

## Electronic Supplementary Information

### A Vapochromic Strategy for Ammonia Sensing Based on a Bipyridinium Constructed Porous Framework

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#### Section 1. Materials and General Procedures

##### 1.1 Materials and instruments

All chemicals were obtained from commercial sources and were of GR/AR grade unless otherwise noted. The solvent taken in the spectrum testing experiment was spectrally pure acetonitrile. The IR (KBr pellet) spectra were recorded (400-4000 cm<sup>-1</sup> region) on an ABB Bomem MB-102 FT-IR spectrometer. UV-Vis spectral measurement was carried out at room temperature by using a Perkin-Elmer Lambda 950 spectrometer, with a BaSO<sub>4</sub> plate as a standard (100% reflectance). A xenon lamp (Beijing, 500 W) was used for photochemical reaction. Elemental analysis of C, H and N was performed on a Vario EL III CHNOS elemental analyzer. <sup>13</sup>C NMR spectra were recorded on a Bruker-BioSpin AVANCE III HD solid-state NMR Spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex600 diffractometer with Cu K $\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) at a scan speed of 2° min<sup>-1</sup>. Raman spectra were recorded on a Labram HR Evolution spectrometer made by Horiba Jobin Yvon Corporation. The electron spin resonance (ESR) signal was recorded by a Bruker A300 spectrometer. X-ray Photoelectron Spectroscopy (XPS) measurement was performed on a Thermo Fisher ESCALAB 250Xi spectrometer.

##### 1.2 X-ray crystallographic study

Data collection were performed on an Agilent Diffraction SuperNova dual diffractometer, with Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) at 100 K for **PB-I**. Absorption corrections were performed using a multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares on F<sup>2</sup> using the SHELXTL-2016 program package.<sup>[1]</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms of the ligands were located by geometrical calculations, and their positions and thermal parameters were fixed during structural refinement. Structure refinement after modification of the data for the water molecules with the SQUEEZE routine of PLATON<sup>[2]</sup> led to better refinement and data convergence. The empirical formulae were confirmed by element analysis.

Crystal data for **PB-I**: C<sub>44</sub>H<sub>32</sub>Cd<sub>2</sub>I<sub>2</sub>N<sub>4</sub>O<sub>8</sub>;  $M_r = 1223.33$ ; Triclinic *P*-1;  $a = 9.1985(5)$ ,  $b = 18.3882(8)$ ,  $c = 18.6209(8) \text{ \AA}$ ,  $\alpha = 73.643(4)$ ,  $\beta = 75.844(4)$ ,  $\gamma = 79.276(4)^\circ$ ,  $V = 2907.0(3) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ;  $Z = 2$ ;  $D_c = 1.398 \text{ g cm}^{-3}$ ;  $\mu$  (Cu K $\alpha$ ) = 14.551 mm<sup>-1</sup>;  $F(000) = 1180$ ; 19937 reflections collected, of which 11479 unique ( $R_{\text{int}} = 0.0482$ ); GOF = 1.043;  $R_1 = 0.0462$  and  $wR_2 = 0.1037 [I > 2\sigma(I)]$ .

References:

[1] G. M. Sheldrick, Crystal structure refinement with SHELXL, *Acta Cryst.*, **2015**, C71, 3-8.

[2] A. L. Spek, *J. Appl. Crystallogr.*, **2003**, 36, 7.

### 1.3 Synthesis and Characterization of Crystal materials.

Synthesis of  $[\text{Cd}_2(\text{pbpy})(\text{bdc})_2\text{I}_2]\cdot 4\text{H}_2\text{O}$  **PB-I**:  $\text{H}_2\text{bpdc}$  (20 mg, 0.12 mmol), **pbpy** $\cdot 2\text{ClO}_4$  (62 mg, 0.1 mmol), KI (20 mg, 0.12 mmol) and  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (70 mg, 0.22 mmol) were dissolved in the *N,N*-dimethylformamide solution (6 mL) in a Teflon vessel of the hydrothermal bomb and stirred for 30 min. The vessel was sealed, placed in an oven and heated at 90 °C for 2 days, and then the reaction mixture was filtrated after cool to room temperature. The filter liquor was let to volatilize for several days, finally the colorless block crystals (**PB-I**) were obtained in 47% yield. Elemental analysis calc. for  $\text{C}_{44}\text{H}_{40}\text{N}_4\text{O}_{12}\text{I}_2\text{Cd}_2$ : C, 40.79; H, 3.11; N, 4.32; found: C, 40.69; H, 3.44; N, 4.41 %.

## Section 2. Additional Data and Pictures

**Table S1.** The interplanar angles and the bending angles ( $\angle\text{N-C-C}$ ) recorded in the ligand A and ligand B of the crystals. The crystals **1** and **2** are represented for Cl<sup>-</sup>/Br<sup>-</sup> halogen anions constructed Cd-based isomorphous complexes, respectively.<sup>[3]</sup>

Complex	Ligand A			Ligand B		
	interplanar angle $\phi\text{A} / ^\circ$	halogen $\cdots\text{N}^+$ distance / Å	$\angle\text{N-C-C} / ^\circ$	interplanar angle $\phi\text{B} / ^\circ$	halogen $\cdots\text{N}^+$ distance / Å	$\angle\text{N-C-C} / ^\circ$
<b>1</b>	32.6	4.04	111.1	2.9	4.22	111.9
<b>2</b>	31.1	3.97	111.2	1.8	4.38	110.7
<b>PB-I</b>	<b>29.9</b>	<b>4.08</b>	<b>110.3</b>	<b>36.7</b>	<b>4.54</b>	<b>111.8</b>

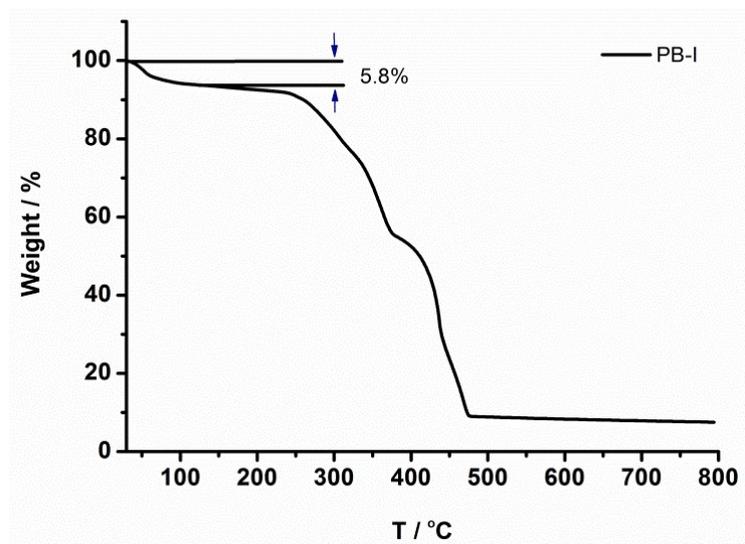
Reference:

[3] C. Chen, L.-X. Cai, B. Tan, Y.-J. Zhang, X.-D. Yang and J. Zhang, *Chem. Commun.*, **2015**, 51, 8189-8192.

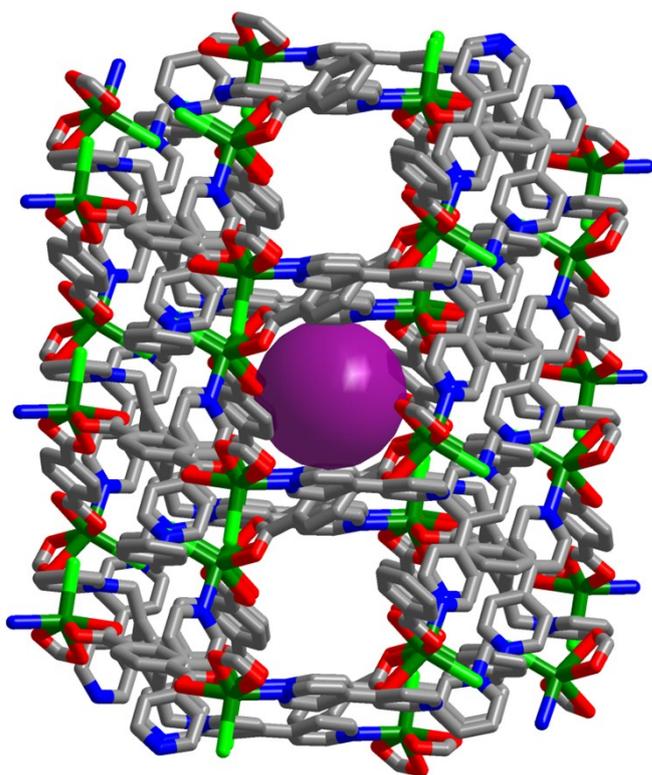
**Table S2.** Elemental analyses of **PB-I** and ammonia treated sample (abbreviated as **PB-I-N**).

Complex	Empirical formula	Calculated (%)			Experiment (%)		
		N	C	H	N	C	H
<b>PB-I</b> $[\text{Cd}_2(\text{pbpy})(\text{bdc})_2\text{I}_2]\cdot 4\text{H}_2\text{O}$	$\text{C}_{44}\text{H}_{40}\text{N}_4\text{O}_{12}\text{I}_2\text{Cd}_2$	4.32	40.79	3.11	4.41	40.69	3.44
<b>PB-I-N</b> $[\text{Cd}_2(\text{pbpy})(\text{bdc})_2(\text{NH}_3)_2]\cdot 2\text{I}\cdot 1.5\text{NH}_3\cdot 5\text{H}_2\text{O}$	$\text{C}_{44}\text{H}_{52.5}\text{N}_{7.5}\text{O}_{13}\text{I}_2\text{Cd}_2$	7.65	38.49	3.85	7.29	38.30	3.51

The primary sample **PB-I** was exposed to ammonia vapor (25% ammonium hydroxide) for one minute, then a color change to yellow occurred and gave a sample that was labeled as **PB-I-N**, which exhibits the empirical formula of  $[\text{Cd}_2(\text{pbpy})(\text{bdc})_2(\text{NH}_3)_2]\cdot 2\text{I}\cdot 1.5\text{NH}_3\cdot 5\text{H}_2\text{O}$ . That is, the **PB-I** can capture one water molecule and 3.5 ammonia molecules per unit cell.



**Fig. S1** The TG curve of PB-I.



**Fig. S2** The frontal view of the cage-like pore space with a quadrature opening.

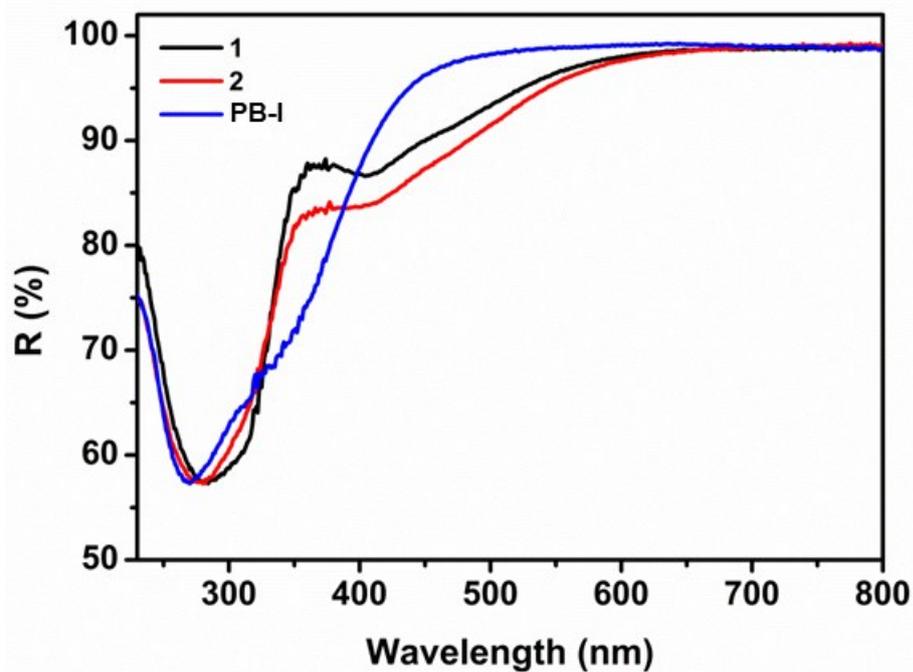


Fig. S3 The UV-Vis diffuse reflectance spectra for 1, 2 and PB-I.

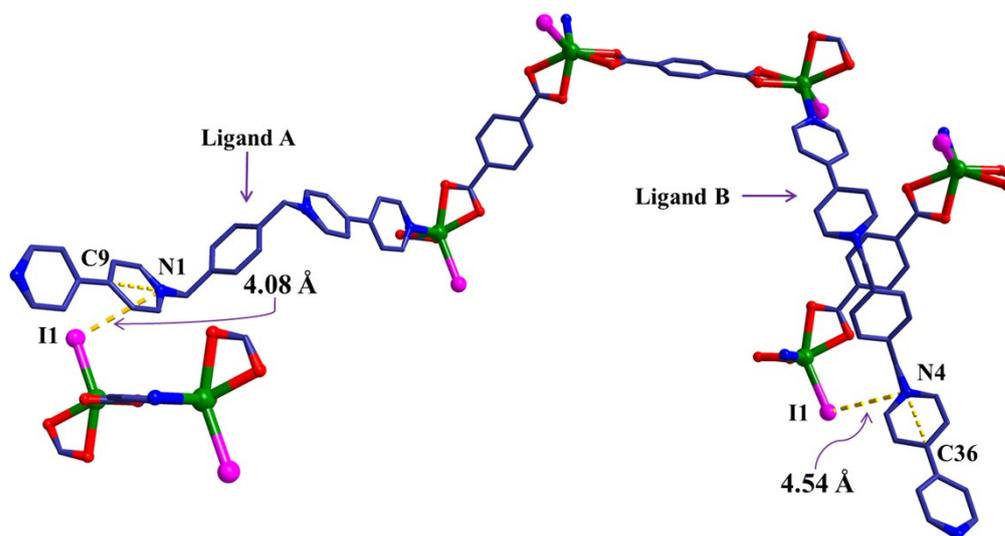
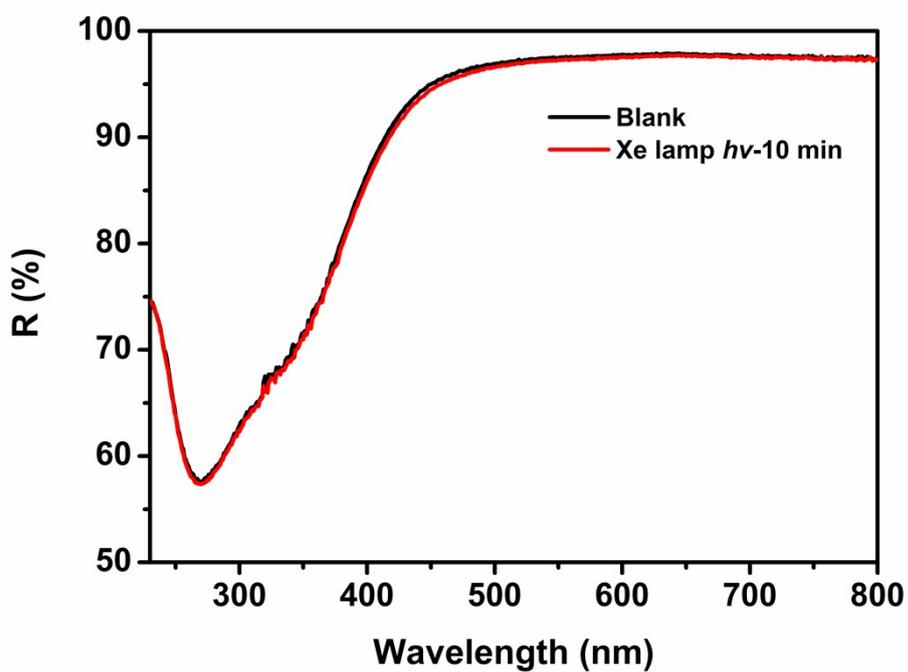
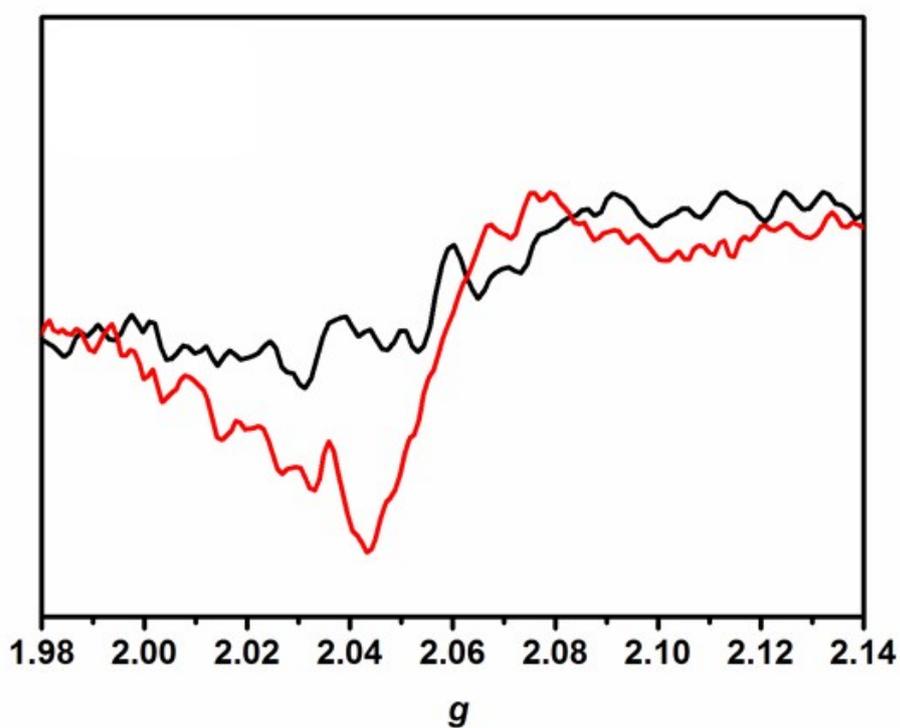


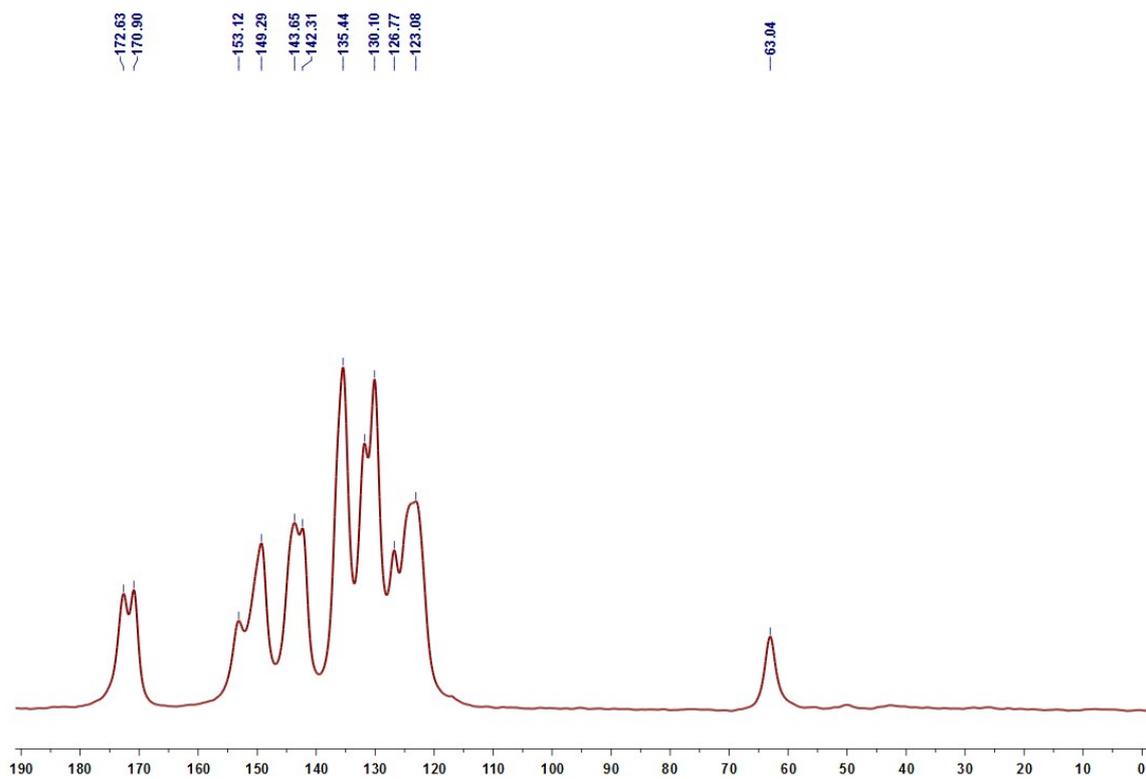
Fig. S4 The distances between donor atom (I) and acceptors (pyridinium) in the solid state are 4.08 Å in (ligand A) and 4.54 Å in (ligand B), respectively.



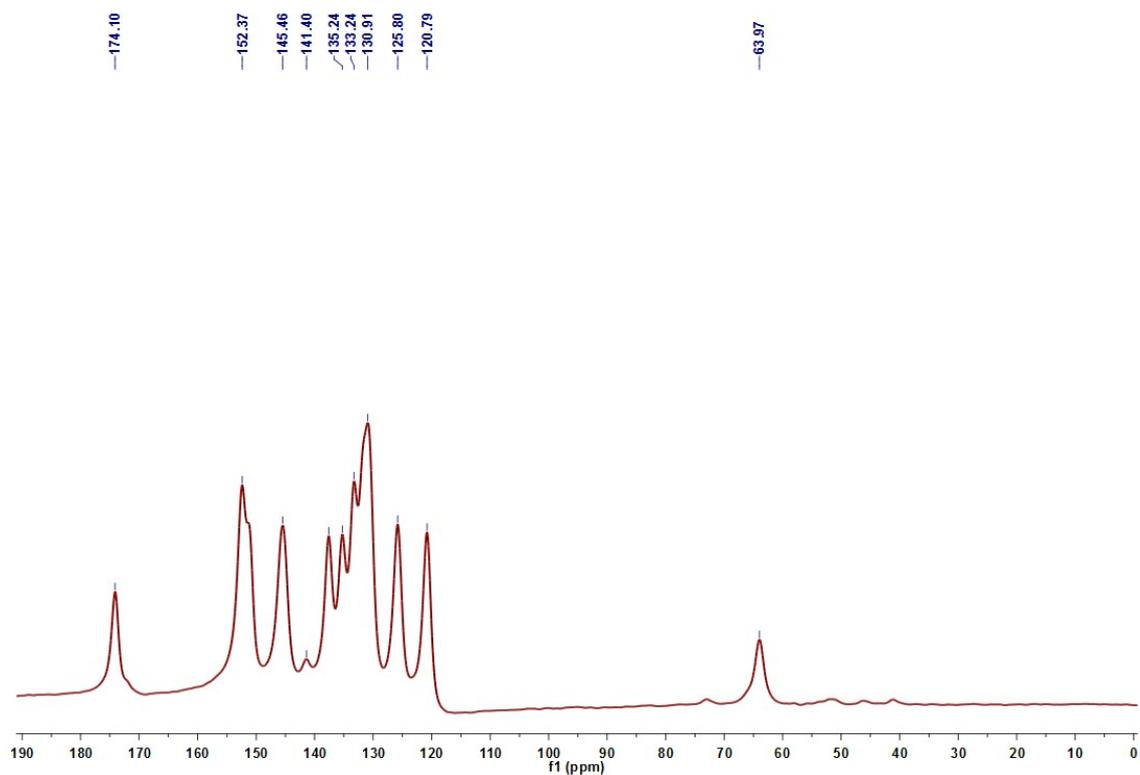
**Fig. S5** The UV-Vis diffuse reflectance spectra for **PB-I** before (black) and after (red) a 500 W xenon lamp irradiated for 10 minutes.



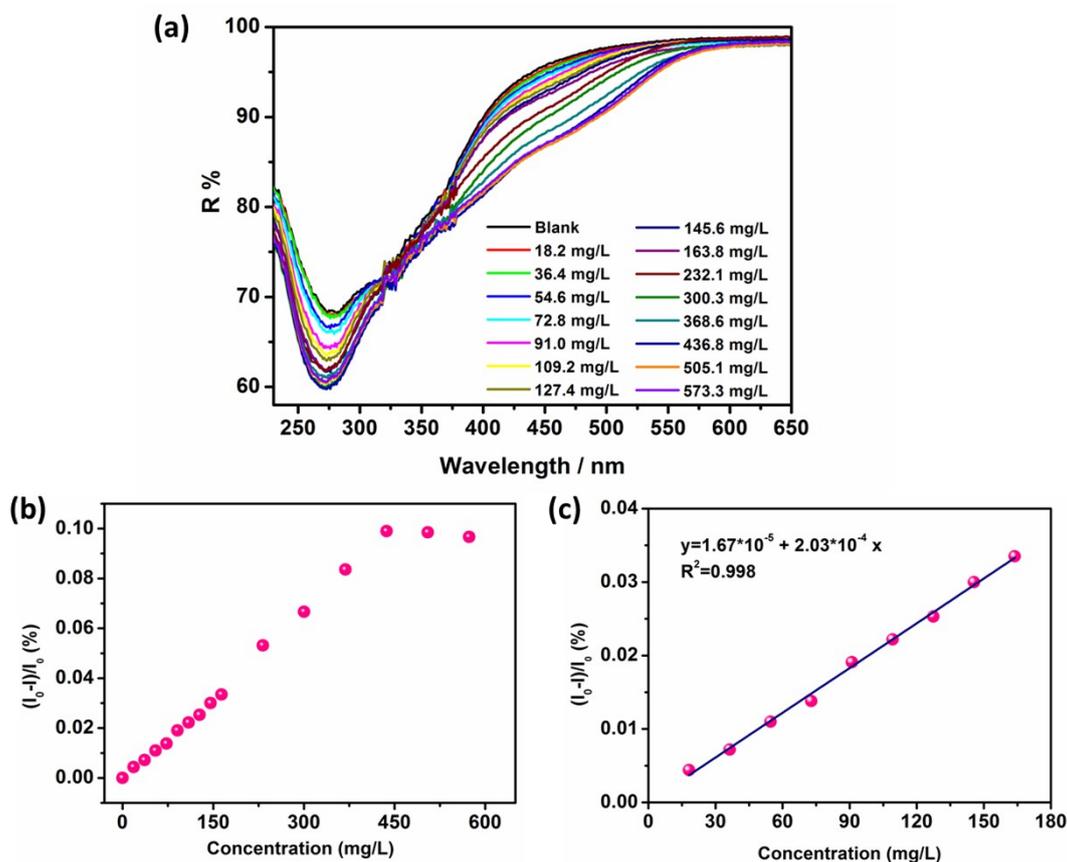
**Fig. S6** ESR spectra for crystal **PB-I** before (black) and after (red) ammonia treatment.



**Fig. S7** The solid state  $^{13}\text{C}$  NMR spectrum of **PB-I**.



**Fig. S8** The solid state  $^{13}\text{C}$  NMR spectrum of **PB-I** after ammonia treatment.



**Fig. S9** (a) The concentration dependent coloration process of **PB-I**. (b) A plot showing the relative diffuse reflection enhancement (measured at 420 nm) of **PB-I** with increasing the ammonia concentration. (c) The data points in the concentration range (18.2–163.8  $\text{mg} \cdot \text{L}^{-1}$ ) are fitted in linear relationship  $y = 2.03 \times 10^{-4} x + 1.67 \times 10^{-5}$  ( $R^2 = 0.998$ ).

As we know, the density of 25% ammonium hydroxide is  $0.91 \text{ g/cm}^3$  with a low boiling ( $37.7 \text{ }^\circ\text{C}$ ). In order to get a credible detection limits, we have designed a concentration-dependent vapochromic experiment with increasing concentration gradient. The **PB-I** sample (**PB-I** 5 mg, with 5 mg  $\text{BaSO}_4$  as the diluent, mixed and pressed into plate) was placed in a jar (500 mL), and 40  $\mu\text{L}$  25% ammonium hydroxide ( $18.2 \text{ mg} \cdot \text{L}^{-1}$ ) was added with a pipette. The jar was placed into a constant temperature oven ( $50 \text{ }^\circ\text{C}$ ) for 1 min ensuring the ammonia completely volatilized. And then gradually increase the ammonia concentration. We got the concentration dependent UV-Vis spectra as follow (Fig. S9a).

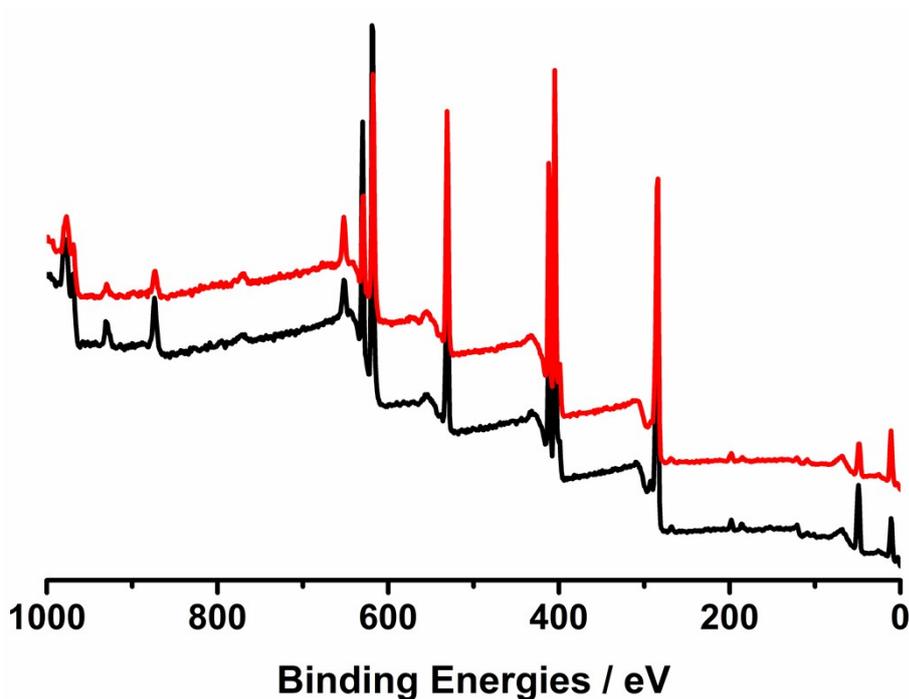
The diffuse reflection intensity vs. ammonia concentration curve in the concentration range ( $18.2\text{--}163.8 \text{ mg} \cdot \text{L}^{-1}$ ) can be well fitted in linear relationship (Fig. S9c). The slope of the line indicates that **PB-I** possesses a favorable sensitivity to detect ammonia. The detection limit was calculated as [Eqs. (1)–(2)]:

$$3\sigma/\text{slope} \quad (1)$$

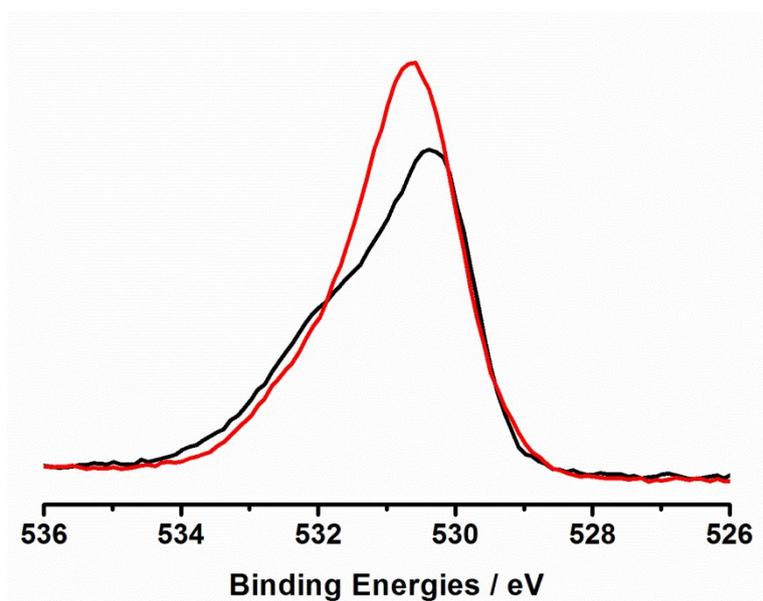
$$\sigma = 100 \times (I_{SE}/I_0) \quad (2)$$

where  $I_{SE}$  is the standard error of the diffuse reflection intensity measurement, as determined by the baseline measurement of the blank sample monitored at 420 nm, and  $I_0$  is the measured diffuse reflection intensity of **PB-I**. The slope was obtained from the linear fit of the ammonia concentration dependent diffuse reflection intensity (monitored

at 420 nm) curve in the region of 18.2–163.8 mg·L<sup>-1</sup>, and the detection limit of ammonia was calculated to be 14.8 mg·L<sup>-1</sup>.



**Fig. S10** XPS survey spectra for **PB-I** before (black) and after (red) ammonia treatment.



**Fig. S11** O 1s XPS core-level spectra for **PB-I** before (black) and after (red) ammonia treatment. Due to the complicated interference of lattice water, it cannot be properly deconvoluted in O 1s XPS core-level spectra. However, it is clearly observed that the maximum peak at 530.4 eV is shifted to 530.7 eV after ammonia treatment (Fig. S9), suggesting ammonia molecules may break the Cd···O coordination bonds.