	3.91µM	4.27 µM	4.40µM

Table S4 Comparison of various CPs sensors for the detection of $Cr_2O_7^{2-}$/CrO_4^{2-}.

	CPs-based fluorescent Materials	Analyte	Quenching constant (K_{SV}, M^{-1})	Detection Limits (LOD, μM)	Media	Ref.
1	$[Zn(btz)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	4.23×10^3, 3.19×10^3	2/10	water	S3
2	$[Zn(ttz)H_2O]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.19×10^3, 2.35×10^3	2/20	water	
3	$[Zn(IPA)(L)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.37×10^3, 1.0×10^3	12.0/18.3	water	S4
4	$[Cd(IPA)(L)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.91×10^3, 1.20×10^3	2.26/2.52	water	
5	{$[Eu_2L_{1.5}(H_2O)_2EtOH]$·DMF}	$Cr_2O_7^{2-}$	1.53×10^3	10	DMF	S5
6	$[Zn_2(TPOM)(NH_2\text{-}BDC)_2]\cdot4H_2O$	($Cr_2O_7^{2-}$/CrO_4^{2-})	7.59×10^3, 4.45×10^3	3.9/4.8	DMF	S6
7	$Eu(CBIP)(HCOO)(H_2O)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.76×10^3, 1.54×10^3	1.0/1.2	water	S7
8	$[Cd(4\text{-}tkpvb)(5\text{-}tert\text{-}BIPA)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	2.5×10^4, 4.78×10^4	0.12/0.08	water	S8
9	{$[Tb(TATAB)(H_2O)_2]$·NMP·H_2O}$_n$	$Cr_2O_7^{2-}$	11 106	5	water	S9
10	$[Eu_2(tpbpc)_4\cdot CO_3\cdot H_2O]$·DMF·solvent	CrO_4^{2-}	4.85×10^3	0.33	water	S10
11	$[Cd(\mu_3\text{-}Hcpboda)(1,4\text{-}bib)]_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.62×10^4, 7.61×10^3	2.29/3.91	water	This work
12	{$[Cd_3(\mu_4\text{-}cpboda)_2(\mu_{1,1}\text{-}OH_2)_2(phen)_2]$·2DMF·1.5$H_2O$}$_n$	($Cr_2O_7^{2-}$/CrO_4^{2-})	1.38×10^4, 1.43×10^4	4.27/4.4	water	

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; [3] H_2IPA = isophthalic acid; TPOM = tetrakis(4-pyridyloxymethylene)methane, NH_2–BDC = 2-aminoterephthalic acid; H_2CBIP = 5-((2′-cyano-[1,1′-biphenyl]-4-yl)methoxy)isophthalicacid; 4-tkpvb= 1,2,4,5-tetrakis(4-pyridylvinyl)benzene; 5-tert-H2BIPA = 5-tert-butyl-isophthalic acid. H_3TATAB = 4,4′,4′′-s-triazine-1,3,5-triyltri-m-aminobenzoic acid, NMP = N-methyl-2-pyrrolidone; Htpbpc = 4-[4,2;6,4]-terpyridin-4-yl-biphenyl-4-carboxylic acid.

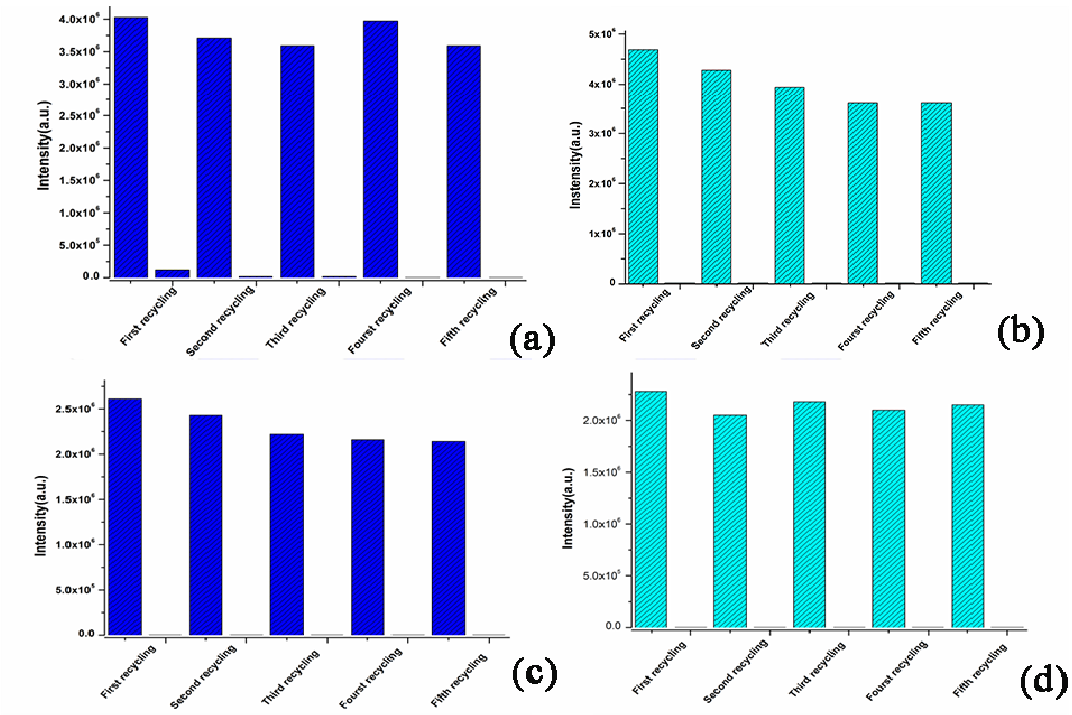
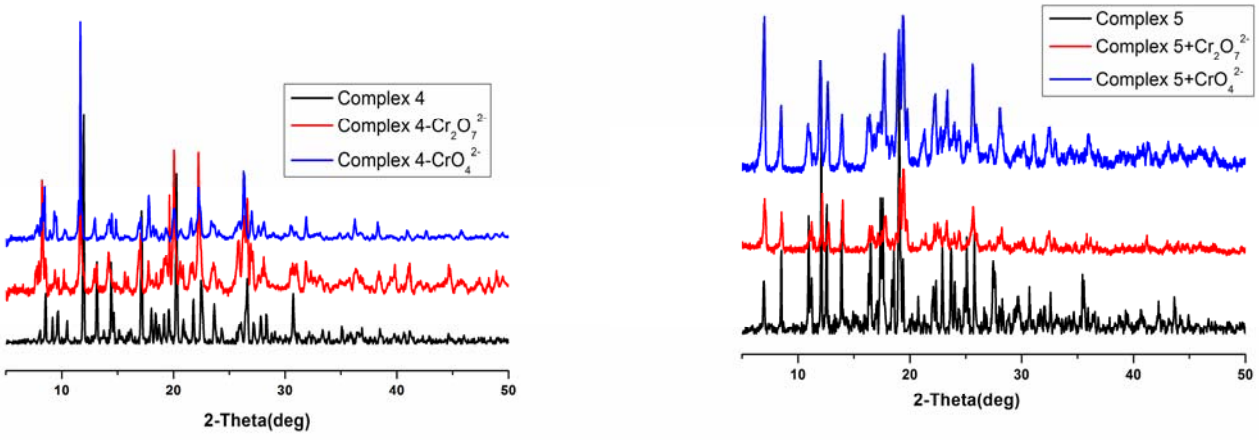
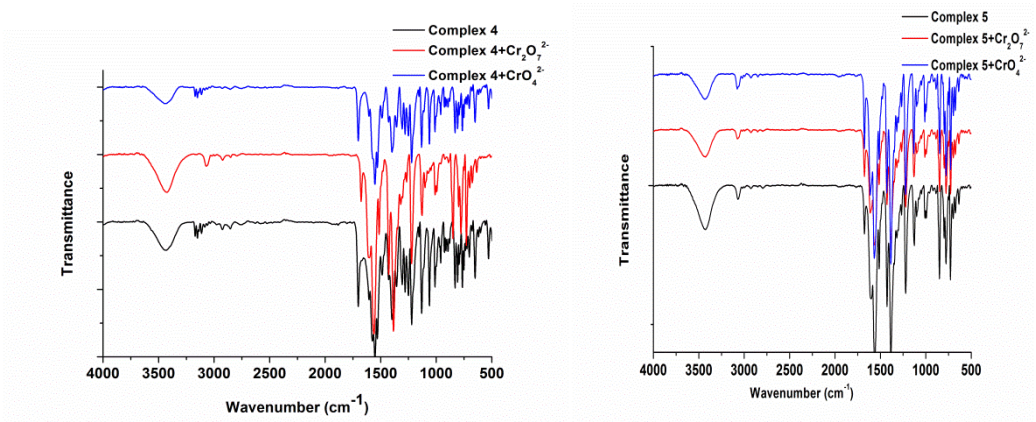


Fig. S7 The luminescence intensity of complex **4** and **5** for the recognition of $Cr_2O_7^{2-}$ (a) in **4**, (c) in **5**, CrO_4^{2-} (b) in **4**, (d) in **5,** after five recycling processes .



(a) (b)

Fig. S8 The PXRD patterns of simulated complexes **4** and **5 ,** the PXRD patterns of **4** and **5** for the recognition of $Cr_2O_7^{2-}$ and CrO_4^{2-} after five recycling processes



(a) (b)

Fig. S9 The IR spectra of complexes **4** and **5**, the IR spectra of **4** and **5** for the recognition of $Cr_2O_7^{2-}$ and CrO_4^{2-} after five recycling processes

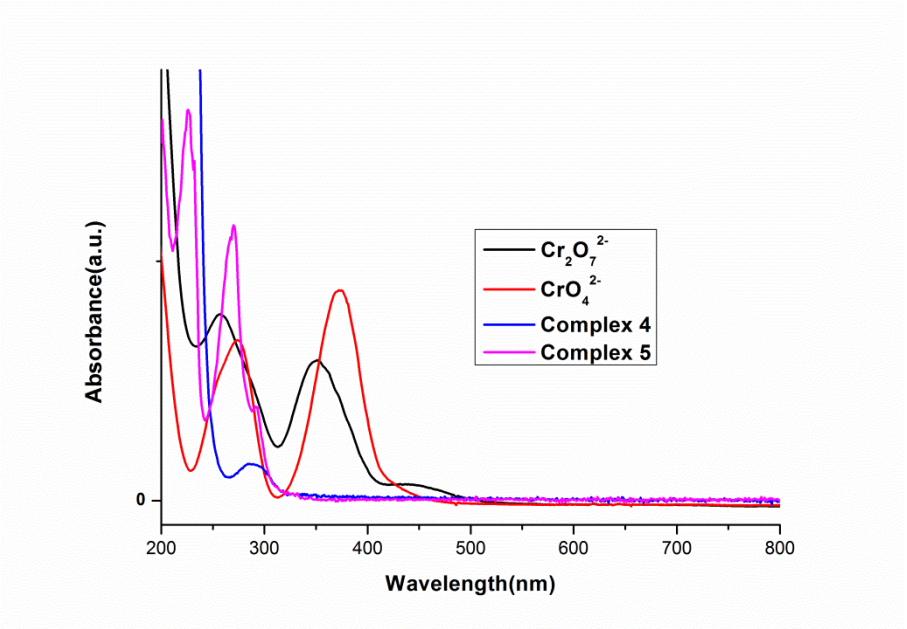
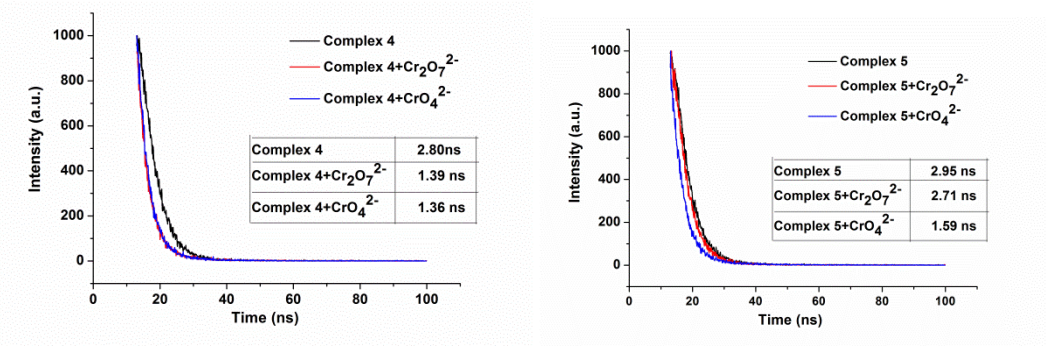
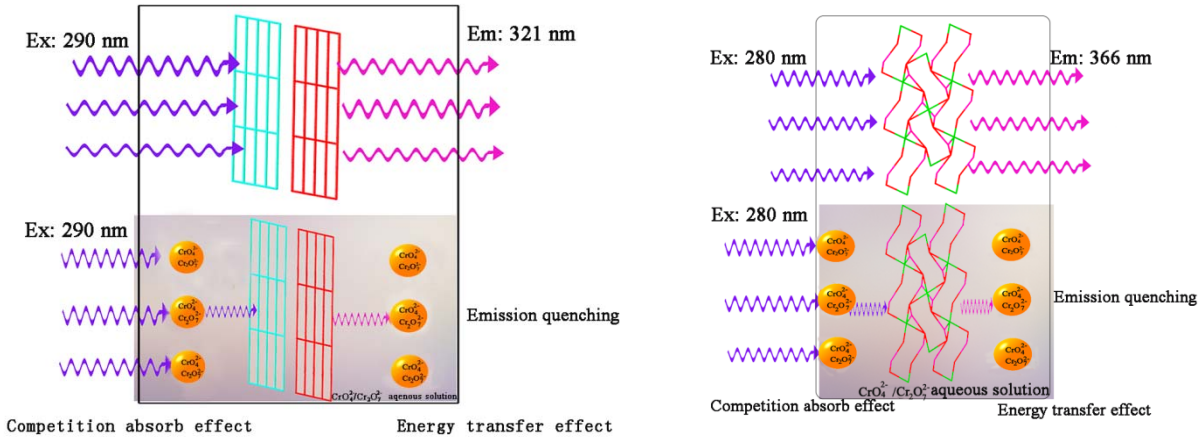


Fig. S10 Liquid UV-vis spectra of complexes **4** and **5**, $Cr_2O_7^{2-}$ and CrO_4^{2-} in the aqueous solution



(a) (b)

Fig. S11 The luminescence decay lifetimes of the complexes **4**, **5** and Cr^{VI} treated materials.



(a) (b)

Figure. S12 The possible quenching mechanism for detecting $Cr_2O_7^{2-}$/CrO_4^{2-} by complexes **4** (a) and **5** (b).[S11]

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