A pillar-layer MOF for detection of small molecule acetone and metal ions in dilute solution

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Experimental Section

Materials and Measurements

All starting materials and solvents were reagent grade, commercially available and used without further purification. L was synthesized according to the reported procedures.[1] Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. TG analyses were performed on a Perkin−Elmer Thermal Analysis Pyris Diamond heated from room temperature to 850 ºC under a N_2 atmosphere at a rate of 10 ºC min^{-1}.

Synthesis of Cd(5-aip)L·3DMA (1)

A mixture of $Cd(NO_3)_2$•$4H_2O$ (0.1542 g, 0.50 mmol), bpy (0.2 g, 1 mmol), 5-aminoisophthalic acid (0.09 g, 0.50 mmol), 3,5-di(pyridin-4-yl)-4H-1,2,4-triazol-4-amine (0.11 g, 0.50 mmol) and N,N'-dimethylacetamide/ethanol (5:1 = mL) was heated at 90 (°C) for 72 hours. Colorless crystals of **1** were collected in 70% yield based on $Cd(NO_3)_2$•$4H_2O$. Elemental Anal. Calcd for $C_{32}H_{42}CdN_{10}O_7$ (791.16): C, 48.58; H, 5.35; N, 17.70. Anal. Found: C, 48.54; H, 5.33; N, 17.66%.
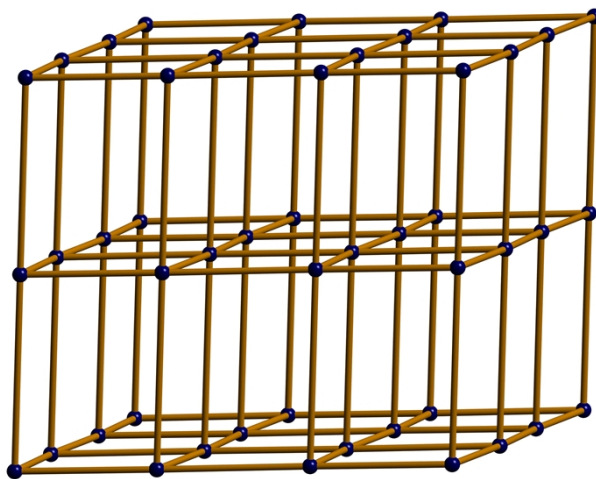

Fig. S1 The simple cubic (a-polonium) network of compound **1**.

Luminescent measurements

The PL properties of **1** in various solvent were investigated at room temperature. The strongest emission wavelengths were located at 418 nm when excited at 352 nm. The **1**-solvent were prepared by introducing 5 mg of **1** powder into 5 mL of acetonitrile, DMA, DMF, acetone, 1, 3-propanediol, cyclohexane, tetrahydrofuran, methanol and ethanol. After sonication treatment 90 min, aging for 6 h, the fluorescence spectra were measured. For the experiment of sensing metal ions, the **1**-M^{2+} emulsions were prepared by introducing 5 mg of **1** powder into 5 mL of M^{x+} (M = Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} or Ag^+) solution. After sonication treatment 90 min, aging for 6 h, the luminescent spectra were measured. The width of the excitation slit was 2.5 nm and the emission slit was 2.5 nm.
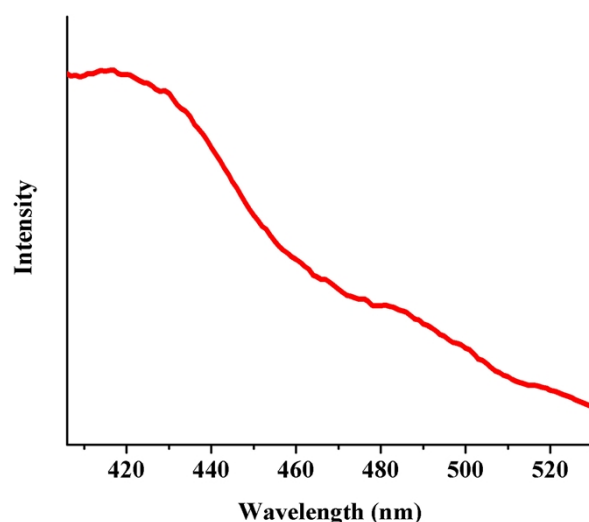

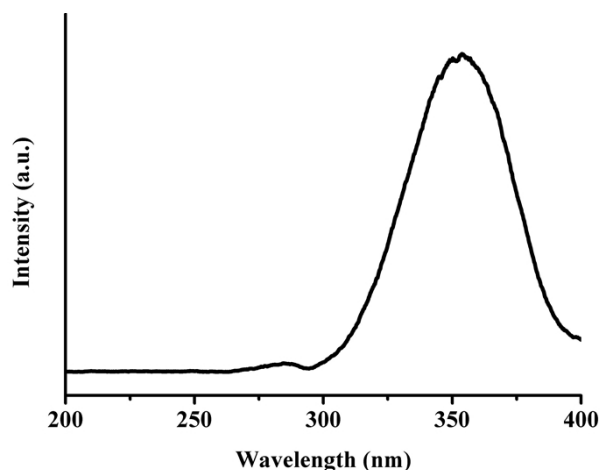**Fig. S2** Luminescent spectra of **1** in the solid state, λ_{ex} = 352 nm.

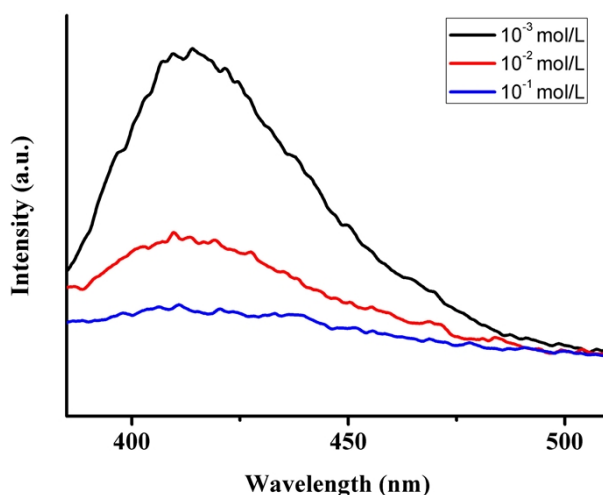**Fig. S3** Excitation spectrum (λ_{em} =418 nm) of **1** in DMA.

Fig. S4 The luminescence spectra of solid **1** activated in dilute solutions of $Ni(NO_3)_2$ at different concentrations.
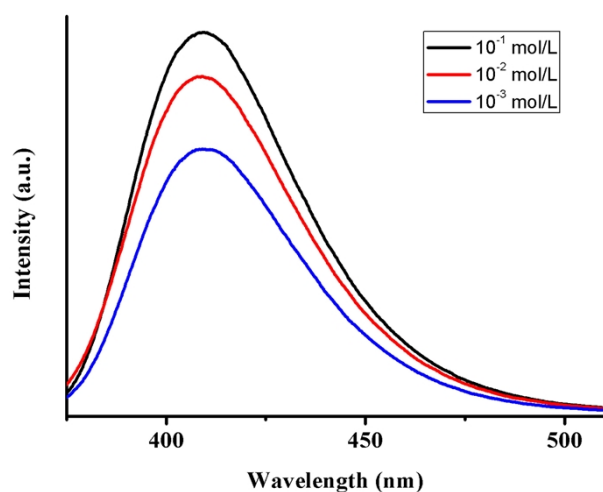

Fig. S5 The luminescence spectra of solid **1** activated in dilute solutions of $Cd(NO_3)_2$ at different concentrations.

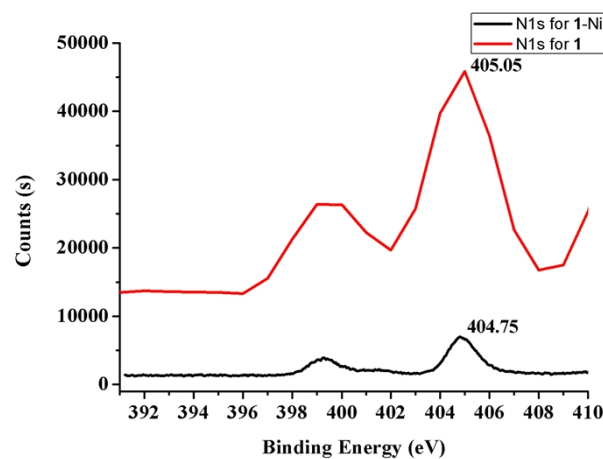**Fig. S6** N1s X-ray photoelectron spectroscopy (XPS) spectra of the **1** (red) and **1**-Ni^{2+}
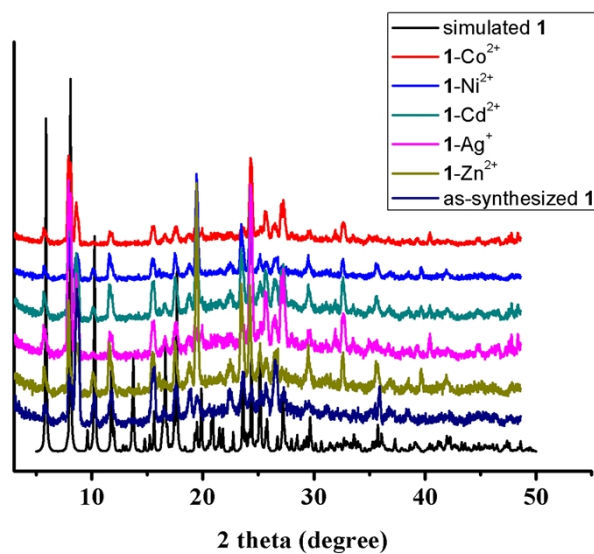
(black).

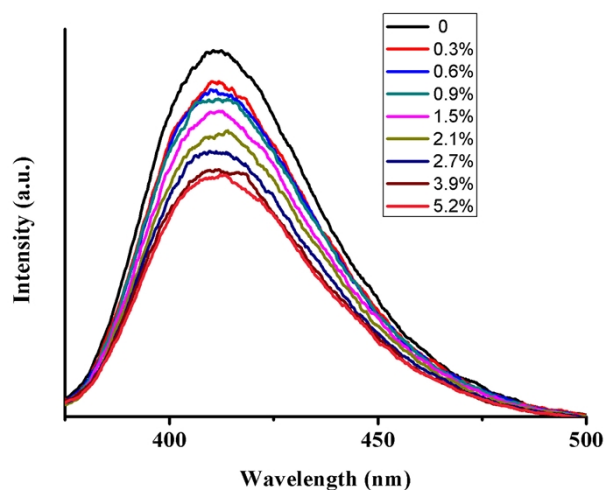**Fig. S7** Powder X-ray diffraction patterns of compound **1**.

Fig. S8 Emission spectra of the dispersed **1** in DMA in the presence of various contents of acetone solvent (vol. %) (excited at 352 nm).
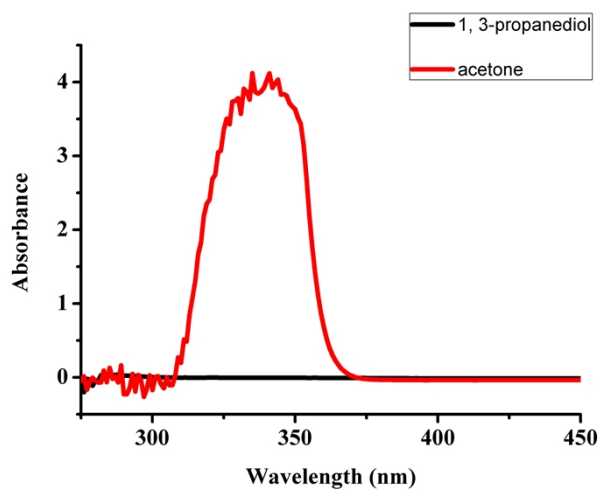
The detection limit of the **1**-DMA system with acetone

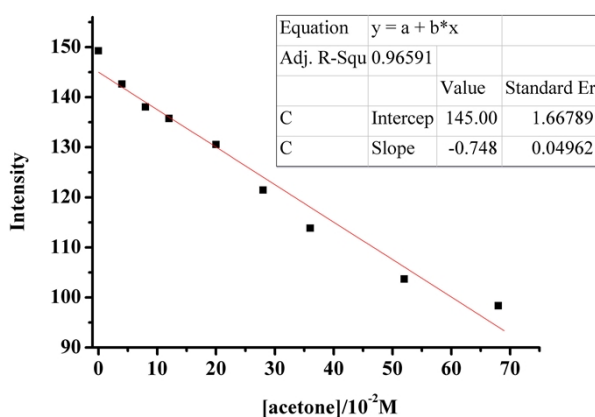| Equation	y = a + b*x		
Adj. R-Squ	0.96591		
		Value	Standard Er
C	Intercep	145.00	1.66789
C	Slope	-0.748	0.04962

Fig. S10 Plot of the intensity at 418 nm for a mixture of **1**-DMA and acetone in the range 0–70 10^{-2} M.

The result of the analysis as follows:

Linear Equation: $Y = -0.748 \times X + 145$ $\qquad$ R = 0.96591

$S = 7.48 \times 10^3$ $\qquad$ $\delta = 4.107$ $\qquad$ K = 3.3

$LOD = K \times \delta / S = 1.812 \times 10^{-3}$ M

The preparation of the samples for ICP and TGA analysis:

Several groups of parallel experiments were carried out at the same time.

The finely ground sample of **1** (5 mg) are immersed in 5 mL of $M(NO_3)_x$ (M = Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+} or Ag^+) solution. After sonication treatment 90 min, aging for 6 h, the sample were filtered out and washed several times. Then the prepared samples were collected for ICP analysis.

Table S1 ICP results for metal-ion-incorporated samples.

Metal ions	Cd/M Mol ratio
Zn^{2+}	1:0.00228
Co^{2+}	1:0.00813
Cd^{2+}	1:0.00287
Ni^{2+}	1:0.00147
Ag^+	1:0.00666

ICP analysis shows that **1** exhibits different loaded amount toward metal ions. Among these metal ions, the ionic radius increases in the order $Ag^+ > Cd^{2+} > Zn^+ > Ni^{2+} > Co^{2+}$. The loaded amount increases in the order $Co^{2+} > Ag^{2+} > Cd^+ > Zn^{2+} > Ni^{2+}$. This

experimental result perhaps can be assigned to not only the size and charge of cations, but also the preferred affinity between cations and nitrogen atoms from the framework.[2]
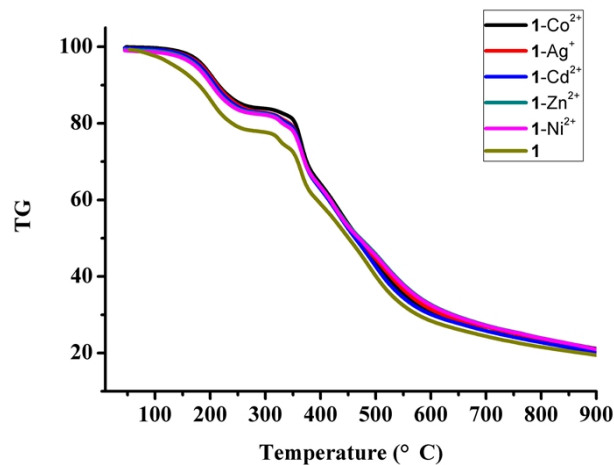

Fig. S11 The TGA curve of compounds **1** and **1**-M^{2+}.

The entire TG curves show three weight loss stages: a sequential weight loss from 100 to 260 °C corresponding to the escape of solvent molecules, almost no weight loss from 260 to 320 °C, and then a steady weight loss from 320 to 900 °C probably due to the decomposition of the ligands.

Single-crystal X-ray diffraction data collection of the compound **1** was performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) at room temperature. All the four crystal structures were solved and refined with full-matrix least-squares techniques (SHELXL-97)[3] within WINGX.[4] Anisotropic thermal parameters were employed to refine all non-hydrogen atoms. The hydrogen atoms of organic ligands were fixed at idealized positions as rigid groups. Hydrogen atoms attached to nitrogen atoms were bound at idealized positions. The data was collected on a Bruker Apex CCD diffractometer at 298(2) K for **1**, with graphite-monochromated MoKa radiation (λ = 0.71073 Å). In **1**, the guest molecules were highly disordered and could not be modeled properly, thus the SQUEEZE routine of PLATON was applied to remove the contributions to the scattering from the solvent molecules. The reported refinements are of the guest-free structures using the *.hkp files produced using the SQUEEZE routine. The detailed crystallographic data and structure refinement parameters are listed in Table S1.

Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC reference numbers 1040849 for **1**.

Table S2 Crystal data and structure refinement for **1**.

Compound	**1**
formular	$C_{32}H_{42}CdN_{10}O_7$
weight	791.16
space group	$P2_1/c$
a [Å]	15.136(5)
b [Å]	17.265(5)
c [Å]	14.239(5)
α [deg]	90
β [deg]	95.717(5)
γ [deg]	90
ρ_{cald} [gcm^{-3}]	1.419
V [Å^3]	3702(2)
Z	4
wavelength (Å)	0.71069
F (000)	1632
Reflns collcd/unique	19117/6556
GOF on F^2	0.911
[a]R_1[$I> 2\sigma(I)$]	0.0483
[b]wR_2(all data)	0.0770

[a]$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b]w$R_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

1. F. Bentiss, M. Lagrenee, M. Traisnel, B. Mernari and H. Elattari, *J. Heterocyclic Chem.*, 1999, **36**, 149.

2. X. Z. Song, S. Y. Song, S. N. Zhao, Z. M. Hao, M. Zhu, X. Meng, L. L. Wu and H. J. Zhang, *Adv. Funct. Mater.*, 2014, **24**, 4034.

3. G. M. Sheldrick, SHELXS97, Programs for X-ray Crystal Structure Solution, University of Göttingen: Göttingen, Germany, 1997.

4. L. J. Farrugia, WINGX, A Windows Program for Crystal Structure Analysis, University of Glasgow: Glasgow, U.K., 1988.