

Electronic Supplementary Information

Ammonia detection by using flexible Lewis acidic sites in luminescent porous frameworks constructed from a bipyridinium derivative

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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 spectrum pure acetonitrile. The IR (KBr pellet) spectra were recorded (400-4000 cm⁻¹ region) on an ABB Bomem MB-102 FT-IR spectrometer. Thermogravimetric (TG) analysis was performed on a Mettler-Toledo TGA/SDTA851e thermal analyzer in a flowing air atmosphere at a heating rate of 10°C min⁻¹ from 30 to 800 °C. Elemental analysis of C, H and N was performed on a Vario EL III CHNOS elemental analyzer. ¹H NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz). The chemical shifts were measured relative to TMS (0.00 ppm) for DMSO-D₆ as indicated. Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex diffractometer with Cu K α ($\lambda = 1.5406 \text{ \AA}$) at a scan speed of 4° min⁻¹. The photoluminescence spectra were determined by a FLS920 and FLS980 fluorescence spectrometer at room temperature. The quantum yields of solid compounds were determined by an absolute method with an integrating sphere. Raman spectra were recorded on a Labram HR Evolution spectrometer made by Horiba Jobin Yvon Corporation.

1.2 X-ray crystallographic study

Data collection were performed on an Agilent Diffraction SuperNova dual diffractometer, with Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$) at 100 K for **1** and **2**. Absorption corrections were performed using a multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares on F2 using the SHELX-97 program package.^[1] 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^[2] led to better refinement and data convergence. The empirical formulae were confirmed by element analysis (EA).

Crystal data for **1**: C₄₄H₃₂Cd₂Cl₂N₄O₈; *Mr* = 1040.47; Triclinic *P*-1; *a* = 8.9041(9), *b* = 17.9362(15), *c* = 18.9879(7) Å, α = 100.842(5), β = 102.263(7), γ = 103.409(8)°, *V* = 2791.2(4) Å³; *T* = 100(2) K; *Z* = 2; *D_c* = 1.238 g·cm⁻³; μ (Cu K α) = 7.460 mm⁻¹; *F*(000) = 1136; 17414 reflections collected, of which 9300 unique (*R*_{int} = 0.0714); GOF = 1.042; *R*₁ = 0.0835 and *wR*₂ = 0.1849 [*I* > 2 σ (*I*)].

Crystal data for **2**: C₄₄H₃₂Br₂Cd₂N₄O₈; *Mr* = 1129.36; Triclinic *P*-1; *a* = 9.0867(7), *b* = 18.0356(10), *c* = 18.8207(12) Å, α = 102.462(5), β = 103.387(7), γ = 100.625(6)°, *V* = 2839.3(3) Å³; *T* = 100(2) K; *Z* = 2; *D_c* = 1.321 g·cm⁻³; μ (Cu K α) = 8.009 mm⁻¹; *F*(000) = 1108; 19057 reflections collected, of which 10969 unique (*R*_{int} = 0.0549); GOF = 1.065; *R*₁ = 0.0612 and *wR*₂ = 0.1368 [*I* > 2 σ (*I*)].

Referee:

[1] (a) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structure, University of Göttingen, Göttingen, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structure, University of Göttingen, Göttingen, 1997.

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

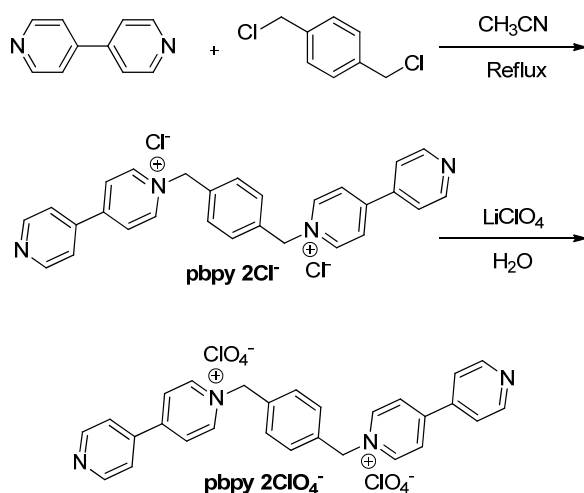
1.3 Synthesis and characterization of crystal materials.

Synthesis of **pbpy·2Cl**: To a stirring solution of 4,4'-bipyridine (10.2 g, 65.0 mmol) in acetonitrile (35 mL), 1,4-bis-(chloromethyl)-benzene (4.0 g, 22.8 mmol) was added and the reaction temperature was increased to 100 °C and maintained refluxing for 24 h. Then the reaction mixture was isolated by filtration and washed with acetonitrile to obtain a pale yellow solid **pbpy·2Cl** (10.9 g, yield 98%). ¹H NMR (400 MHz, DMSO-D₆): δ 5.89 (s, 4H), 7.67 (s, 4H), 8.01 (q, *J* = 4.5 Hz, 4H), 8.65 (d, *J* = 7.0 Hz, 4H), 8.87 (q, *J* = 4.5 Hz, 4H), 9.34 (d, *J* = 7.0 Hz, 4H).

Synthesis of **pbpy·2ClO₄**: To a stirring solution of **pbpy·2Cl** (2.45 g, 5.0 mmol) in deionized water (20 mL), lithium perchlorate (1.98 g, 11.0 mmol) was added and stirred for 10 minutes. Then the mixture was filtrated and followed by washing with excess distilled water to obtain a yellow powder **pbpy·2ClO₄** (2.9 g, yield 94%).

Synthesis of [Cd₂(pbpy)(bdc)₂Cl₂]₂·5H₂O **1**: H₂bpdc (20 mg, 0.12 mmol), **pbpy·2Cl** (50 mg, 0.1 mmol) and Cd(NO₃)₂·4H₂O (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 allowed to cool slowly to room temperature within 2 days. Yellowish block crystals (**1**) were obtained in 86% yield. Elemental analysis calc. for C₄₄H₄₂N₄O₁₃Cl₂Cd₂: C, 46.74; H, 3.74; N, 4.96; found: C, 46.35; H, 3.94; N, 5.35 %.

Synthesis of [Cd₂(pbpy)(bdc)₂Br₂]₂·8H₂O **2**: H₂bpdc (20 mg, 0.12 mmol), **pbpy·2ClO₄** (62 mg, 0.1 mmol) and Cd(NO₃)₂·4H₂O (70 mg, 0.22 mmol) were dissolved in the *N,N*-dimethylformamide solution (8 mL) in a Teflon vessel of the hydrothermal bomb, an excess KBr (30 mg, 0.25 mmol) was added to the mixture afterwards and stirred for 30 min. The vessel was sealed, placed in an oven and heated at 90 °C for 2 days, finally allowed to cool slowly to room temperature within 2 days. The reaction was filtered and the filtrate was allowed to stand at room temperature and orange petaloid crystals of **2** were obtained within a few days (yield: 61%). Elemental analysis calc. for C₄₄H₄₈N₄O₁₆Br₂Cd₂: C, 41.50; H, 3.80; N, 4.40; found: C, 41.04; H, 3.91; N, 4.35 %.



Scheme 1 Synthesis of the bipyridinium salts **pbpy·2Cl** and **pbpy·2ClO₄**.

Section 2. Additional Data and Figures

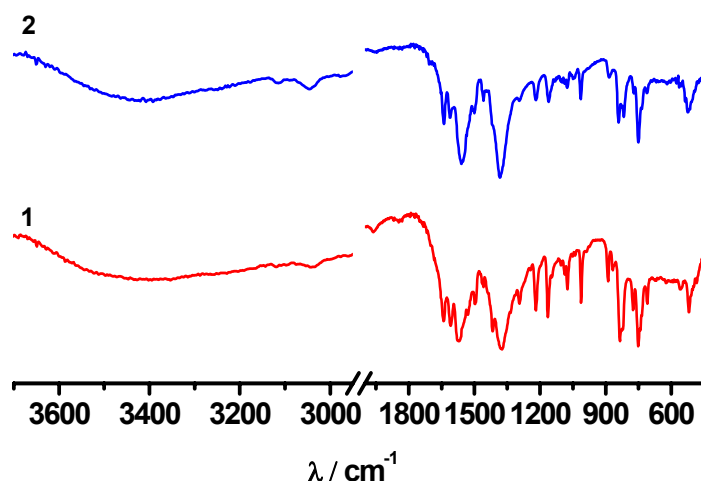


Fig. S1 FT-IR spectra of compounds 1 and 2.

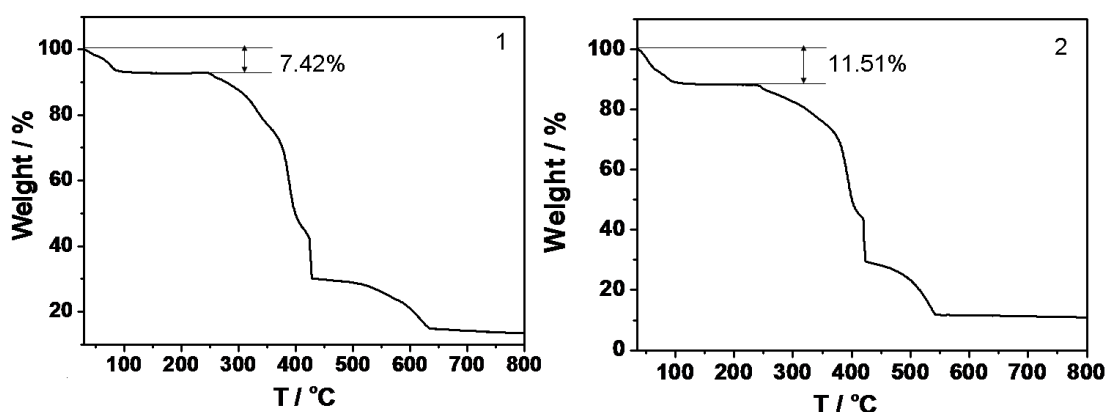


Fig. S2 The TG plots of compounds 1 and 2. The first weight loss of 7.42% and 11.51% of the total weight below 110 °C in 1 and 2 corresponds well to the release of five water molecules in 1 (calc. 7.97%) and eight water molecules in 2 (calc. 11.31%). The molecular skeletons remain stable up to about 250 °C, and then begin to decompose subsequently above this temperature.

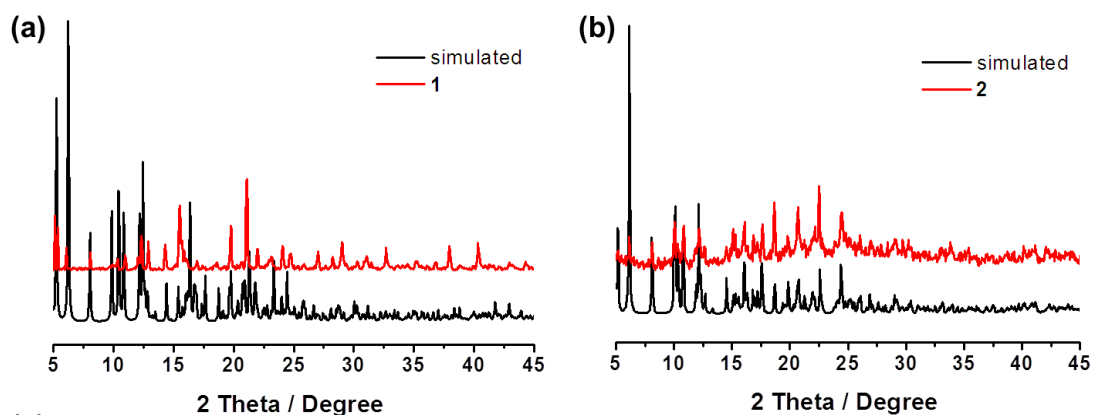


Fig. S3 The calculated and experimental XRPD patterns of compounds 1 (a) and 2 (b).

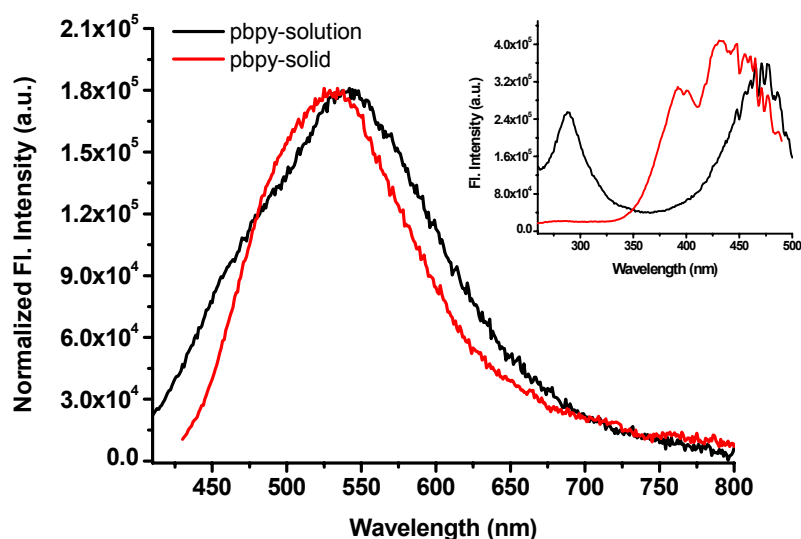


Fig. S4 The fluorescence spectra of **pbpy·2Cl** (2.5×10^{-5} mol/L) measured in acetonitrile (dark line) and the fluorescence spectrum of **pbpy·2Cl** measured in solid state (red line). The inset was the excitation spectra of the ligand in solution and in the solid-state measured in 540 nm and 534 nm, respectively.

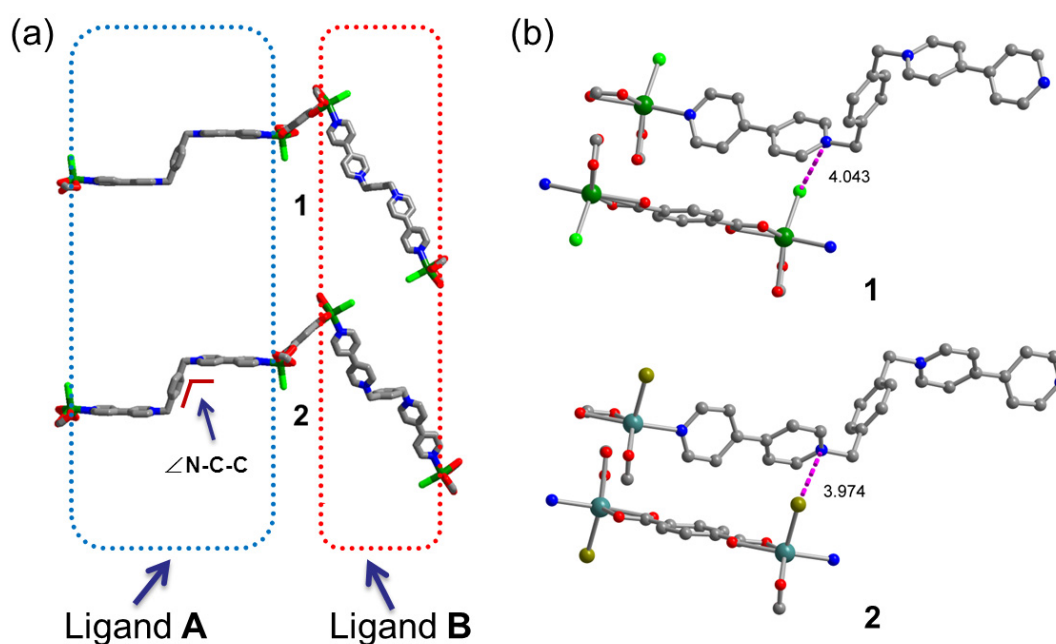


Fig. S5 (a) The coordination environment in compounds **1** and **2**. The two inequivalent pbpy ligands are marked as ligand **A** and ligand **B**, respectively. The bending angles (\angle N-C-C) are 111.6 and 111.2° in **1**, 111.1 and 110.5° in **2**. The dihedral angle between the pyridine and pyridinium rings is 32.55° in **1**, and 31.05° in **2**, respectively. Another set is not given due to the disorder of some carbon atoms. (b) The distances between donor atoms (Cl/Br) and acceptors (pyridinium) in the solid state are 4.06 Å in **1** and 3.97 Å in **2**, respectively. The distances between the carboxylate oxygen atom and the pyridinium nitrogen atom are 3.09 Å in **1** and 3.08 Å in **2**. The dihedral angles between the adjacent pyridinium ring and the benzenedicarboxylate moiety is 37.17° with the centroid distance of 4.51 Å in **1** and 40.74° with the centroid distance of 4.72 Å in **2**.

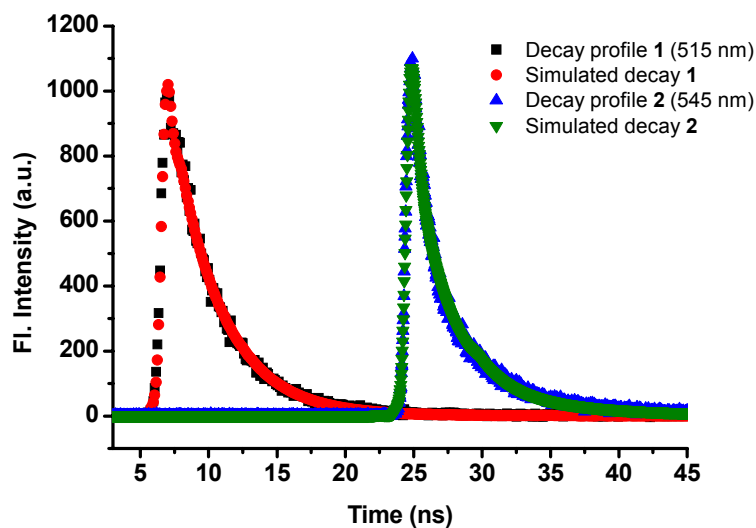


Fig. S6 Fluorescence decay curves of compounds 1 and 2.

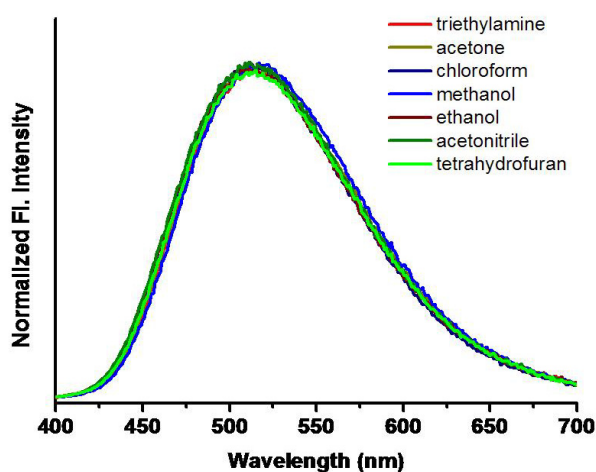


Fig. S7 Normalized solid-state emission spectra of 1 fumigated for 20 minutes in triethylamine, acetone, chloroform, methanol, ethanol, acetonitrile and tetrahydrofuran, respectively. Their emission peaks keep unchanged as compared with the pristine sample (515 nm).

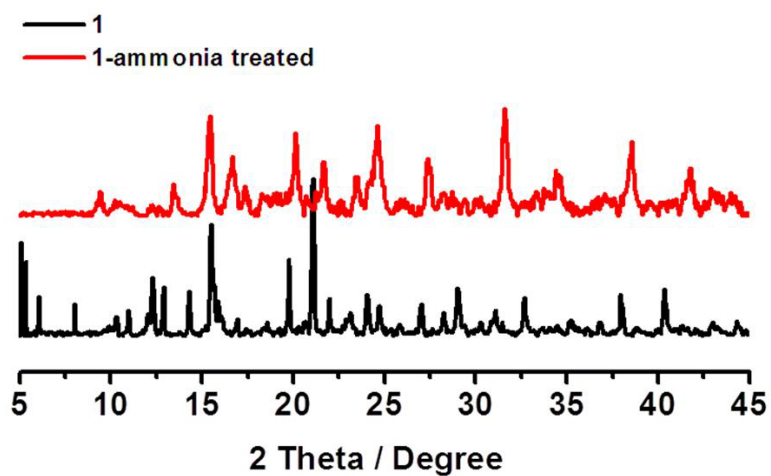


Fig. S8 The PXRD patterns of 1 and its ammonia treated sample.

Table S1. Optical properties of the compounds under study: PL maxima (λ), PL quantum yields and decay times (Φ_{PL} , τ).

compd	λ (nm)	τ (ns)	Φ_{PL} (%)
1	515	0.10 (8.89%)	32.8
		3.41 (91.11%)	
2	545	0.17 (13.99%)	3.3
		7.98 (25.84%)	
		2.42 (60.17)	