Supplementary Information

Six cobalt(II), zinc(II), nickel(II) and copper(II) complexes based on bis-benzimidazolyl bidentate ligands with phenolyl ether linkers: synthesis, structural studies and recognition for HSO_4^-

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1. General procedures

All solvents, regents were purchased commercially and were not further purified before use. A Bruker AVANCE III spectrometer was used to record NMR spectra. HRMS was obtained on the mass spectrometer (A VG ZAB-HS). The elemental analyses were obtained by using a Perkin-Elmer 2400C Elemental Analyzer. IR spectra (KBr), fluorescence spectra and UV spectra were gotten by a Bruker Equinox 55 spectrometer, a RF-5301PC fluorescence spectrophotometer (Shimadzu) and a JASCO-V570 spectrometer, respectively. The elemental analyses were performed using a Perkin-Elmer 2400C Elemental Analyzer. The solid-state fluorescence spectra were obtained using a Fluorolog-3 fluorescence spectrophotometer from Horiba Jobin Yvon. The powder X-ray diffraction patterns were recorded using aD/Max-IIIA diffractometer with a Cu-target tube (λ = 1.5418 Å) and a graphite monochromator. Thermogravimetric analysis (TG) was performed in N_2 at a heating rate of 20 °C min^{-1} using a NETZSCH TG209F3.

2. X-ray data collection and structure determinations

A Bruker Apex II CCD diffractometer was utilized to collected diffraction data for complexes **1-6**. SADABS and SAINT the program were used.[1] All structures were solved by direct methods by using the SHELXS program of the SHELXTL package and refined with SHELXL.[2] Fig.s were generated by using Crystal-Maker.[3] Further details were listed in Table S1 and Table S2.

3. CCDC numbers for complexes 1-6.

CCDC 2350976-2350979 and 2350981-2350982 for complexes **1-6** contain the supplementary crystallographic data. These data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

4. Summary of crystallographic data for complexes 1-6.

Table S1. Summary of Crystalographic Data for Complexes 1-3

	1	2	3
chemical formula	$C_{29}H_{24}N_6O_8Co$	$C_{29}H_{24}N_6O_8Zn$	$C_{62}H_{56}N_{12}O_{16}Ni_2$
fw	643.47	649.91	1342.61
Cryst syst	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a /Å	15.662(1)	15.603(1)	7.842(4)
b /Å	8.770(5)	8.651(8)	11.923(6)
c /Å	20.845(1)	20.841(1)	16.445(9)
α/deg	90	90	89.7(1)
β/deg	99.8(1)	101.0(1)	87.6(1)
γ/deg	90	90	73.4(1)
V /Å^3	2821.1(3)	2761.4(4)	1473.1(1)
Z	4	4	1
D_{calcd}, Mg/m^3	1.515	1.563	1.513
Abs coeff, mm^{-1}	0.672	0.954	0.722
F(000)	1324	1336	696
Cryst size, mm	0.22 × 0.20 × 0.18	0.15 × 0.14 × 0.13	0.15 × 0.14 × 0.05
θ_{min}, θ_{max}, deg	1.98, 25.01	1.33, 25.01	1.24, 25.00
T /K	296(2)	296(2)	296(2)
no. of data collected	13997	13575	7389
no. of unique data	4979	4874	5101
no. of refined params	397	397	415
goodness-of-fit on F^2 [a]	1.009	1.051	1.049
Final R indices[b] [$I > 2\sigma(I)$]			
R_1	0.0386	0.0297	0.0276
wR_2	0.0916	0.0821	0.0693
R indices (all data)			
R_1	0.0550	0.0356	0.0304
wR_2	0.1028	0.0887	0.0720

[a] Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. [b] R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = $1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table S2. Summary of Crystalographic Data for Complexes 4-6

	4	5	6
chemical formula	$C_{29}H_{24}N_4O_6SCu$ ·DMF	$C_{32}H_{30}N_4O_6SCu$ ·CH_3OH	$C_{36}H_3N_4O_{62}Co$
fw	693.22	694.24	675.59
Cryst syst	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a /Å	10.546(8)	10.846(1)	11.126(1)
b /Å	12.516(9)	11.864(1)	14.273(1)
c /Å	12.968(9)	14.141(2)	19.771(1)
α/deg	68.8(1)	68.9(2)	90
β/deg	79.6(1)	72.7(2)	94.6(2)
γ/deg	72.3(1)	73.9(2)	90
V /Å^3	1517.1(1)	1591.7(4)	3129.9(5)
Z	2	2	4
D_{calcd}, Mg/m^3	1.518	1.449	1.434
Abs coeff, mm^{-1}	0.847	0.806	0.603
F(000)	718	722	1404
Cryst size, mm	0.15 × 0.14 × 0.05	0.22 × 0.21 × 0.20	0.12 × 0.11 × 0.10
θ_{min}, θ_{max}, deg	1.69, 25.01	1.87, 25.01	2.03, 25.01
T /K	173(2)	296(2)	150(2)
no. of data collected	7667	8160	15616
no. of unique data	5301	5582	5497
no. of refined params	436	448	434
goodness-of-fit on F^2 [a]	1.067	1.020	1.049
Final R indices[b] [$I > 2\sigma(I)$]			
R_1	0.0983	0.0367	0.0289
wR_2	0.2347	0.0941	0.0727
R indices (all data)			
R_1	0.2223	0.0445	0.0328
wR_2	0.2993	0.0994	0.0752

[a] Goof = $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined. [b] R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; wR2 = $1/[\sigma^2(F_o^2) + (0.0691P) + 1.4100P]$ where $P = (F_o^2 + 2F_c^2)/3$.

5. The data of hydrogen bonds, π-π interactions and C-H···π contacts of complexes 1-6.

Table S3. H-Bonding Geometry (Å, °) for complexes 1-3, 5 and 6

	D-H···A	D-H	H···A	D···A	D-H···A
1	C(15)-H(15A)···O(5)^{i}	0.969(3)	2.613(3)	3.068(4)	108.9(8)
2	C(15)-H(15A)···O(5)^{i}	0.970(2)	2.595(2)	3.002(3)	105.4(1)
3	C(17)-H(17A)···O(8)^{i}	0.970(1)	2.244(1)	3.202(2)	168.9(1)
	C(7)-H(7)···O(5)^{ii}	0.930(1)	2.644(1)	3.370(2)	135.3(1)
5	C(31)-H(31)···O(5)^{i}	0.930(3)	2.681(3)	3.523(5)	150.7(4)
6	C(21)-H(21)···O(6)^{i}	0.930	2.432(1)	3.124(2)	171.1(6)

Symmetry code: i: *x*, -0.5 - *y*, 0.5 + *z* for **1**. i: -*x*, -*y*, 1 - *z* for **2**. i: *x*, *y*, -1+*z*; ii: 1-*x*, 2-*y*, 1-*z* for **3**. i: 1 -*x*, 1 - *y*, 1 - *z* for **5**. i: 1 + *x*, 2 + *y*, *z* for **6**.

Table S4. Distances (Å) of π-π interactions for 1-6

Complexes	π-π	
	face-to-face	center-to-center
1	3.394(3) (benzimidazole) 3.575(3) (benzimidazole)	3.606(1) (benzimidazole) 3.594(2) (benzimidazole)
2	3.362(3) (benzimidazole) 3.353(3) (benzimidazole)	3.483(3) (benzimidazole) 3.544(2) (benzimidazole)
3	3.437(2) (benzimidazole)	3.458(1) (benzimidazole)
4	3.330(1) (benzimidazole)	3.469(2) (benzimidazole)
5	3.742(4) (benzene)	4.376(4) (benzene)
6	3.412(2) (benzimidazole)	3.562(3) (benzimidazole)

6. The solid-state fluorescence spectra of L_1-L_3 and complexes 1-6

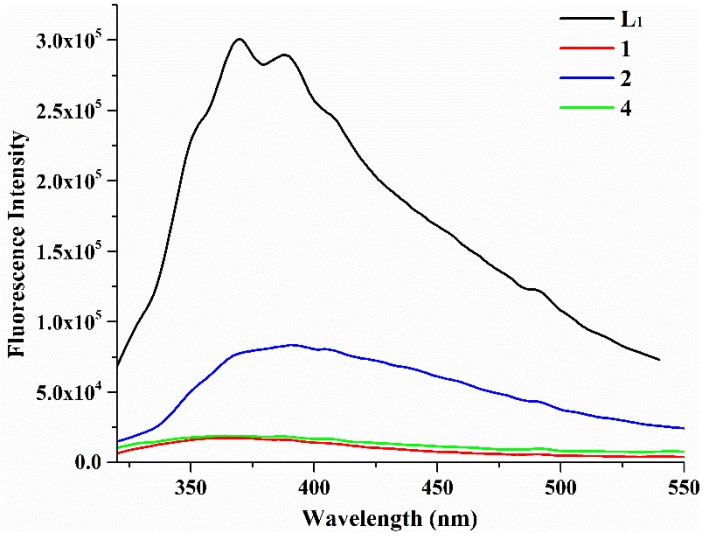

Fig. S1 The solid-state fluorescence spectra of $\mathbf{L_1}$ and complexes **1**, **2** and **4** at room

temperature (λ_{ex} = 300 nm).

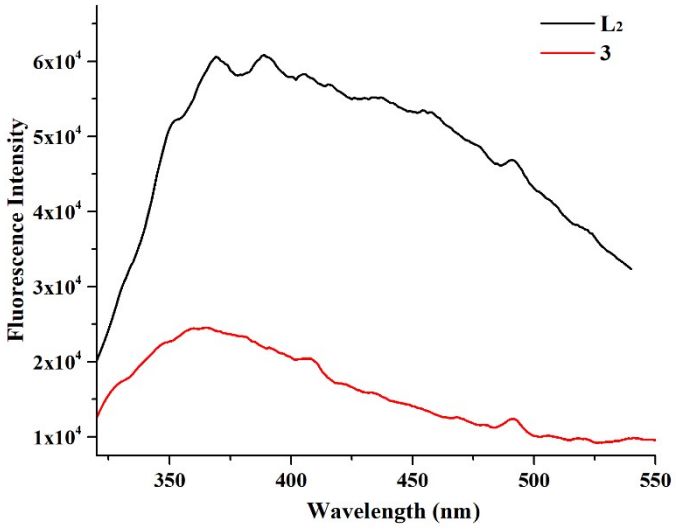

Fig. S2 The solid-state fluorescence spectra of $\mathbf{L_2}$ and complex **3** at room temperature (λ_{ex} = 300 nm).

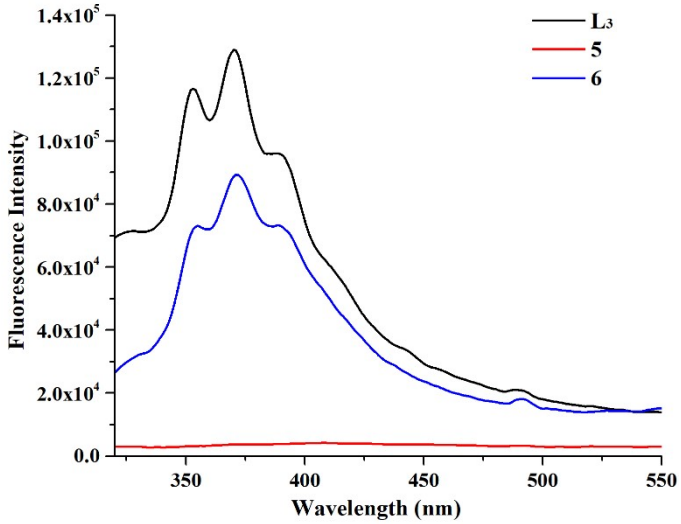

Fig. S3 The solid-state fluorescence spectra of $\mathbf{L_3}$ and complexes **5** and **6** at room temperature (λ_{ex} = 300 nm).

7. The simulated and experimental PXRD patterns for complexes 1-6

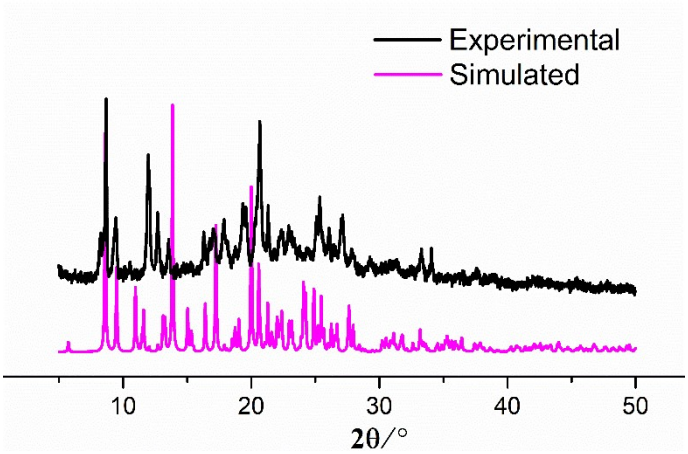

Fig. S4 The simulated (purple) and the experimental (black) PXRD patterns of **1**.

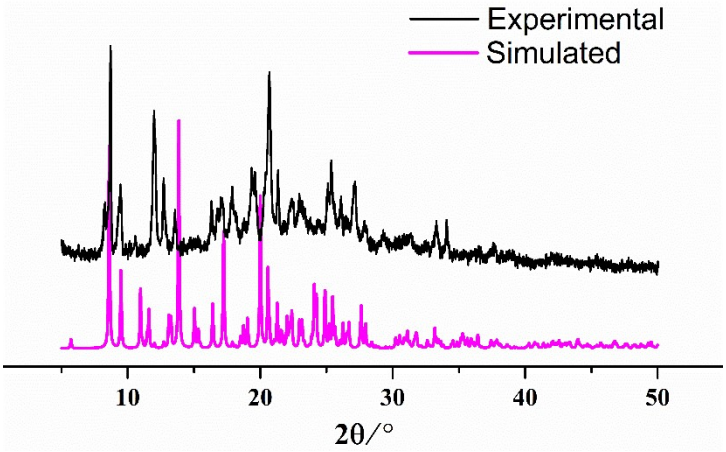

Fig. S5 The simulated (purple) and the experimental (black) PXRD patterns of **2**.

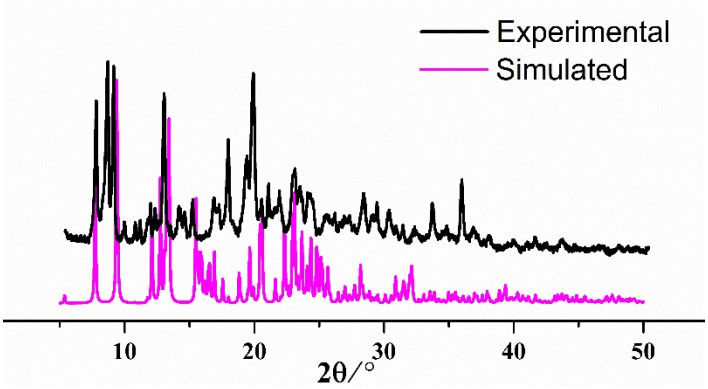

Fig. S6 The simulated (purple) and the experimental (black) PXRD patterns of **3**.

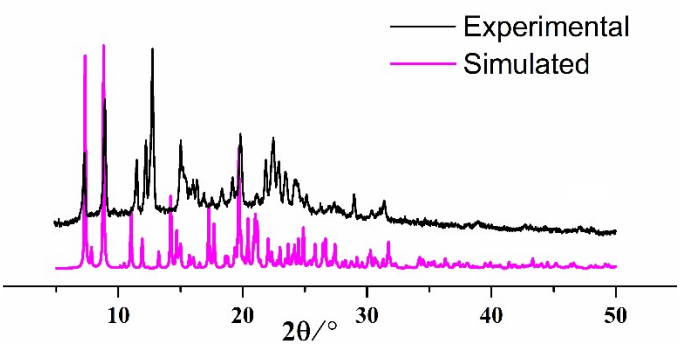

Fig. S7 The simulated (purple) and the experimental (black) PXRD patterns of **4**.

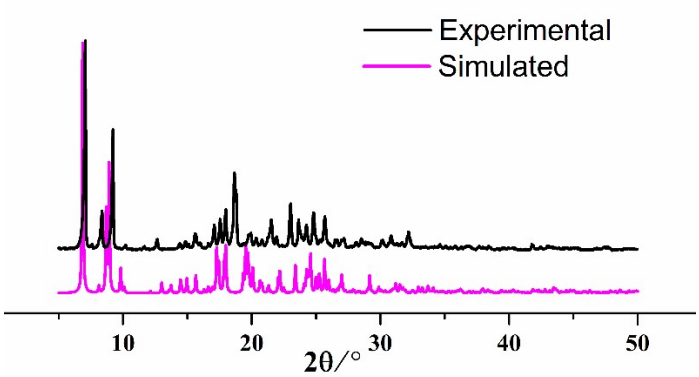

Fig. S8 The simulated (purple) and the experimental (black) PXRD patterns of **5**.

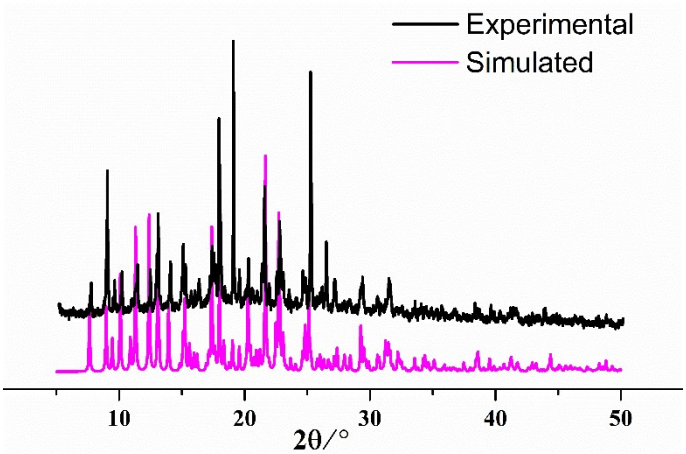

Fig. S9 The simulated (purple) and the experimental (black) PXRD patterns of **6**.

8. The curves of thermogravimetry for complexes 1-6

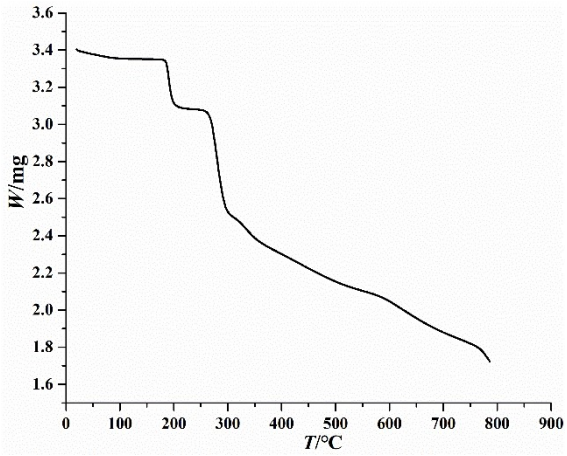

Fig. S10 TG curve from room temperature to 800 ˚C for **1**.

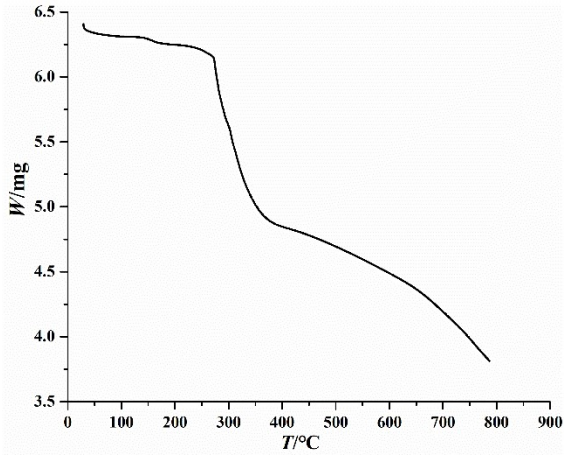

Fig. S11 TG curve from room temperature to 800 ˚C for **2**.

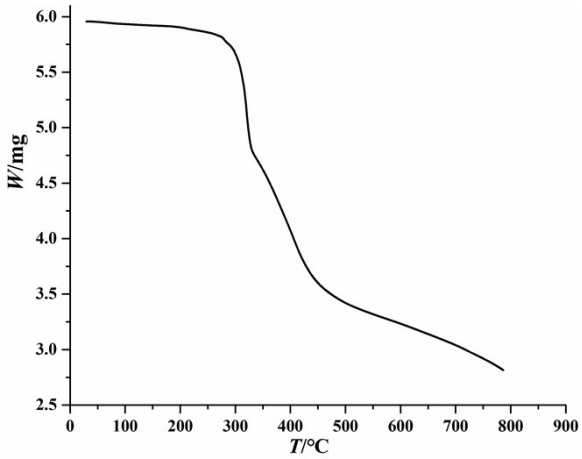

Fig. S12 TG curve from room temperature to 800 ˚C for **3**.

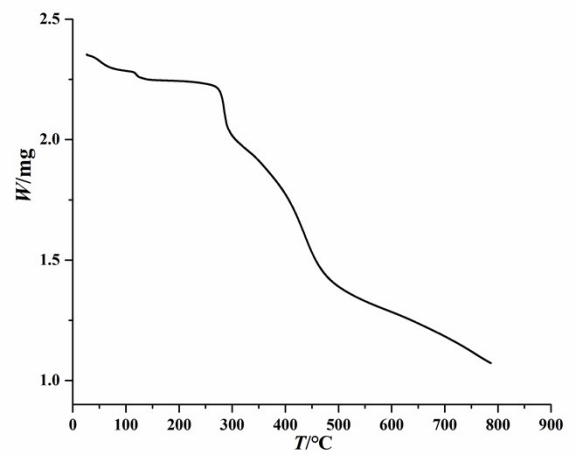

Fig. S13 TG curve from room temperature to 800 ˚C for **4**.

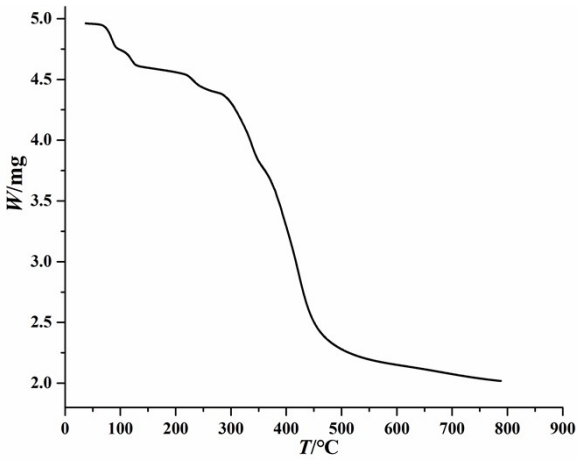

Fig. S14 TG curve from room temperature to 800 ˚C for **5**.

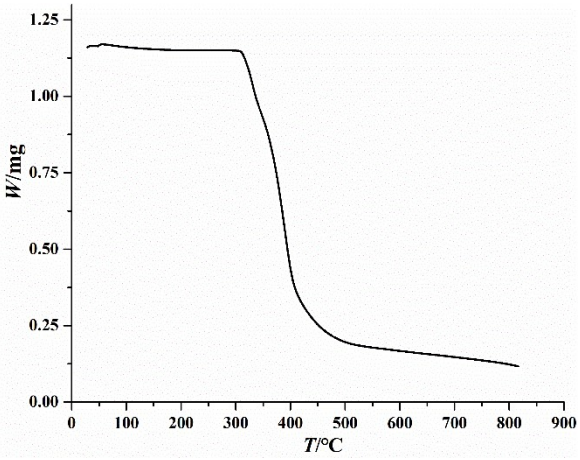

Fig. S15 TG curve from room temperature to 800 ˚C for **6**.

9. The figures of fluorescence and UV/vis spectroscopies for complex 1.

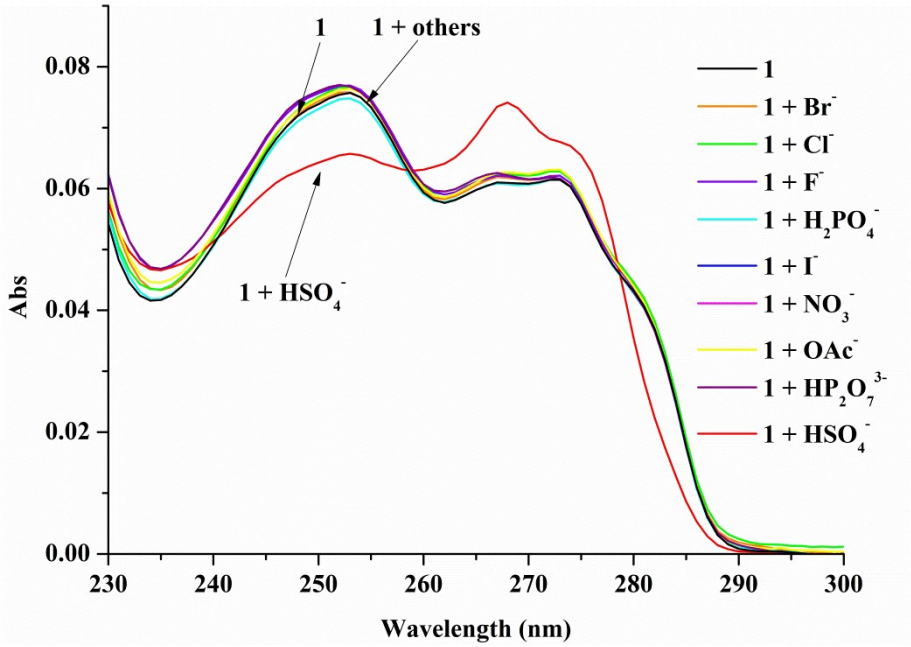

Fig. S16 UV/vis absorption spectra of **1** (5.0×10^{-6} mol/L) with salts (20.0 equiv.) of F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, OAc^-, NO_3^-, HSO_4^-, $P_2O_7^{2-}$ in CH_3CN/H_2O (1:1, v/v) at room temperature.

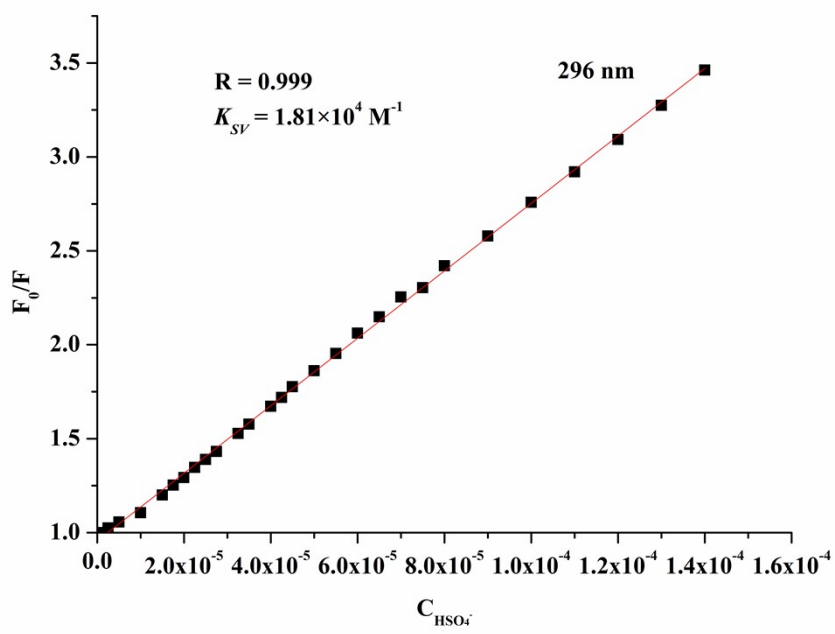

Fig. S17 Fluorescence titration fitting curve of complex **1** to HSO_4^-.

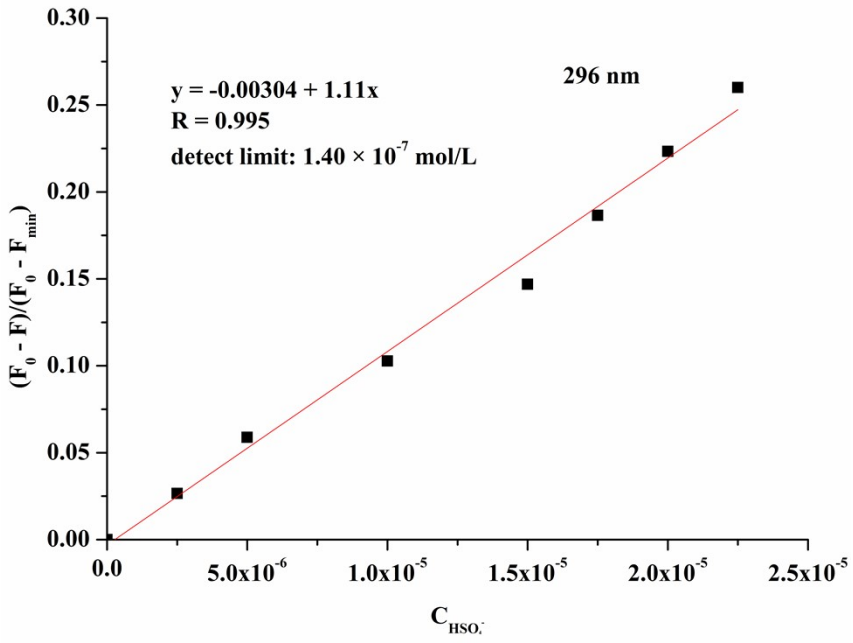

Fig. S18 Detection limit of complex **1** to HSO_4^-.

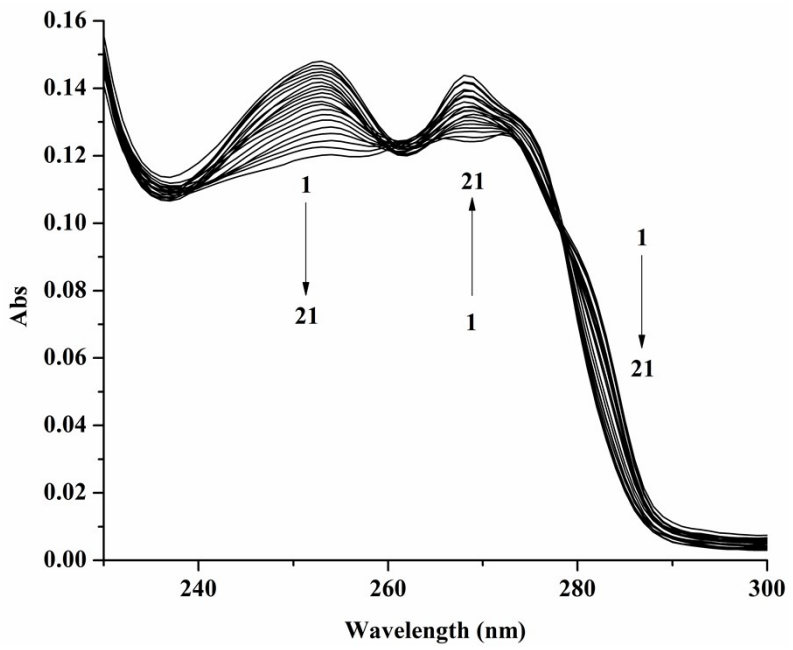

Fig. S19 UV/vis titration of **1** (5.0×10^{-6} mol/L) with diverse $C_{HSO_4^-}$ in CH_3CN/H_2O (v:v ＝ 1:1) at room temperature. The concentrations of HSO_4^- are 0, 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 14, 16, 18, 20, 25, 30, 35 × 10^{-5} mol/L.

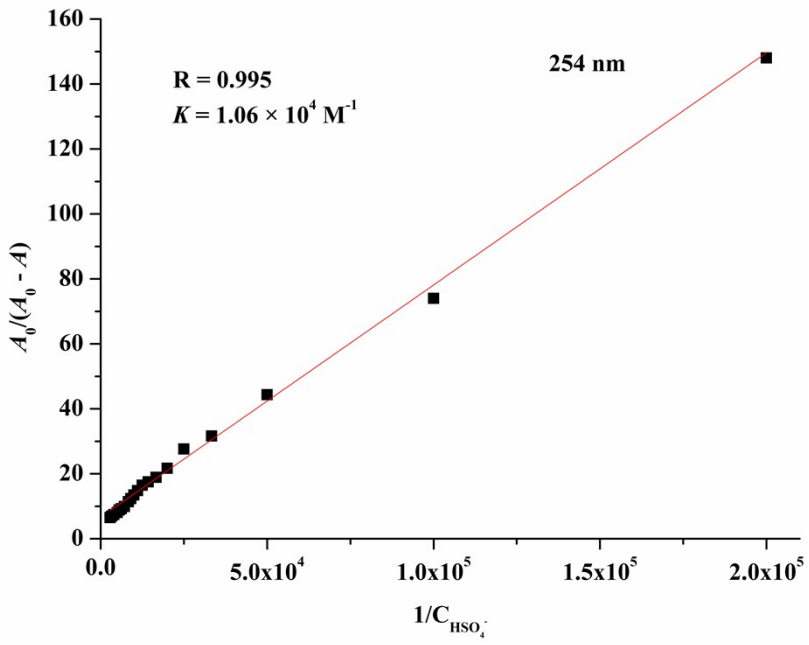

Fig. S20 UV titration fitting curve of complex **1** to HSO_4^-.

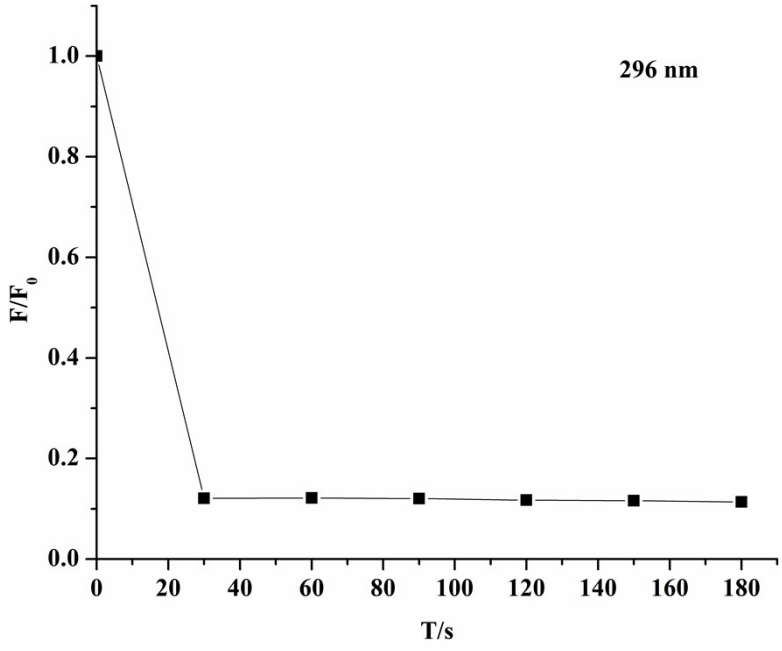

Fig. S21 Fluorescence response time of complex **1** to HSO_4^-.

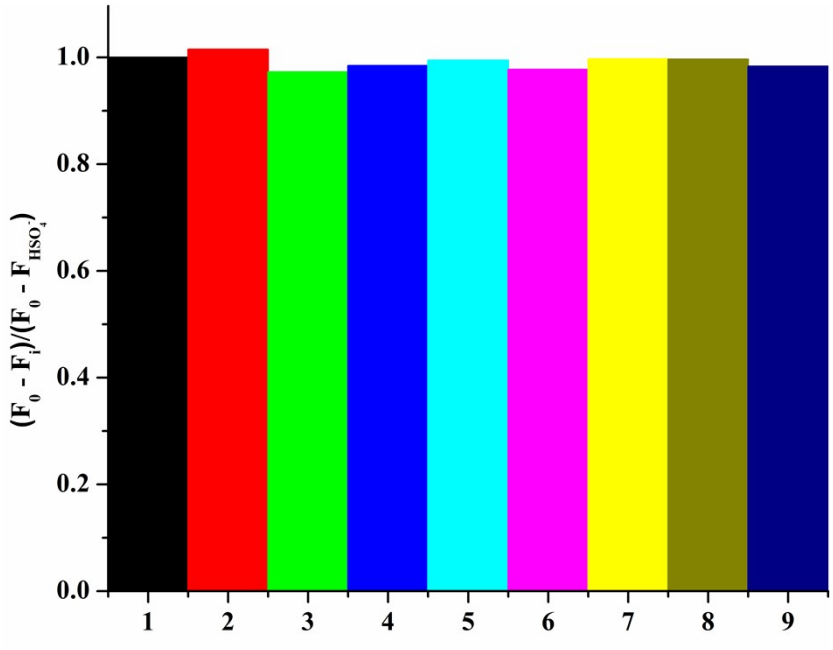

Fig. S22 Histogram of the interference of complex **1** with HSO_4^- at 296 nm (where the horizontal numbers represent the systems 1: **1** + HSO_4^-; 2: **1** + HSO_4^- + F^-; 3: **1** + HSO_4^- + Cl^-; 4: **1** + HSO_4^- + Br^-; 5: **1** + HSO_4^- + I^-; 6: **1** + HSO_4^- + $H_2PO_4^-$; 7: **1** + HSO_4^- + OAc^-; 8: **1** + HSO_4^- + NO_3^-; 9: **1** + HSO_4^- + $HP_2O_7^{3-}$).

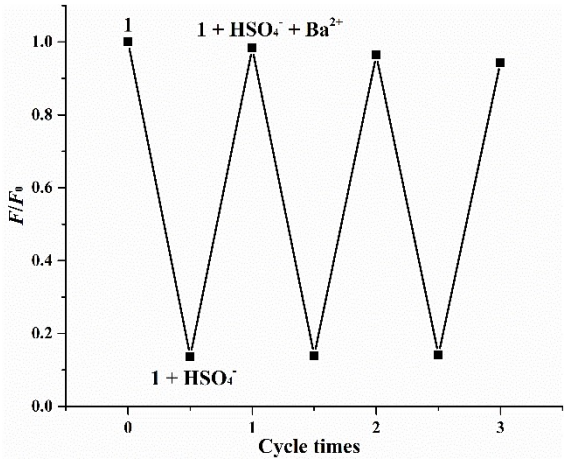

Fig. 23 Reversibility study of complex **1** (5×10^{-6} mol/L) for HSO_4^- (1.0×10^{-4} mol/L) in CH_3CN/H_2O (v/v = 1:1) at 296 nm at room temperature.

10. The Fig. of HRMS for 1 and 1·HSO_4^-

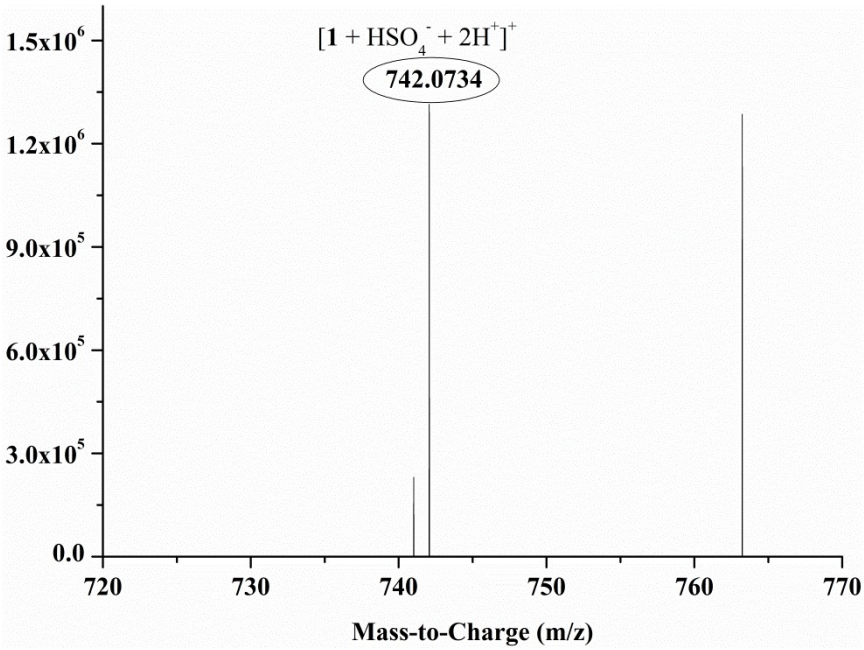

Fig. S24 HRMS of **1**·HSO_4^-.

11. Infrared spectra of 1 and 1·HSO_4^-

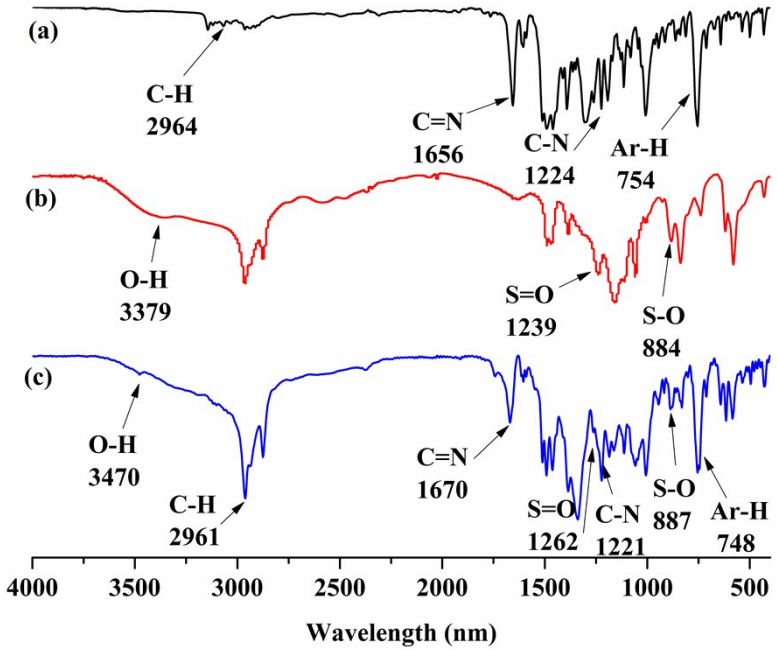

Fig. S25 (a) Infrared image of complex **1**; (b) Infrared image of HSO_4^-; (c) Infrared image of **1**·HSO_4^-

References

S1 AXS, SAINT Software Reference Manual; Bruker: Madison, WI, 1998.

S2 G. M. Sheldrick, SHELXTL NT (Version 5.1), Program for Solution and

Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany), 1997.

S3 D. C. Palmer, Crystal Maker 7.1.5, CrystalMaker Software: Yarnton, UK, 2006.