Electronic Supplementary Material (ESI) for CrystEngComm.

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A new Cd(II)-based metal-organic framework for highly fluorescence sensing of nitrobenzene

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Experimental Section

Materials and Instrumentation

All chemicals were of analytical grade and used without further purification.

Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 II analyzer. The powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator at 298K. Simulated PXRD spectra were carried out by the Mercury (Hg) program available free of charge *via* the Internet at http://www.ccdc.cam.ac.uk/Solutions/CSDSystem/Pages/Mercury.aspx. IR spectra were recorded on a Nicolet-5700 FT-IR spectrophotometer with KBr pellets in the 4000 - 400 cm $^{-1}$ region. The photoluminescence spectra were measured on a Perkin Elmer LS-55 spectrofluorometer. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on a Netzsch STA 449C thermal analyzer with a heating rate of 10 °C min^{-1}.

X-ray diffraction

Single-crystal X-ray diffraction for complex **1** were collected on a Bruker SMART-1000 CCD diffractometer at room temperature with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation in the ω scan mode. The diffraction profiles were integrated by the program SAINT. [S1] All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL program.[S2] All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms on ligands were placed in idealized positions with isotropic thermal parameters. The command "omit -1 50.04" was used to omit some disagreeable reflections during the refinement of the compound **1**. The disordered DMF molecules were restrained using the commands "SIMU", "FLAT", "DFIX" and "ISOR" (see the "_refine_special_details" section in the CIF) to make the displacement parameters more reasonable and obtain reasonable structures. Further details of crystal data and structure refinement for **1** were summarized as follows. Selected bond lengths of **1** were given in Table S2. Full crystallographic data for **1** have been deposited with the CCDC 1025203. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.[S3]

Reference

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

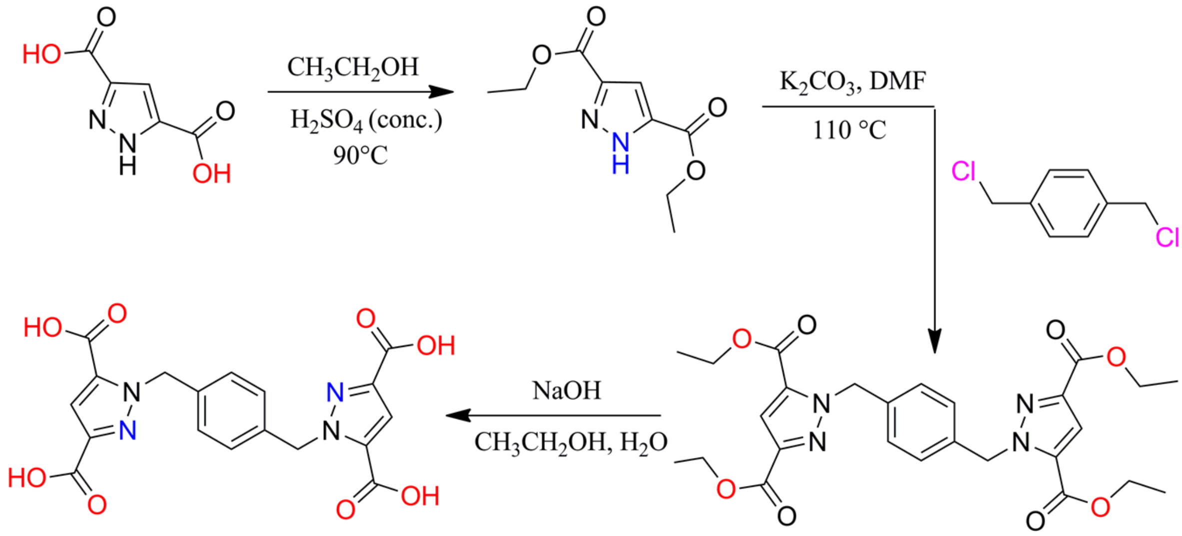
S2 (a) G. M. Sheldrick, SHELXL97, *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997; (b) G. M. Sheldrick, SHELXS97, *Program for Crystal Structure Solution*; University of Göttingen: Göttingen, Germany, 1997.

S3 The checkcif program available at: http://journals.iucr.org/services/cif/checkcif.html.

Crystal data and structure refinement for compound 1

Crystal data for **1** ($Cd_2C_{21}H_{23}N_5O_{12}$): Mr = 762.24, monoclinic, space group $C2/c$, a = 23.2860(2) Å, b = 17.2577(16) Å, c = 18.2221(17) Å, V = 5874.1(9) Å^3, Z = 8, D_{calc} = 1.724 g/cm^3. Reflections collected/unique = 14727 / 5185, R_{int} = 0.1704; $R1$ = 0.0708, $wR2$ = 0.1434 ($I > 2\theta(I)$); $R1$ = 0.1443, $wR2$ = 0.1623 (all data) and GOF = 1.005.

Preparation of H_4L ligand



The ^{1}H-NMR and ^{13}C-NMR spectrum of ligand H_4**L** was recorded in DMSO-d_6 (Fig. S6, Fig. S7).

Figures in Supporting Information

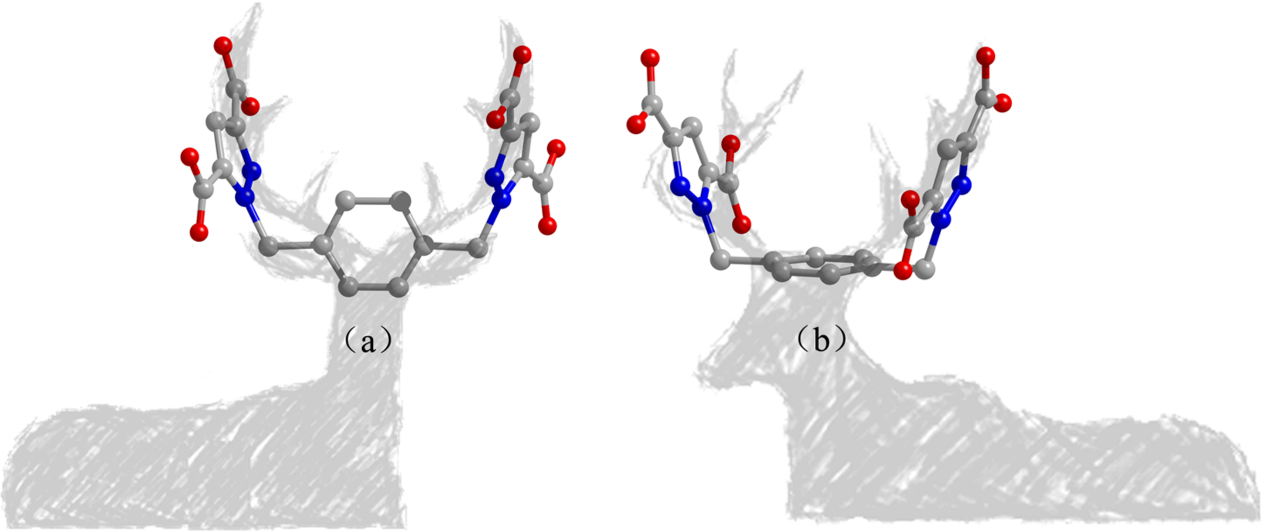


Fig. S1 Two different antler-liked configurations of **L**$^{4-}$ ligand in **1**. Color codes: C (gray), O (red) and N (blue). (Hydrogen atoms are omitted for clarity.)

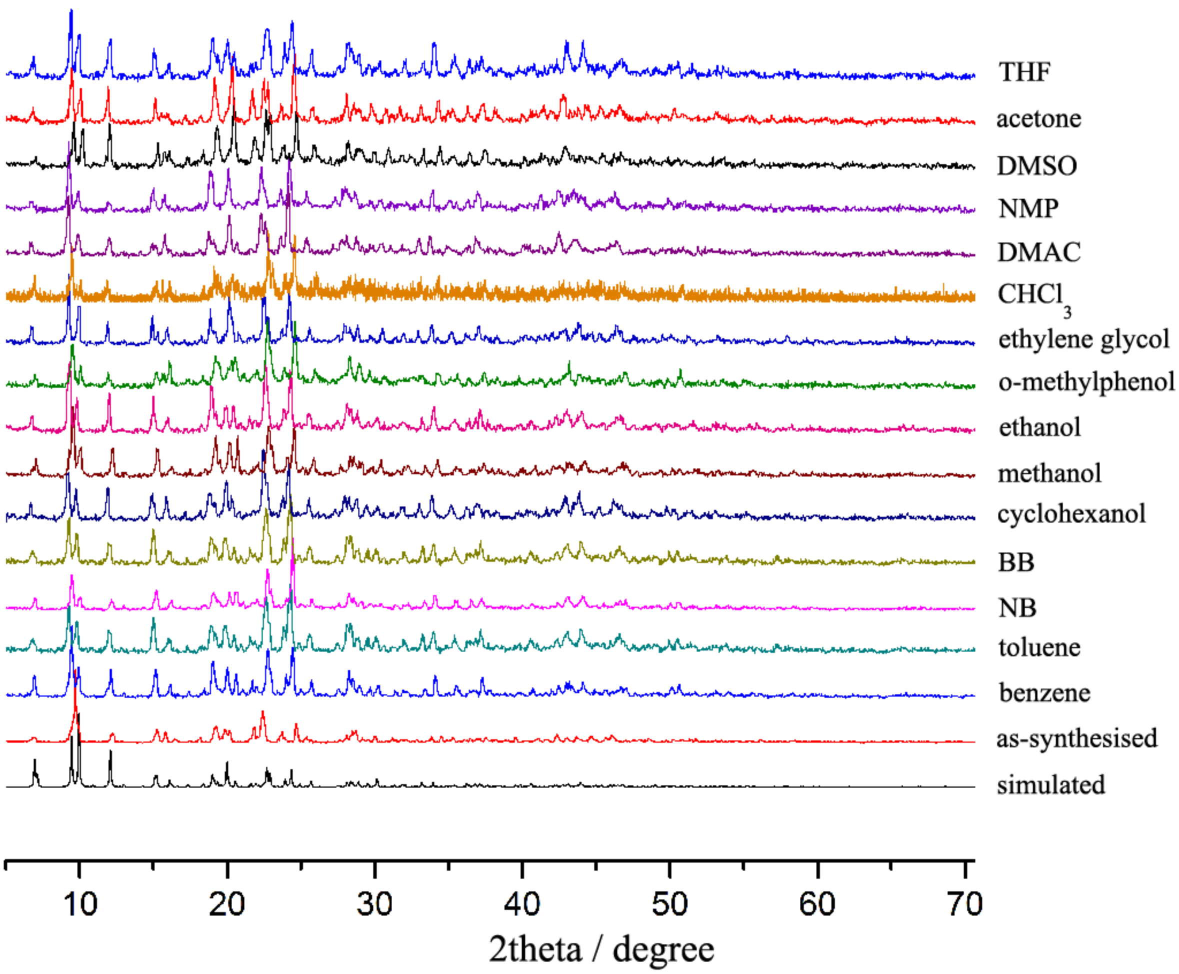


Fig. S2 PXRD patterns of **1** soaked in different analytes.

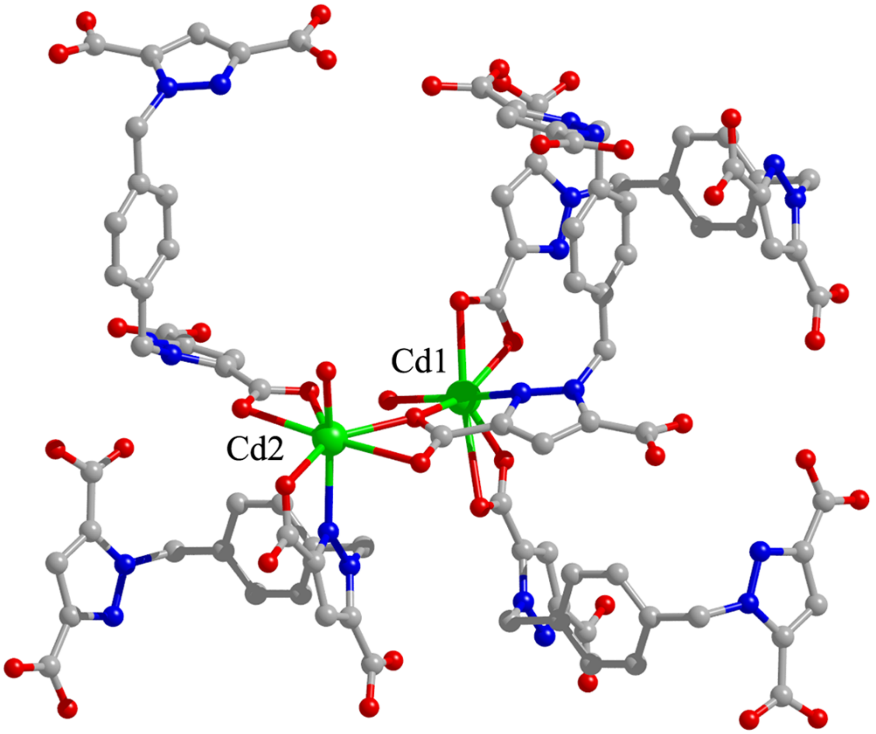


Fig. S3 Coordination geometries of Cd^{2+} ions in **1**. Color codes: Cd (green), C (gray), O (red) and N (blue). (Hydrogen atoms are omitted for clarity.)

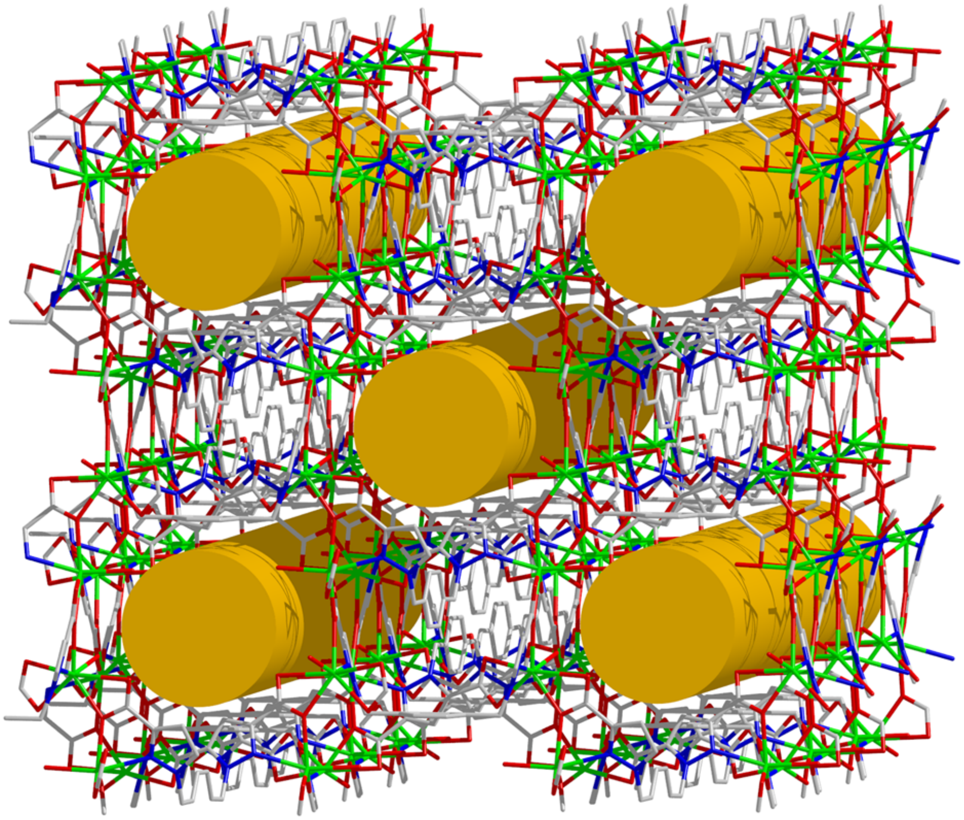


Fig. S4 View of **1** (the orange cylinders represent the voids inside the pores). Color codes: Cd (green), C (gray), O (red) and N (blue). (Hydrogen atoms are omitted for clarity.)

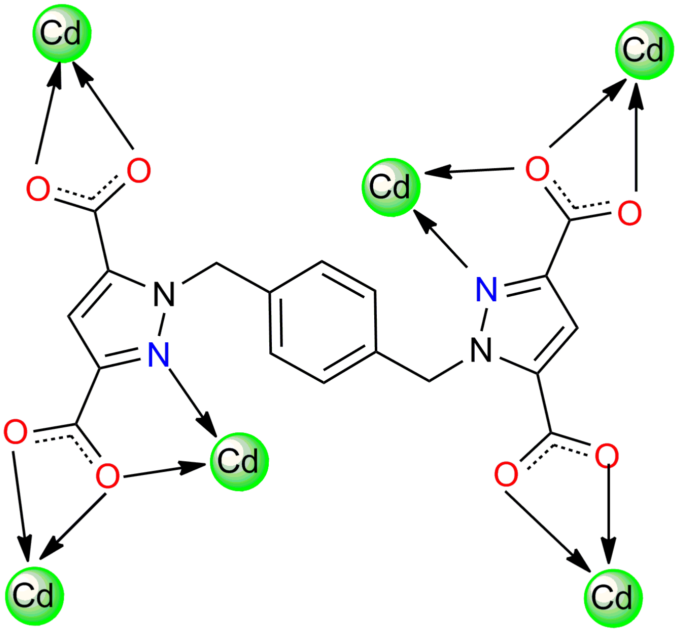


Fig. S5 Schematic representation of the observed coordination modes of **L**$^{4-}$ ligand in **1**.

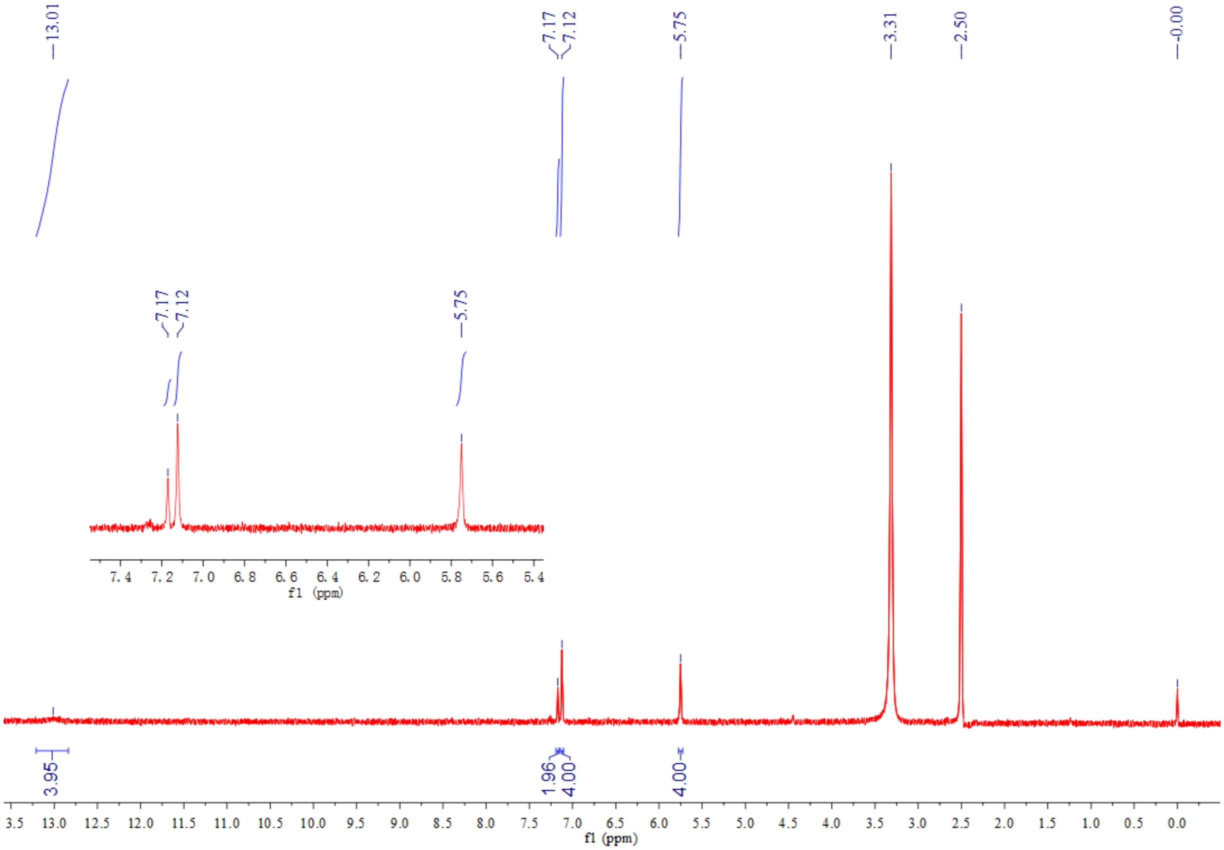


Fig. S6 ^{1}H NMR spectrum of ligand H$_4$**L** recorded in DMSO-d$_6$.

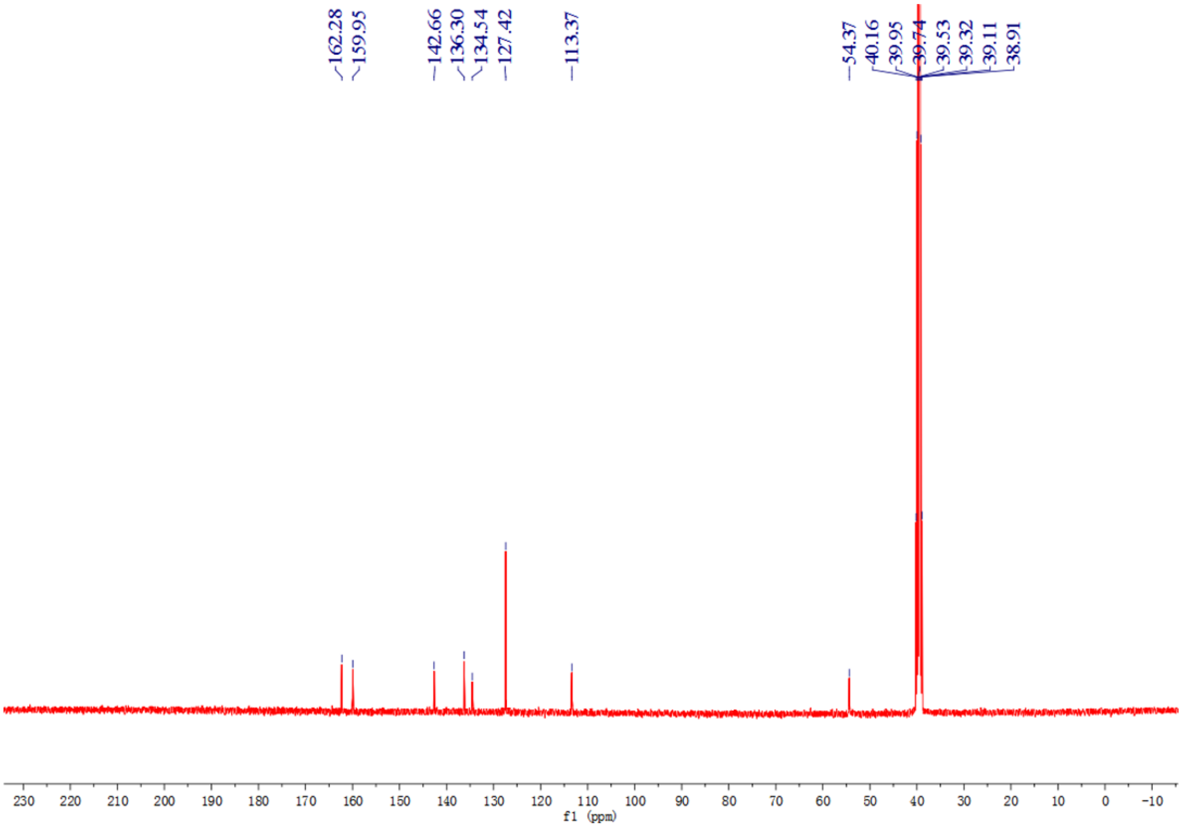


Fig. S7 ^{13}C NMR spectrum of ligand H_4**L** recorded in DMSO-d_6.

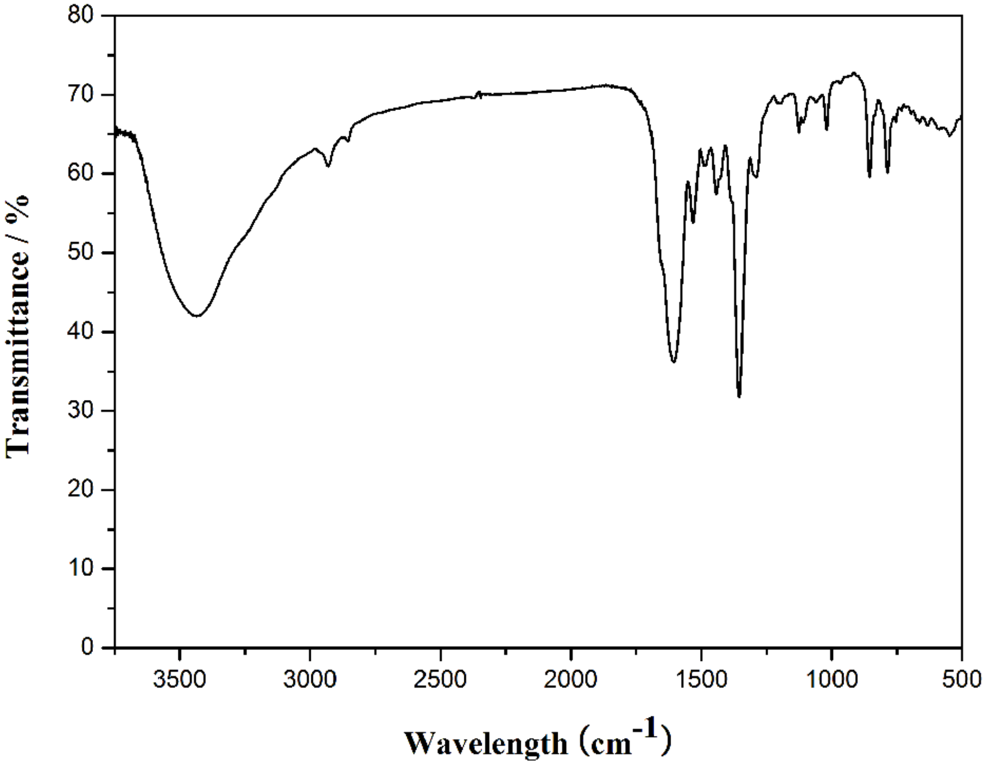


Fig. S8 The FT-IR spectrum of compound **1**.

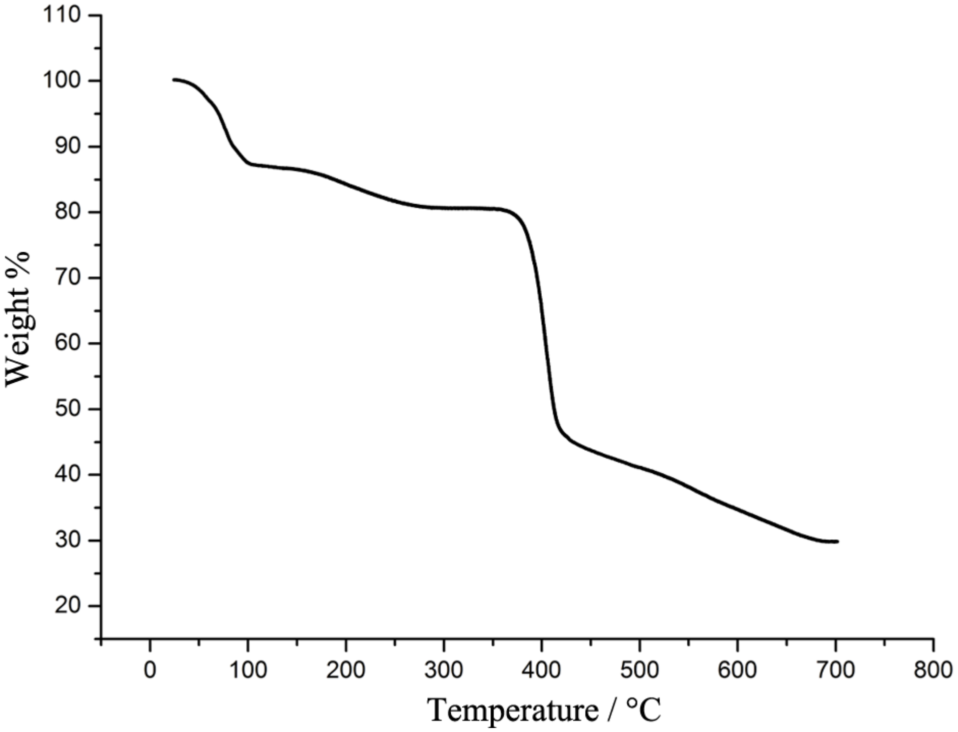


Fig. S9 The TGA curves of compound **1**.

Table S1 HOMO and LUMO energies of toluene, benzene, BB and NB.

	B3LYP/6-31G*		**B3LYP/6-31G****	
Analytes	**HOMO (eV)**	**LUMO (eV)**	**HOMO (eV)**	**LUMO (eV)**
toluene	-6.4045	0.1456	-6.4121	0.1222
benzene	-6.7025	0.0993	-6.7193	0.0729
BB	-6.5830	-0.3426	-6.5901	-0.3654
NB	-7.5915	-2.4284	-7.6015	-2.4354

The former results listed here are only used for comparison.

Table S2 The selected bond lengths [Å] and angles [º] of compound **1**.

Cd(1)-O(5)#1	2.234(8)	Cd(2)-N(3)	2.422(8)
Cd(1)-O(9)	2.270(8)	Cd(2)-O(7)#3	2.433(8)
Cd(1)-O(2)	2.313(7)	Cd(2)-O(1)	2.645(7)
Cd(1)-O(3)#2	2.362(7)	O(3)-Cd(1)#5	2.362(7)
Cd(1)-N(1)	2.409(8)	O(4)-Cd(1)#5	2.429(7)
Cd(1)-O(4)#2	2.429(7)	O(5)-Cd(1)#1	2.234(8)
Cd(2)-O(10)	2.267(8)	O(7)-Cd(2)#6	2.433(8)
Cd(2)-O(2)	2.285(7)	O(8)-Cd(2)#6	2.396(8)
Cd(2)-O(3)	2.295(7)	Cd(2)-O(8)#3	2.396(8)
O(5)#1-Cd(1)-O(9)	92.8(3)	O(3)-Cd(2)-N(3)	70.1(3)
O(5)#1-Cd(1)-O(2)	121.8(3)	O(8)#3-Cd(2)-N(3)	106.0(3)
O(9)-Cd(1)-O(2)	91.3(3)	O(10)-Cd(2)-O(7)#3	85.8(3)
O(5)#1-Cd(1)-O(3)#2	81.7(3)	O(2)-Cd(2)-O(7)#3	133.0(3)
O(9)-Cd(1)-O(3)#2	96.4(3)	O(3)-Cd(2)-O(7)#3	85.9(3)
O(2)-Cd(1)-O(3)#2	154.9(2)	O(8)#3-Cd(2)-O(7)#3	53.5(3)
O(5)#1-Cd(1)-N(1)	101.2(3)	N(3)-Cd(2)-O(7)#3	102.6(3)
O(9)-Cd(1)-N(1)	161.0(3)	O(10)-Cd(2)-O(1)	84.4(3)
O(2)-Cd(1)-N(1)	70.5(3)	O(2)-Cd(2)-O(1)	52.7(2)
O(3)#2-Cd(1)-N(1)	98.2(3)	O(3)-Cd(2)-O(1)	88.2(2)
O(5)#1-Cd(1)-O(4)#2	136.6(3)	O(8)#3-Cd(2)-O(1)	133.4(3)
O(9)-Cd(1)-O(4)#2	90.0(3)	N(3)-Cd(2)-O(1)	84.0(2)
O(2)-Cd(1)-O(4)#2	101.4(2)	O(7)#3-Cd(2)-O(1)	169.0(3)
O(3)#2-Cd(1)-O(4)#2	54.9(2)	O(10)-Cd(2)-O(2)	93.6(3)
N(1)-Cd(1)-O(4)#2	88.5(3)	O(10)-Cd(2)-O(3)	83.9(3)
O(2)-Cd(2)-O(8)#3	80.7(3)	O(2)-Cd(2)-O(3)	140.8(2)
O(3)-Cd(2)-O(8)#3	138.2(3)	O(10)-Cd(2)-O(8)#3	100.6(3)
O(2)-Cd(2)-N(3)	99.6(3)	O(10)-Cd(2)-N(3)	151.8(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,-y+1/2,-z; #2 -x+1/2,y-1/2,-z+1/2; #3 x+1/2,-y+1/2,z+1/2; #4 -x+1,y,-z+1/2; #5 -x+1/2,y+1/2,-z+1/2; #6 x-1/2,-y+1/2,z-1/2; #7 -x,y,-z+1/2.