# Supporting Information

## A Pillar-layer strategy to construct 2D polycatenated coordination polymers for luminescent detection of $Cr_2O_7^{2-}$ and $CrO_4^{2-}$ in aqueous solution

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**Experiment Section**

**Materials and Instruments**

Analytical grade chemicals were obtained commercially and used without further purification. Elemental analyses (C, H and N) were performed using a PE 2400 II elemental analyzer. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000-400 $cm^{-1}$ range. Thermogravimetric analyses (TGA) were performed using a Mettler TGA thermal analyzer under $N_2$ atmosphere with a heating rate of 10 $^{o}C$ $min^{-1}$ in the temperature region of 20-1000 $^{o}C$. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer using graphite monochromatized Cu Kα radiation. $H_2L$ was prepared according to a modified literature method.

**Single-crystal Structure Determination**

Single-crystal X-ray diffraction data for 1-6 were recorded on a Bruker Smart CCD diffractometer with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. The structures of 1-6 were solved by Direct Methods and refined by full-matrix least-squares techniques using the *SHELXL*-2014 program. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms bonded to C and N atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Compound 6 contain spatially delocalized electron densities (346e for 6) in the lattice and the solvent contribution was then modeled using SQUEEZE in the Platon program suite. SIMU was used to model the atoms of C17 and C18 with similar anisotropic parameters in 2. Spatial disorder in 3 was treated by applying PART-1 and PART 0 in the ins file with the site occupation factors changed to 0.5.

**Photoluminescence Sensing Experiments of $CrO_4^{2-}$ and $Cr_2O_7^{2-}$**

The lamellar crystal of compound 6 (1 mg) was ground and the power were dispersed in deionized water (1 mL), and then sonicated for 2 min to get the suspension, which were used for luminescent measurements. The aqueous solutions of $Na_yX$ ($1\times10^{-3}$ M, X = $F^-$, $Cl^-$, $Br^-$, $I^-$, $CO_3^{2-}$, $NO_3^-$, $SO_4^{2-}$, $Ac^-$, $CNS^-$, $ClO_4^-$, $BrO_3^-$, $WO_4^{2-}$, $CrO_4^{2-}$, $Cr_2O_7^{2-}$) were prepared for sensing experiments.

**Paper-Based Fluorescent Sensor**

The filter paper was cut into circles of 1.2 cm in diameter, and then the circles are soaked in the dispersion of compound 6 in DMF for 1 min. The fluorescence-based test papers are dry at room temperature, which are further immersed into different anions aqueous solutions of $CrO_4^{2-}$ and $Cr_2O_7^{2-}$ with different concentrations ($10^{-6}$-$10^{-2}$ M) for 30 s.

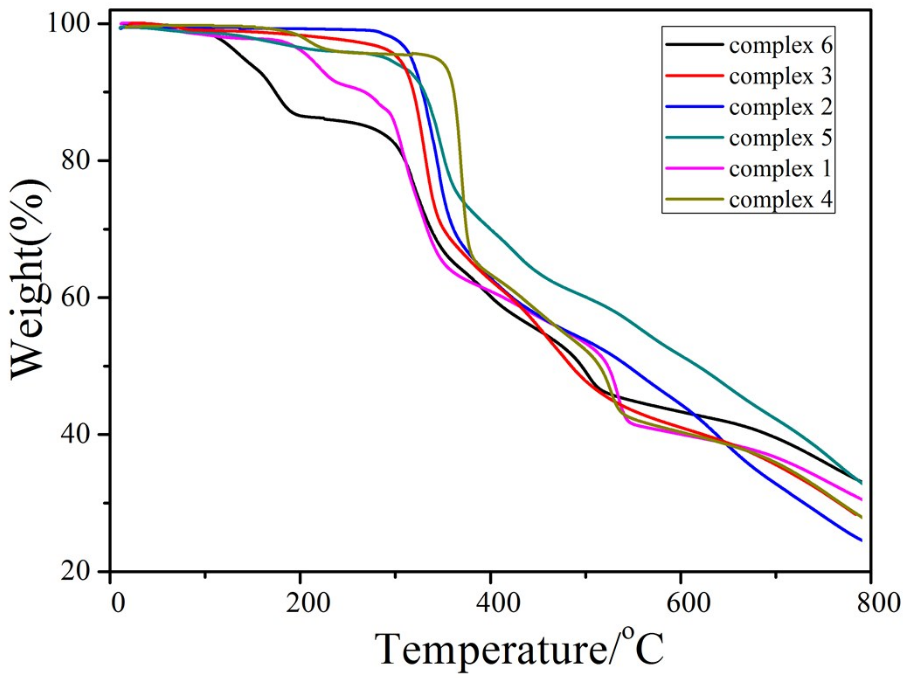
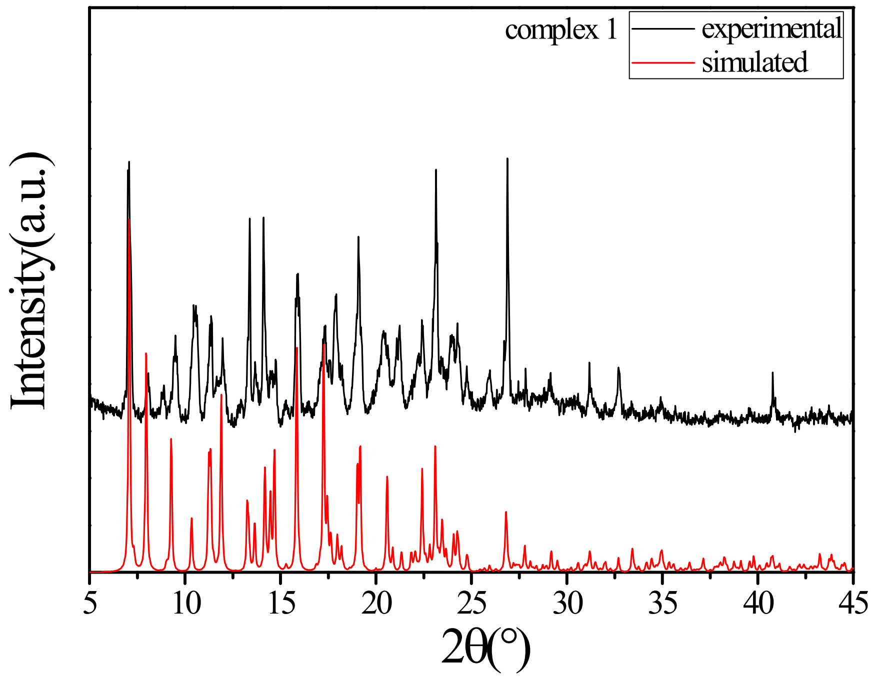



Fig. S1. The thermogravimetric analysis of complexes 1-6.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10
15
20
25
30
35
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45
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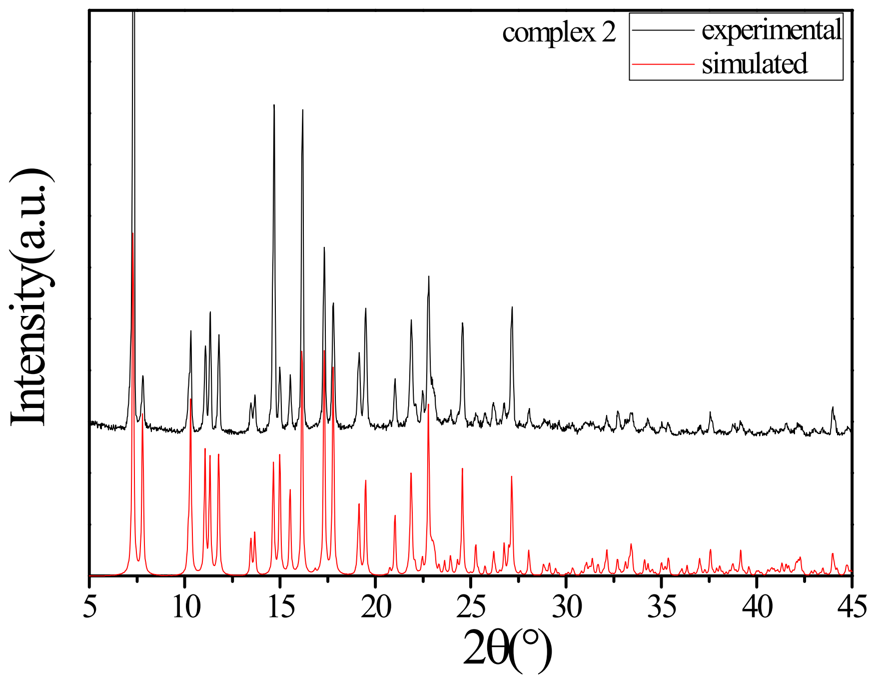
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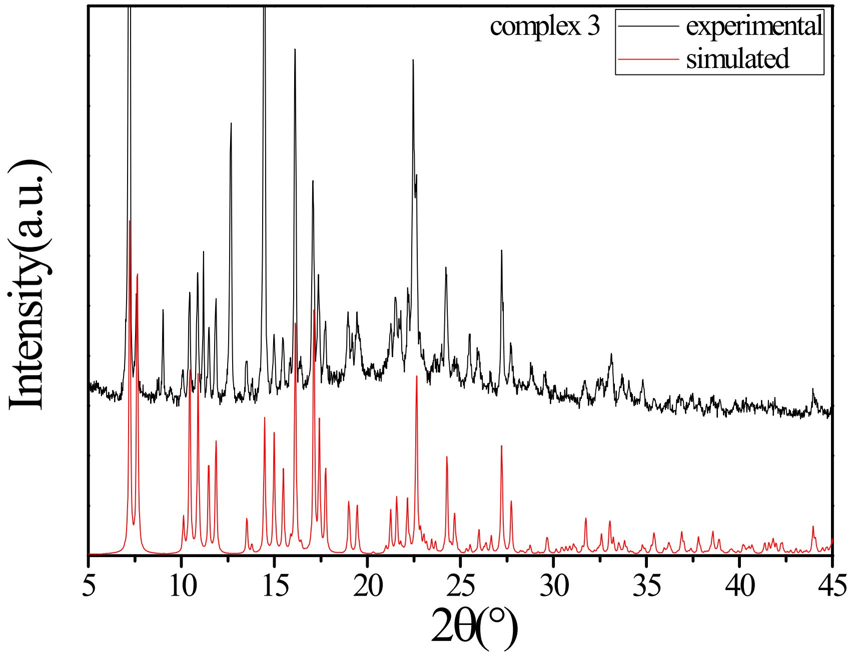
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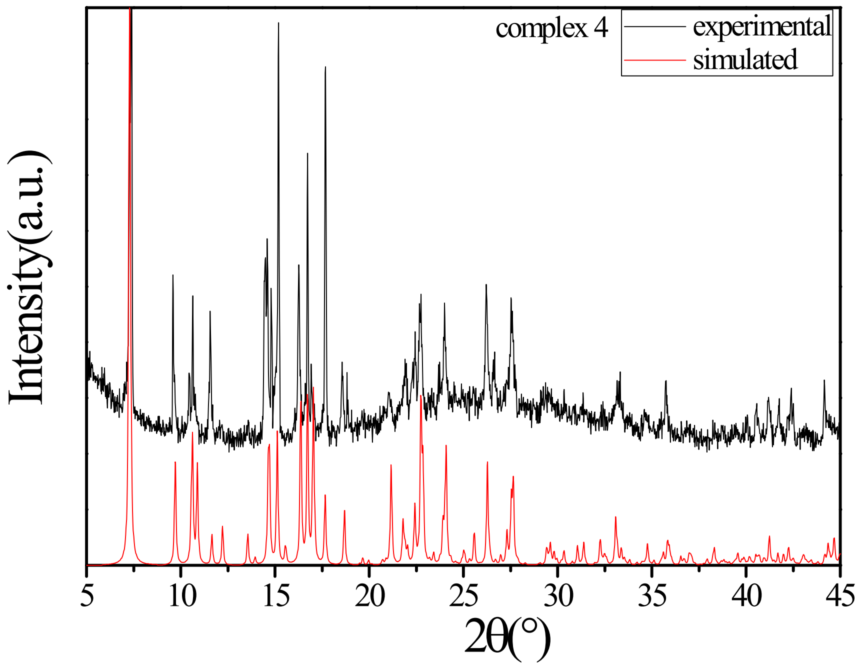
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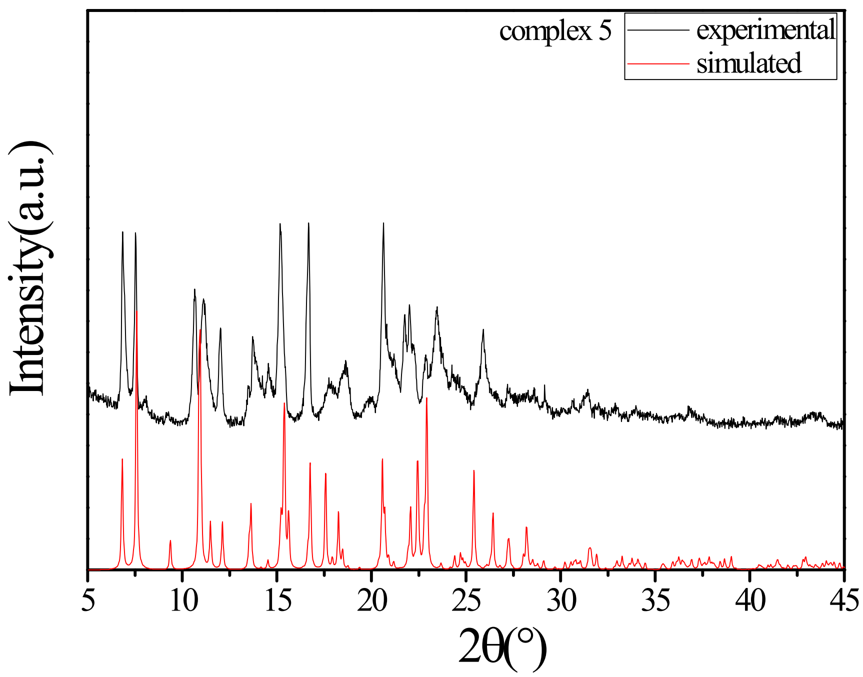


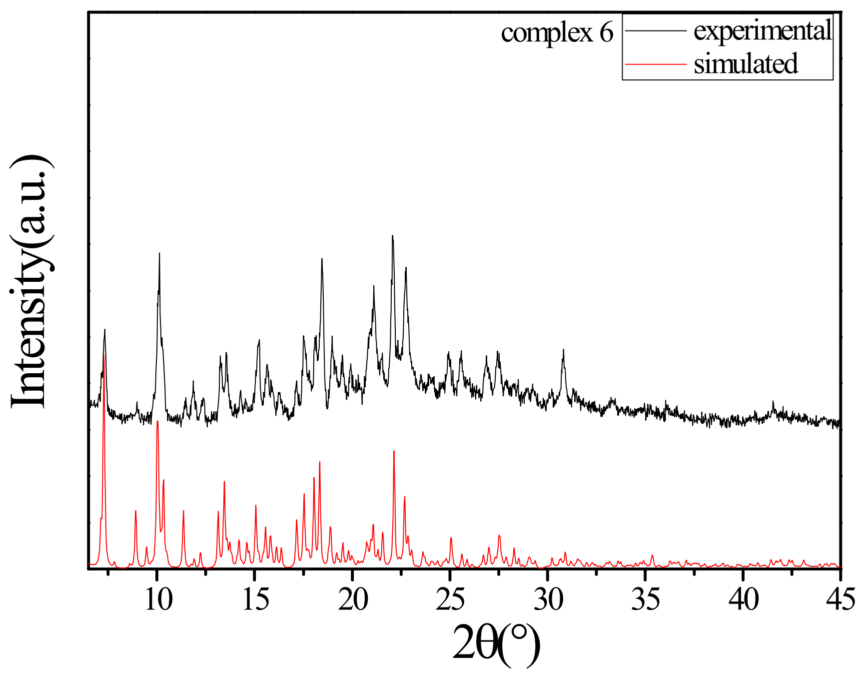




Fig. S2. The PXRD pattern of complexes 1-6.

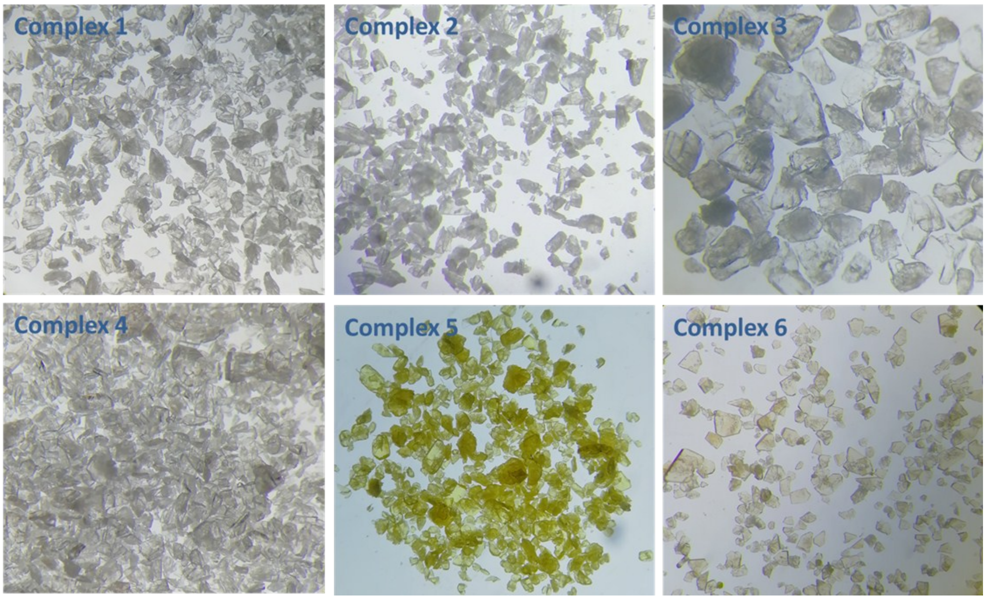
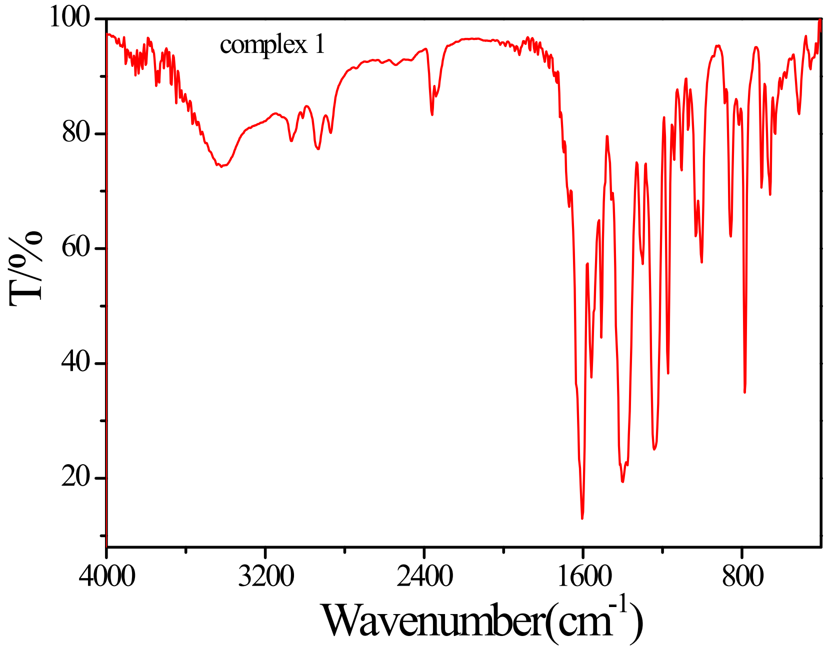
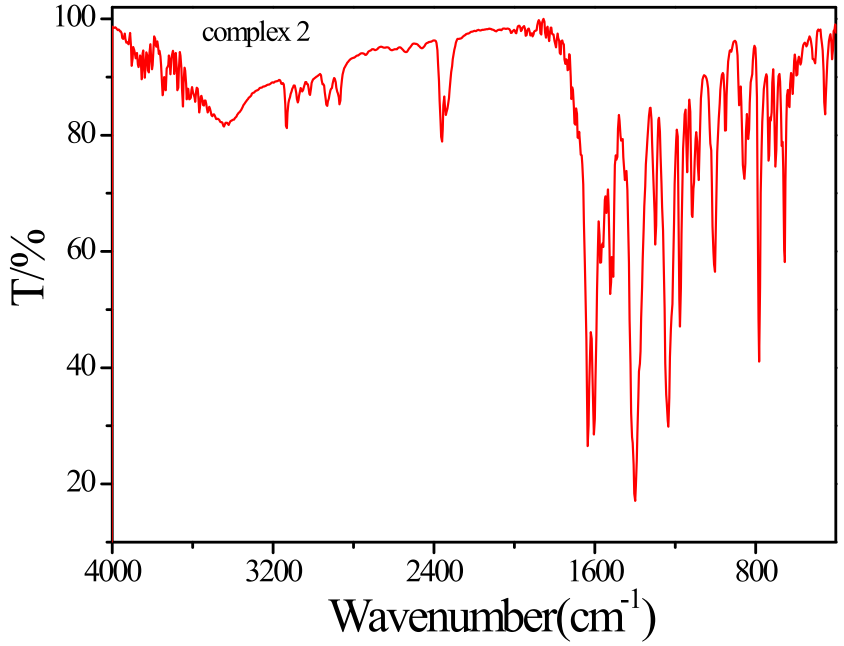



Fig. S3. The microscopic images of complexes 1-6.

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1600
800
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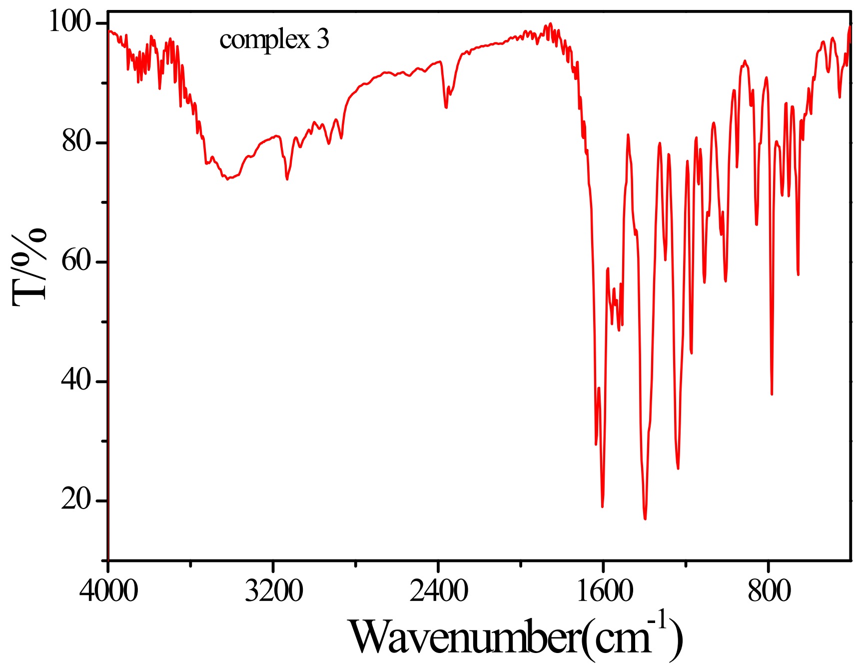
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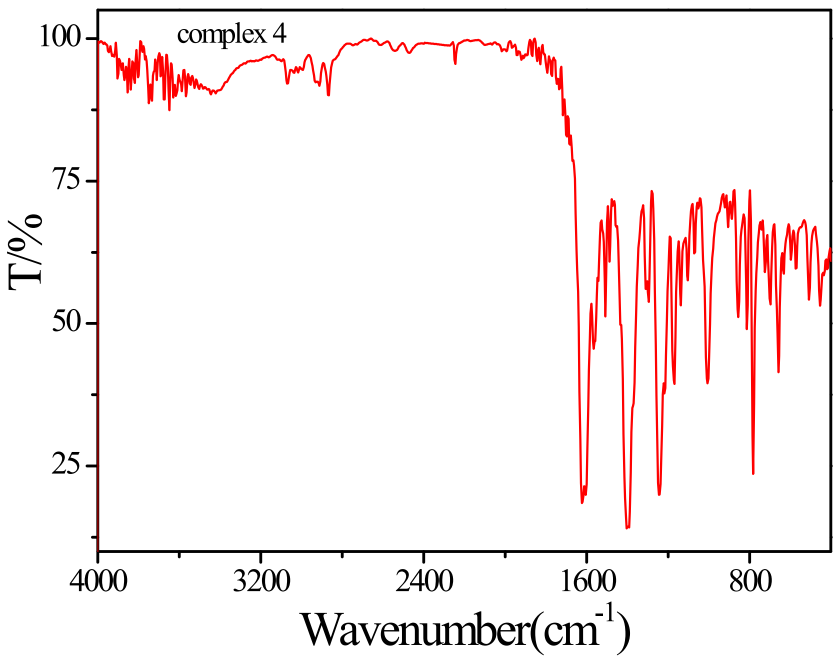
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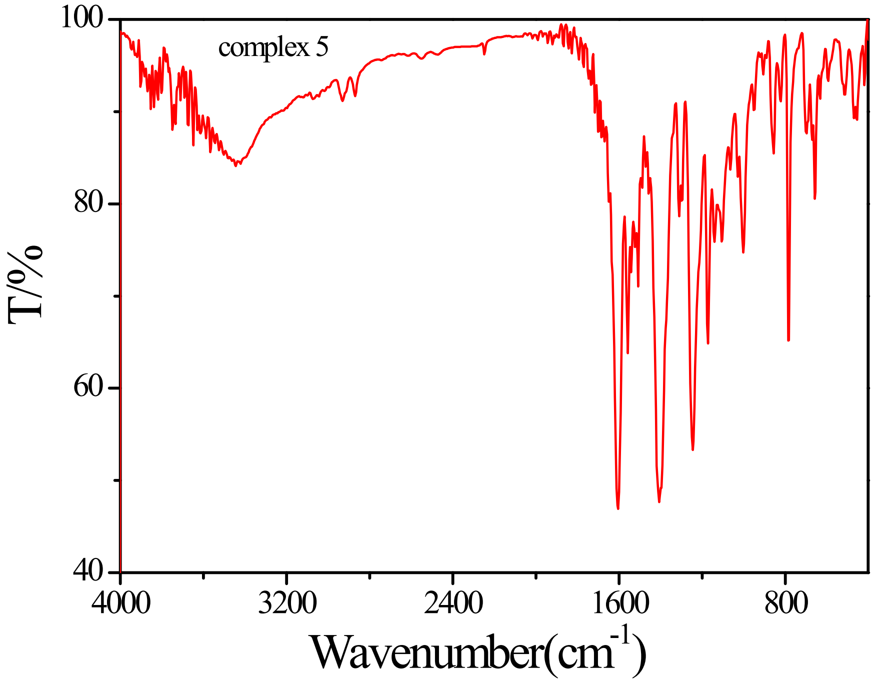
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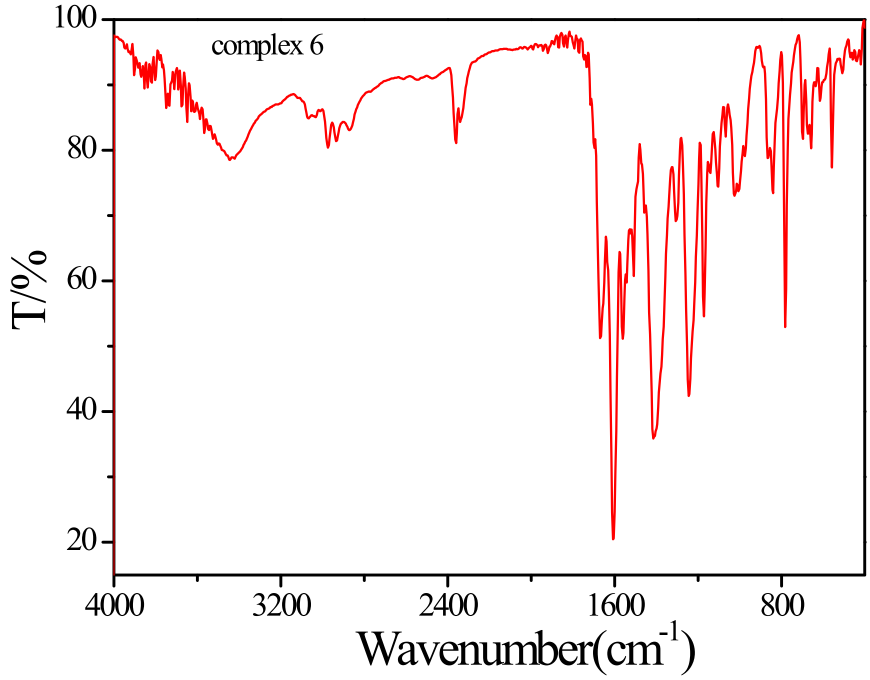



Fig. S4. The IR spectrum of complexes 1-6.

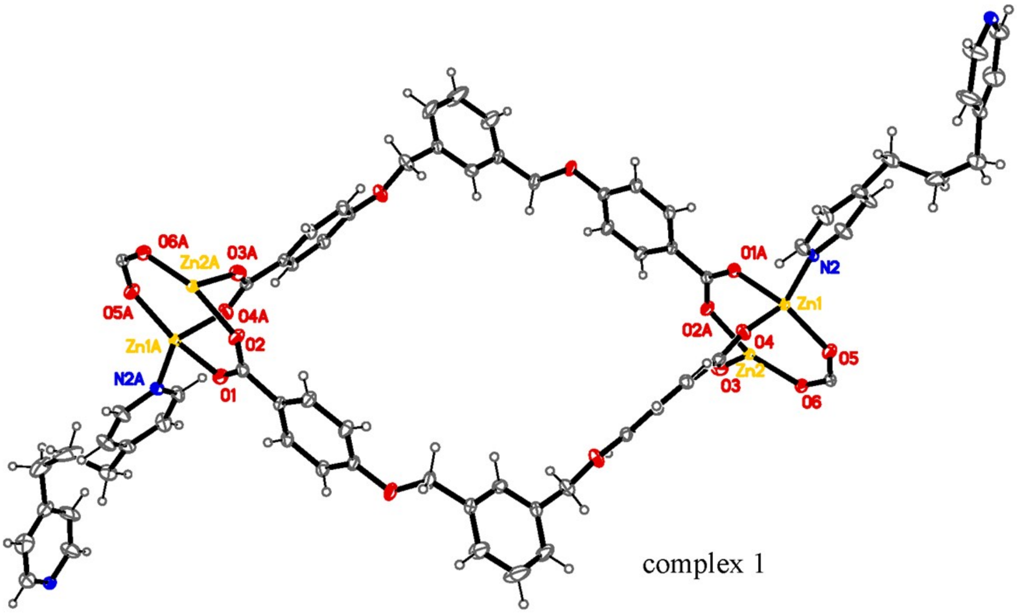



Fig. S5. The coordination model of complex 1.

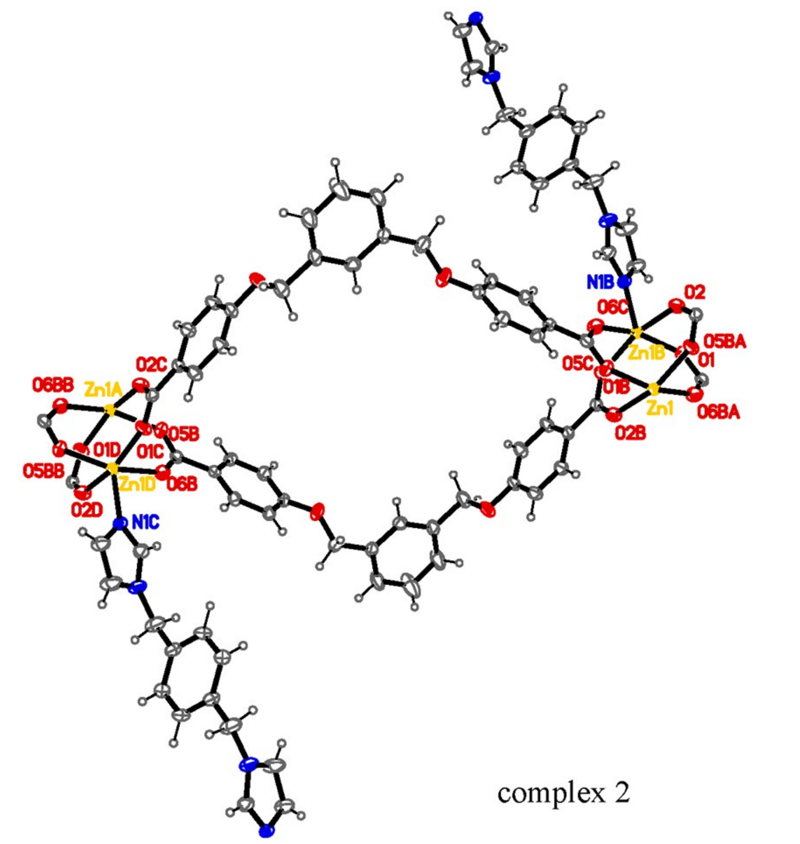



Fig. S6. The coordination model of complex 2.

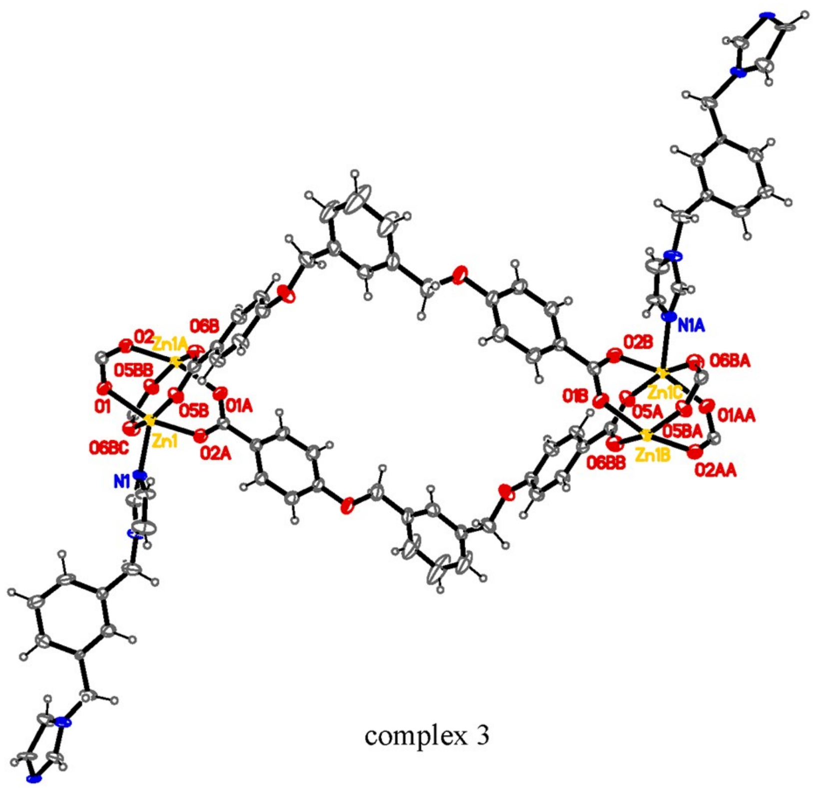



Fig. S7. The coordination model of complex 3.

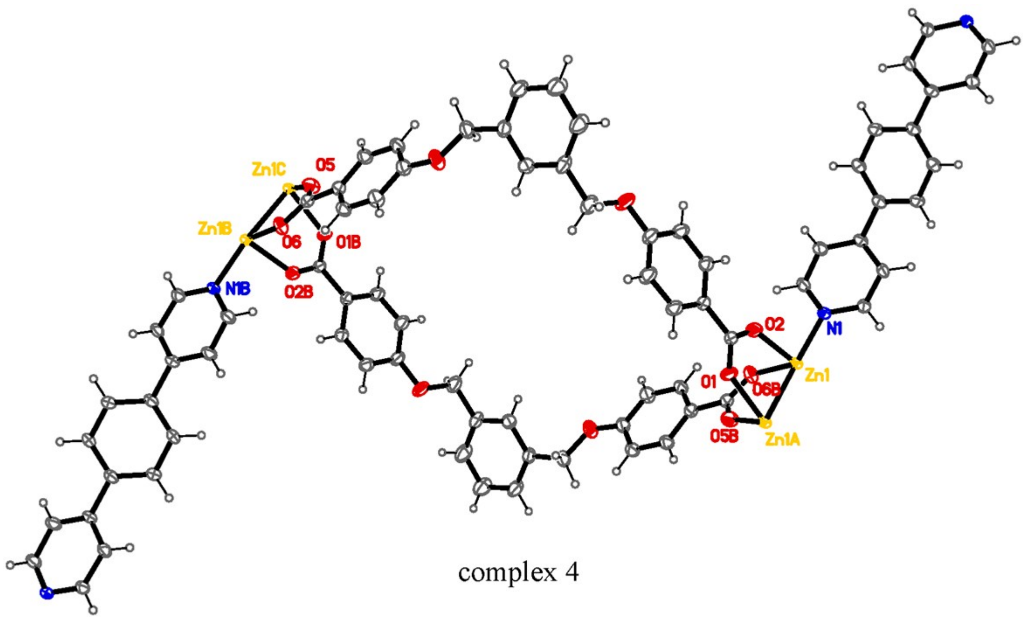



Fig. S8. The coordination model of complex 4.

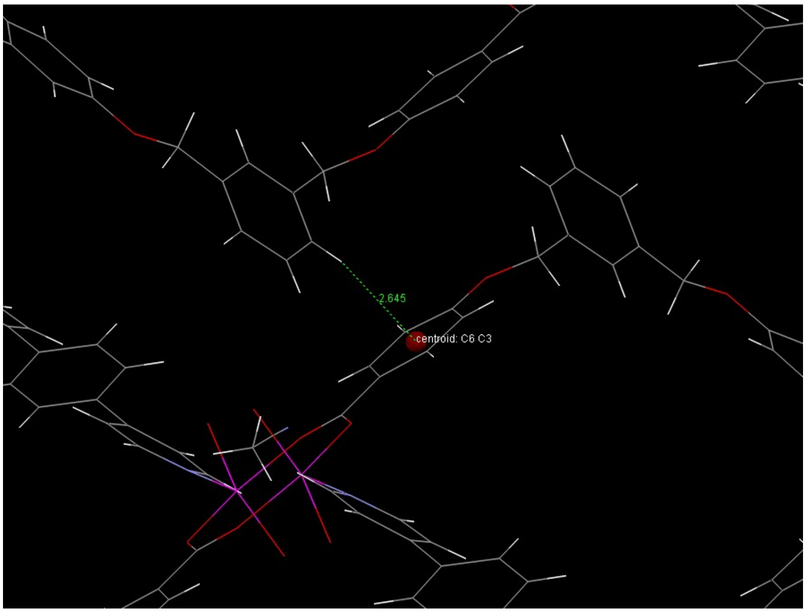



Fig. S9. The C-H···π interactions in complex 4.

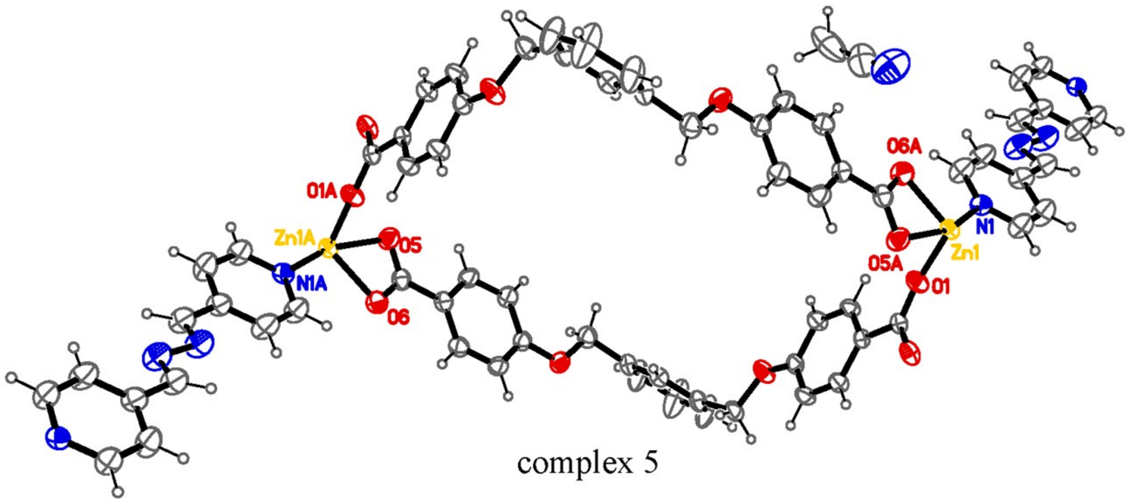



Fig. S10. The coordination model of complex 5.

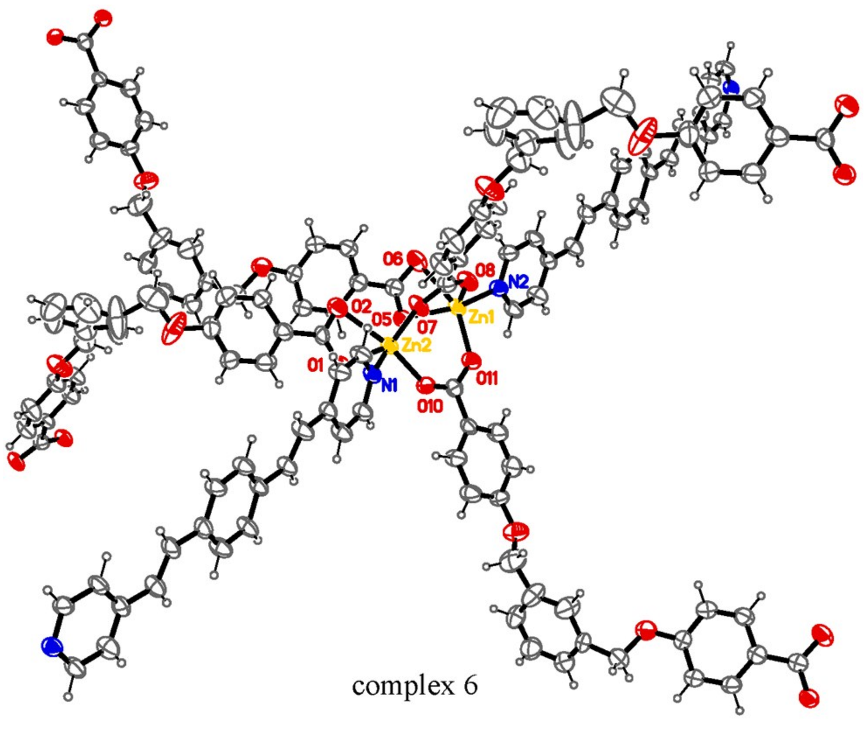



Fig. S11. The coordination model of complex 6.

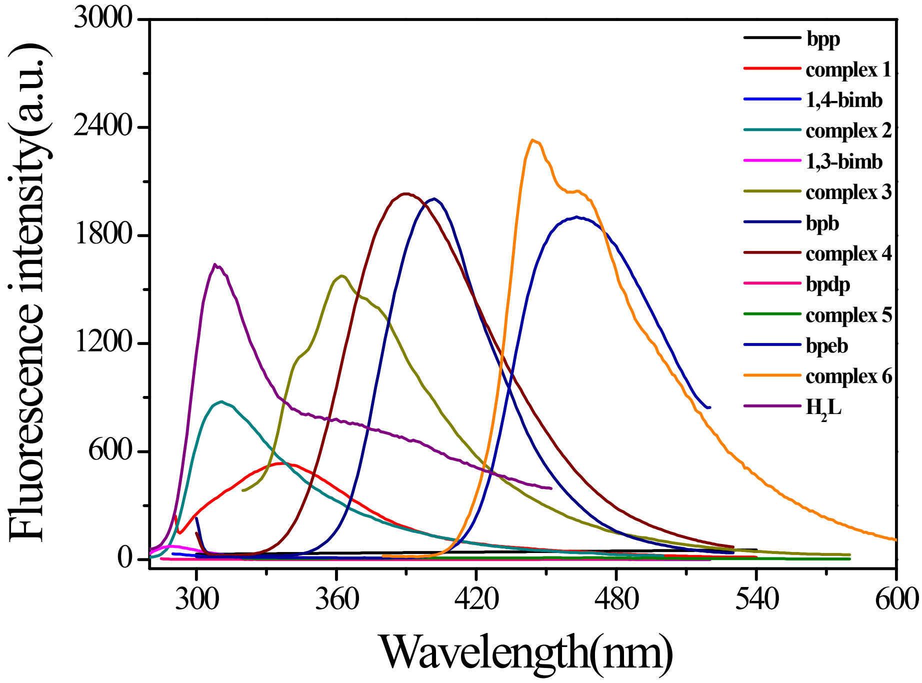
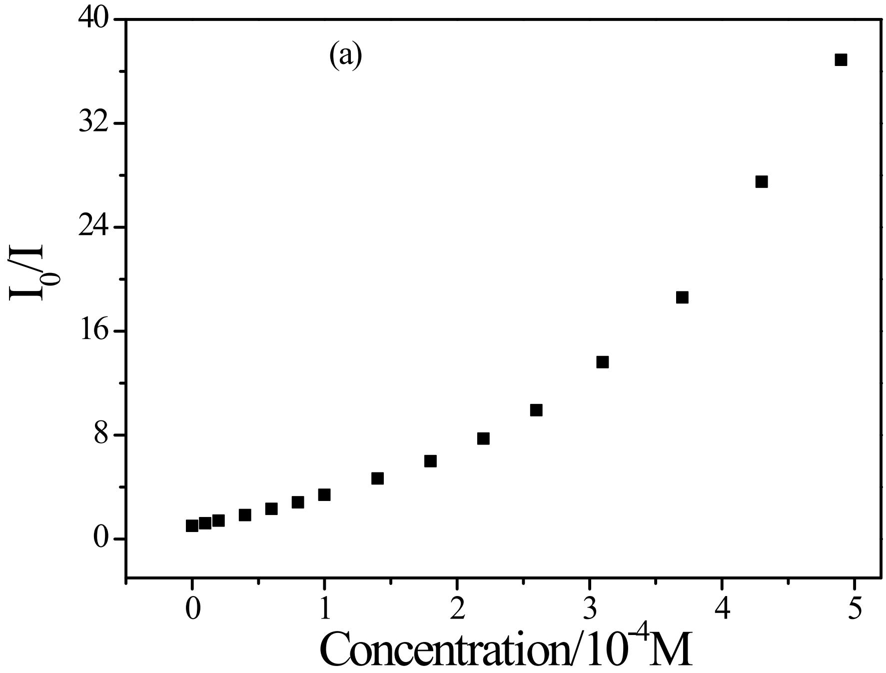



Fig. S12. The solid-state emission spectra of ligands and complexes.



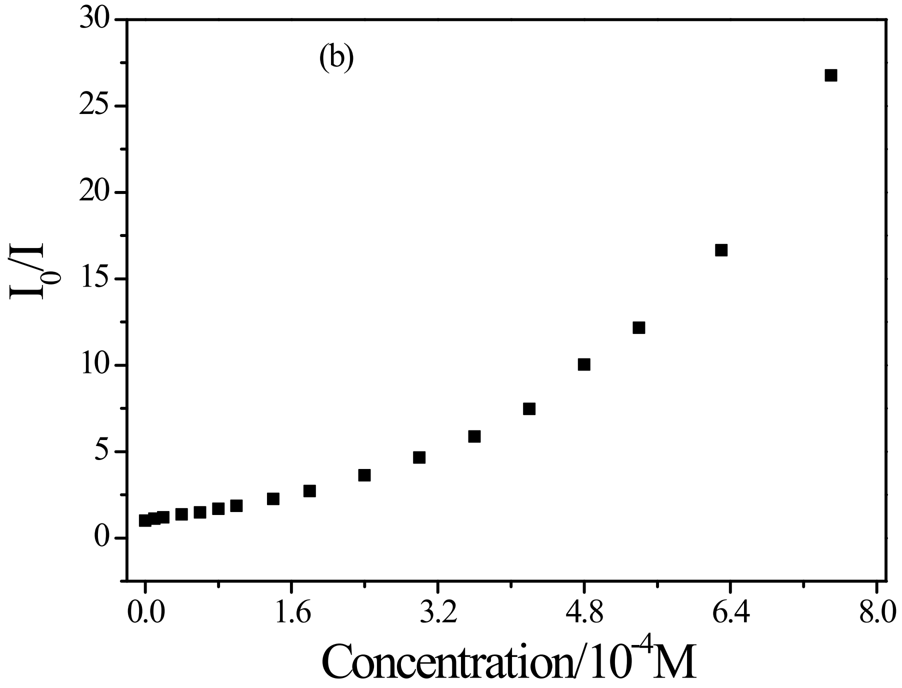



Fig. S13. The Stern-Volmer plot of $I_0/I$ versus the concentration of $Cr_2O_7^{2-}$ (a) and $CrO_4^{2-}$ (b) for complex 6.

Table S1. Comparison of various luminescent CPs for sensing $Cr_2O_7^{2-}/CrO_4^{2-}$ ions.

| | Material | Analyte | Quenching Constant($K_{sv}$,$M^{-1}$) | LOD(M) | Solvent | Ref. |
|---|---|---|---|---|---|---|
| 1 | $[Zn_2(ttz)H_2O]_n$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $2.35\times10^3/2.19\times10^3$ | $2.0\times10^{-5}/20\times10^{-5}$ | water | [1] |
| 2 | $[Zn(btz)]_n$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $3.19\times10^3/4.23\times10^3$ | $1.0\times10^{-5}/ 2.0\times10^{-6}$ | water | [1] |
| 3 | $[Eu(Hpzbc)_2(NO_3)]\cdot H_2O$ | $Cr_2O_7^{2-}$ | --- | $2.2\times10^{-5}$ | ethanol | [2] |
| 4 | $\{[(CH_3)_2NH_2][Eu_4(FDA)_7(DMF)_2\cdot 0.5DMF]\}_n$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $3.56\times10^3/1.25\times10^4$ | $1.12\times10^{-4}/1.14\times10^{-4}$ | water | [3] |
| 5 | $\{[Zn(IPA)(L)]\}_n$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $1.00\times10^3/1.37\times10^3$ | $1.83\times10^{-5}/1.2\times10^{-5}$ | water | [4] |
| 6 | $\{[Cd_3(HL)_2(H_2O)_3]\cdot 3H_2O\cdot 2CH_3CN\}_n$ | $Cr_2O_7^{2-}$ | $6.99\times10^3$ | $1.17\times10^{-4}$ | water | [5] |
| 7 | $\{[Cd(L)(BPDC)]\cdot 2H_2O\}_n$ | $Cr_2O_7^{2-}$ | $6.4\times10^3$ | $3.76\times10^{-5}$ | water | [6] |
| 8 | $\{[Cd_2(bptc)(phen)_2]\cdot 4H_2O\}_n$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $1.09\times10^3/2.09\times10^3$ | $1.06\times10^{-4}/5.89\times10^{-5}$ | water | [7] |
| 9 | $[Eu(L)(HCOO)(H_2O)]_n$ | $Cr_2O_7^{2-}$ | $2.76\times10^3$ | $1.8\times10^{-5}$ | water | [8] |
| 10 | $[Eu(HL)(H_2O)_3]$ | $Cr_2O_7^{2-}$ | $5.50\times10^3$ | $5.1\times10^{-4}$ | water | [9] |
| 11 | $[Zn(L)(bpeb)]$ | $CrO_4^{2-}/Cr_2O_7^{2-}$ | $0.82\times10^4/2.27\times10^4$ | $4.4\times10^{-5}/1.6\times10^{-5}$ | water | This work |

$H_3ttz$ = 1,2,3-tris-[2-(5-tetrazolo)-ethoxy]propane

$H_2btz$ = 1,5-bis(5- tetrazolo)-3-oxapentane

$H_2$pzbc = 3-(1H-Pyrazol-3-yl) benzoic acid
$H_2$FDA = furan-2,5-dicarboxylic acid
{[Zn(IPA)(L)]}$_n$, L = 3- pyridylcarboxaldehyde nicotinoylhydrazone
{[$Cd_3(HL)_2(H_2O)_3$]·$3H_2O$·$2CH_3CN$}$_n$, $H_4$L=1-(3,5-dicarboxylatobenzyl)-3,5-pyrazole dicarboxylic acid
$H_2$IPA = isophthalic acid
{[Cd(L)(BPDC)]·$2H_2O$}$_n$, L = 4,4′-(2,5-bis(methylthio)-1,4-phenylene)dipyridine,
$H_2$BPDC = 4,4′-biphenyldicarboxylic acid
$H_4$bptc = 3,3′,5,5′-biphenyltetracarboxylic acid
phen = 1,10-phenanthroline
[Eu(L)(HCOO)($H_2O$)]$_n$, $H_2$L = 5-((2′-cyano-[1,1′-biphenyl]-4-yl)methoxy)isophthalic acid
[Eu(HL)($H_2O$)$_3$], $H_4$L = 1-(3,5-dicarboxylatobenzyl)-3,5-pyrazole dicarboxylic acid
[Zn(L)(bpeb)], $H_2$L = 1,3-bis(benzoate-4-oxa-methyl)benzene
bpeb = 1,4-bis[2-(4-pyridyl)ethenyl]benzene)

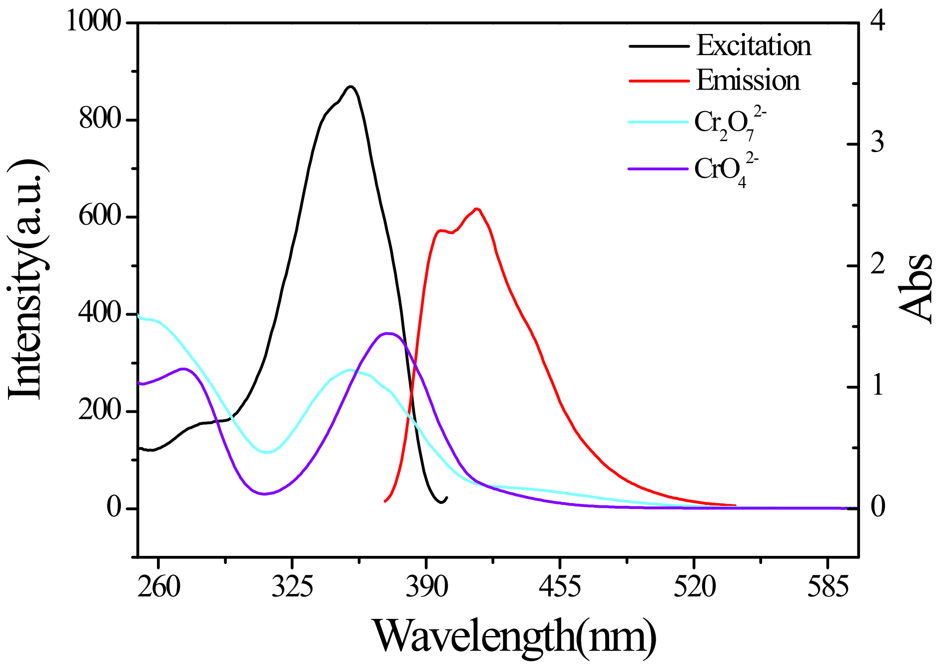



Fig. S14. The UV-vis absorption spectra of $Cr_2O_7^{2-}$ , $CrO_4^{2-}$ , the excitation and emission spectra of complex 6.

## References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[7] Y. N. Lin, X. P. Zhang, W. J. Chen, W. Shi, P. Cheng, *Inorg. Chem.,* 2017, **56**, 11768-11778.
[8] Z. Sun, M. Yang, Y. Ma, L. C. Li, *Cryst. Growth Des.,* 2017, **17**, 4326-4335.
[9] W. Q. Tong, T. T. Liu, G. P. Li, J. Y. Liang, L. Hou, Y. Y. Wang, *New J. Chem.,* 2018, **42**, 9221-9227.