

## Electronic Supplementary Information

### **Metal-Organic Frameworks with Improved Moisture Stability Based on a Phosphonate Monoester: Effect of Auxiliary N-donor Ligands for Framework Dimensionality**

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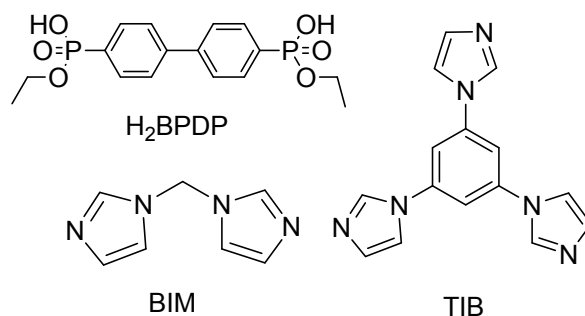
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## Synthesis of organic ligands.



**Scheme S1.** The three organic ligands

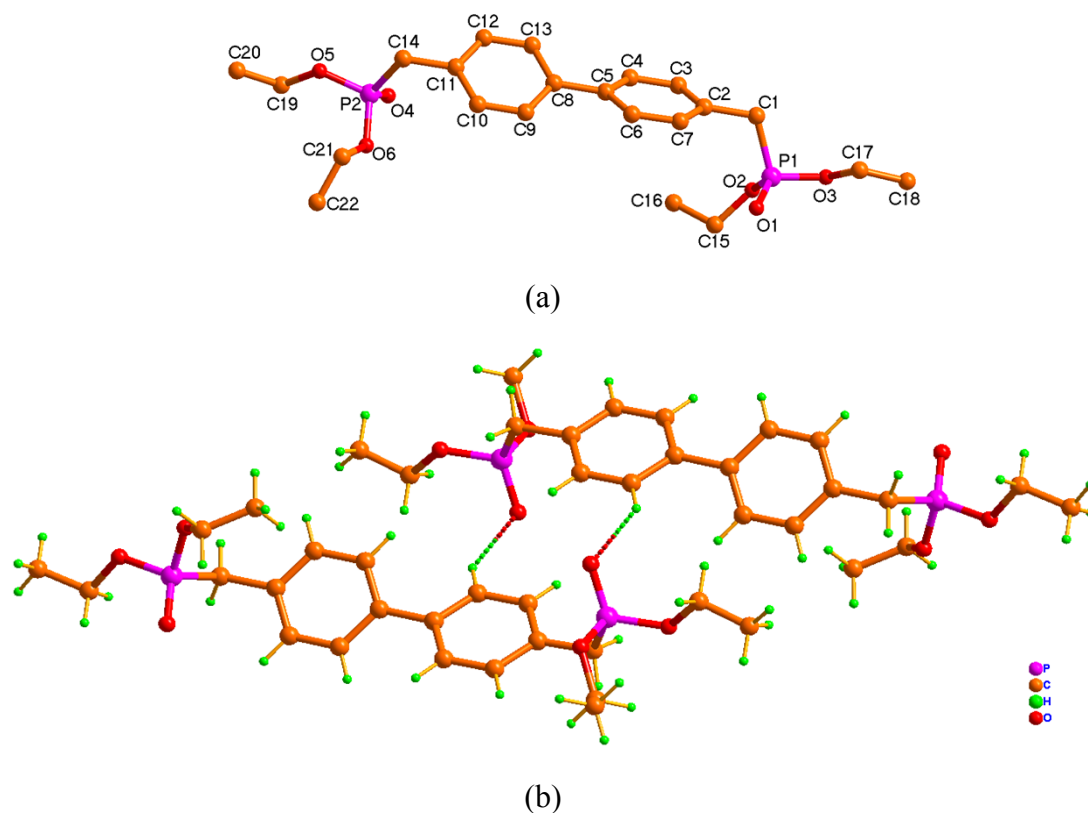
**Synthesis of 4,4'-biphenyldiphosphonate bis(monoethyl ester) (H<sub>2</sub>BPDP):** The H<sub>2</sub>BPDP ligand was synthesized following a modified published procedure.<sup>1</sup> The commercially obtained tetraethyl ([1,1'-biphenyl]-4,4'-diylbis(methylene)) bis(phosphonate) (30 g, 66 mmol) was dissolved in distilled water (50 mL) and concentrated HCl (30 mL), heated to reflux (~90 °C) overnight. The H<sub>2</sub>BPDP was obtained by filtration, washing with water and vacuum drying.

**Synthesis of bis(imidazol-1-yl)methane (BIM):** The BIM ligand was synthesized according to the method reported previously.<sup>2</sup> Typically, KOH (3 g, 53.4 mmol) was ground and dissolved in 20 mL CH<sub>3</sub>CN, to which imidazole (3 g, 44.1 mmol) was added with stirring. After imidazole was fully dissolved, CH<sub>2</sub>Br<sub>2</sub> (3.8 g, 22.1 mmol) was slowly introduced, followed by allowing the reaction temperature to proceed at 60 °C for 5 h and the reaction progress was monitored by using TLC. Until the completion of reaction, the solvent was distilled and the crude product was dissolved in acetone to remove undissolved impurities. After the filtrate was concentrated, cooled and recrystallized, white needle-like crystals was harvested as final product.

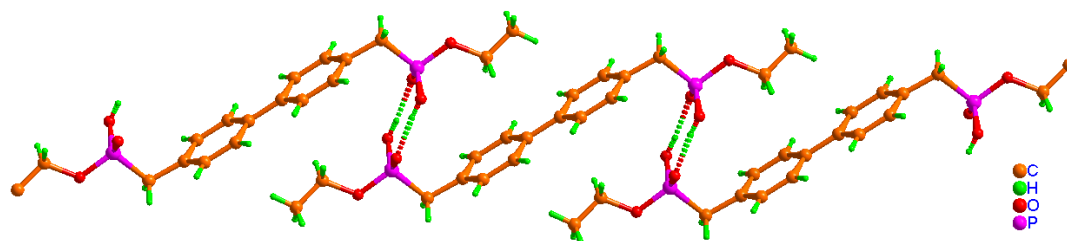
**Synthesis of 1,3,5-tri(1H-imidazol-1-yl)benzene (TIB):** The TIB ligand was synthesized following a modified published procedure.<sup>3</sup> A mixture of 1,3,5-tribromobenzene (126 mg, 0.4 mmol), K<sub>2</sub>CO<sub>3</sub> (221 mg, 1.6 mmol), imidazole (163.4 mg, 2.4 mmol), and CuSO<sub>4</sub> (3 mg, 0.0125 mmol) was charged into a Teflon-lined autoclave (20 mL) under N<sub>2</sub> atmosphere and heated to 150 °C for 1 h, held for 24 h and then cooled down to ambient temperature for 1 h. The crude product was washed with water for three times to colorless. The solid residue was then extracted with methanol, upon removal of the solvent and 50 °C drying, TIB as a colorless solid was obtained.

#### **References:**

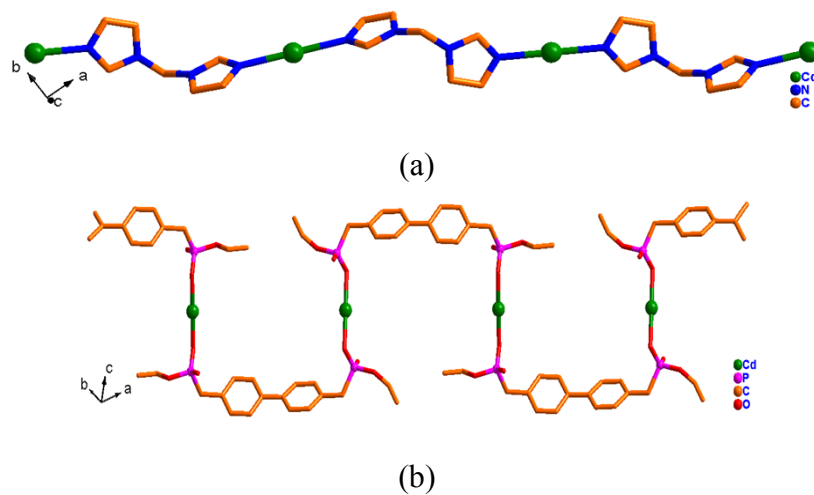
- (1) C. R. Mayer, M. Hervé, H. Lavanant, J.-C. Blais and F. Sécheresse, *Eur. J. Inorg. Chem.*, 2004, 973.
- (2) J. Cai, T. Zhao, G. An, B. Zhou and Q. Hu, *Chem. Bioeng. (in Chinese)*, 2009, **26**, 22.
- (3) A. Rit, T. Pape, A. Hepp and F. E. Hahn, *Organometallics*, 2011, **30**, 334.



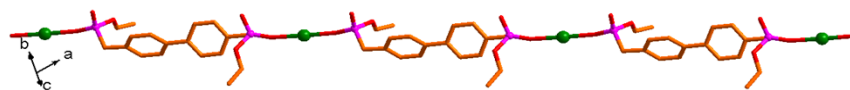
**Fig. S1** (a) Asymmetric unit of 4,4'-biphenyldiphosphonate bis(diethyl ester) molecule. (b) A view showing the partial structure of 4,4'-biphenyldiphosphonate bis(diethyl ester). There are hydrogen bond interactions between molecules [C13–H13A···O4, with the H···O distance and O–H···O angle being 2.63 Å and 145°, respectively. Symmetry code:  $-1-x, 1-y, -z$ ].



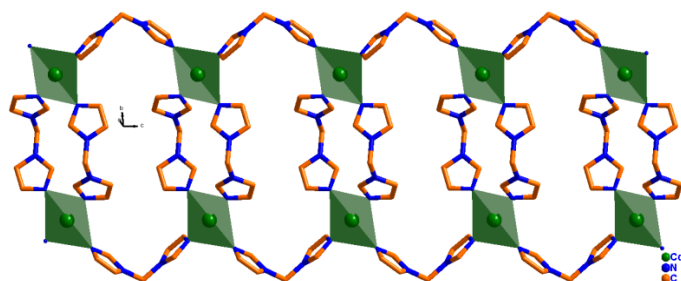
**Fig. S2** A view showing the partial structure of 4,4'-biphenyldiphosphonate bis(monoethyl ester). The molecule itself lies about an inversion centre, and there are strong hydrogen bond interactions between molecules [O2–H2B···O1, with the H···O distance and O–H···O angle being 1.71 Å and 169°, respectively. Symmetry code: -x, -y, 1-z].



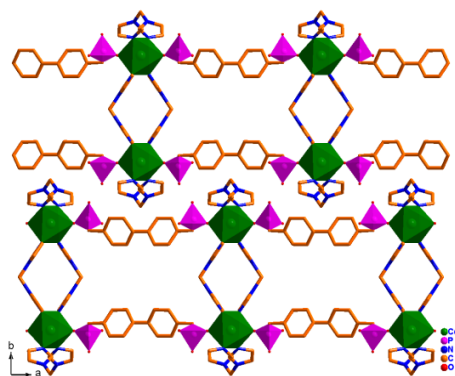
**Fig. S3** View of the 1D chains constructed by Cd(II) and (a) BIM or (b) BPDP ligand in compound **1**.



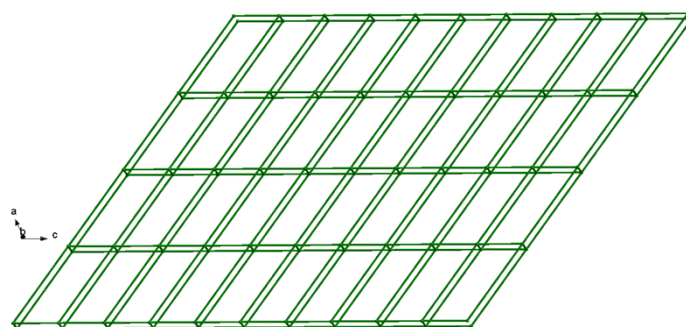
(a)



(b)



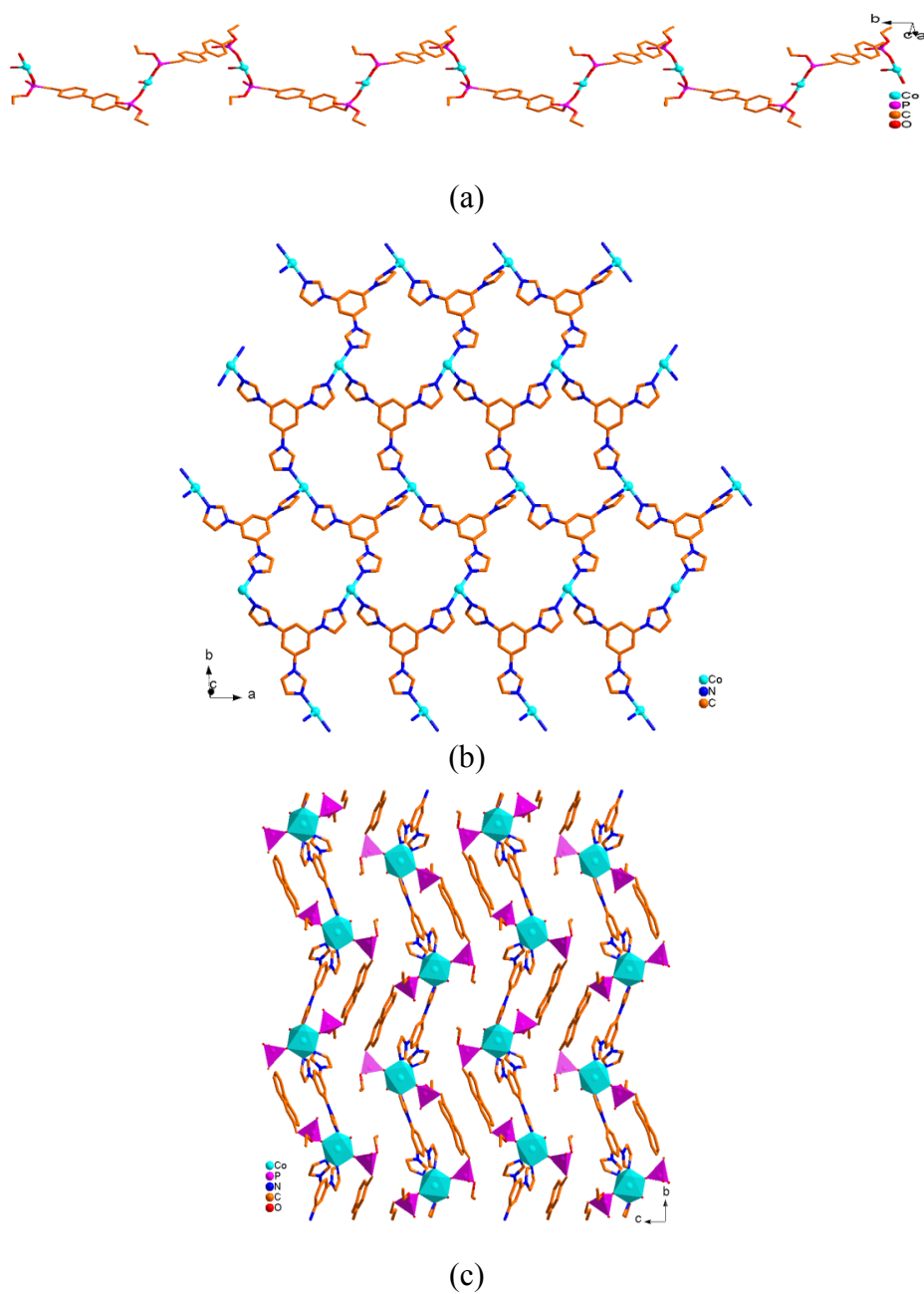
(c)



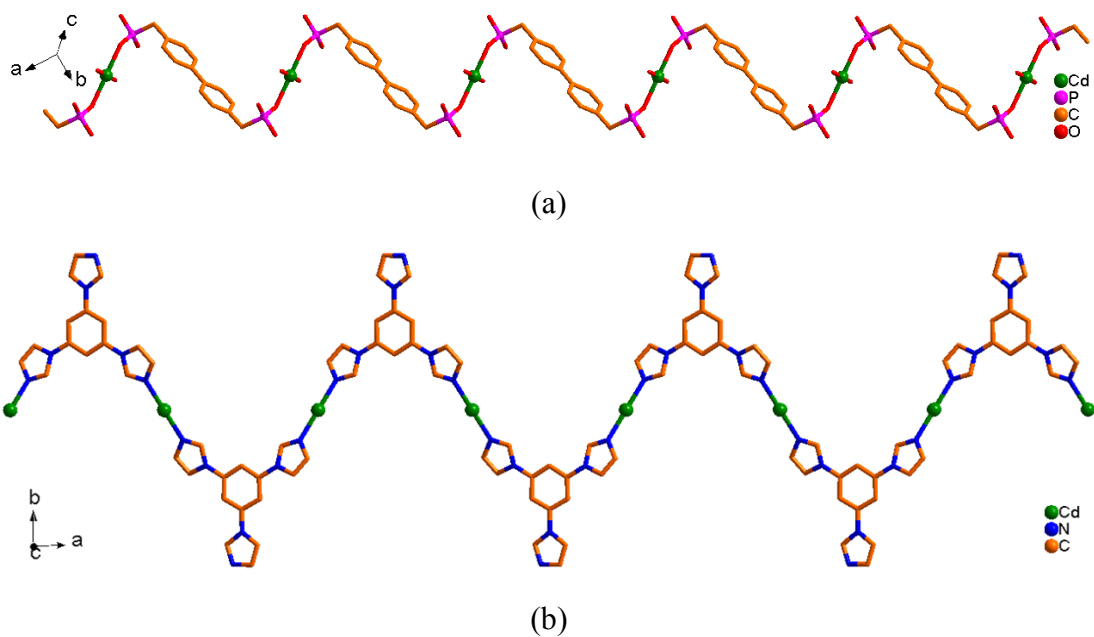
(d)

**Fig. S4** View of (a) the 1D chain constructed by Cd(II) and BPDP ligand, (b) the 1D nanoribbon formed by Cd(II) and BIM, and (c) the layered structure of compound **2**. The ethyl groups in the phosphonate ester ligand and isolated ethanol molecules are

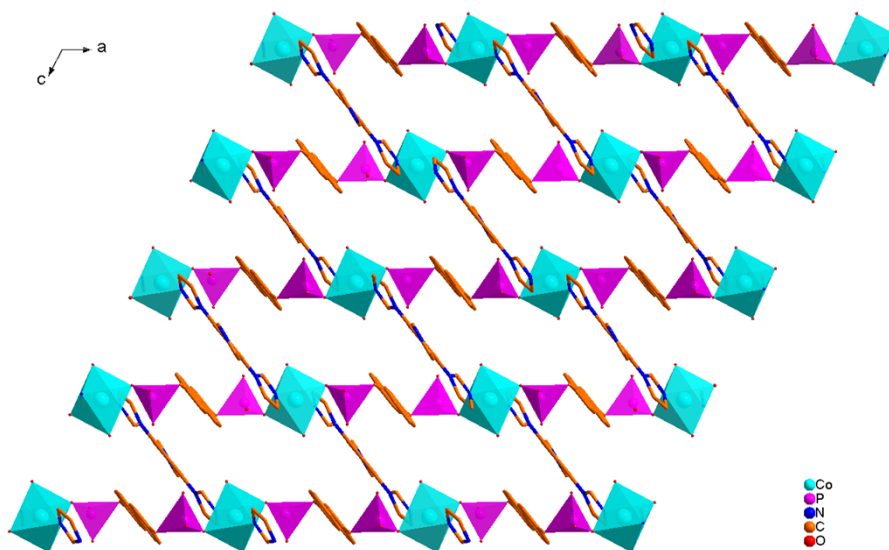
omitted for clarity. (d) The simplified topology with 5-connected nodes for the double layer.



**Fig. S5** View of (a) the 1D chain constructed by Co(II) and BPDP ligand, (b) the 2D Co(II)-TIB layer, and (c) the layered structure of compound 3. The isolated water molecules are omitted for clarity.



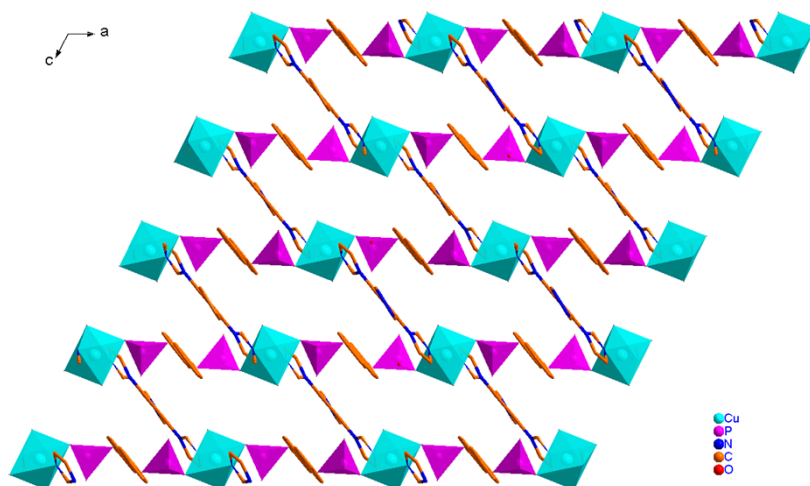
**Fig. S6** View of the 1D wave-like (a) Cd(II)-BPDP and (b) Cd(II)-TIB chains in compound **4**.



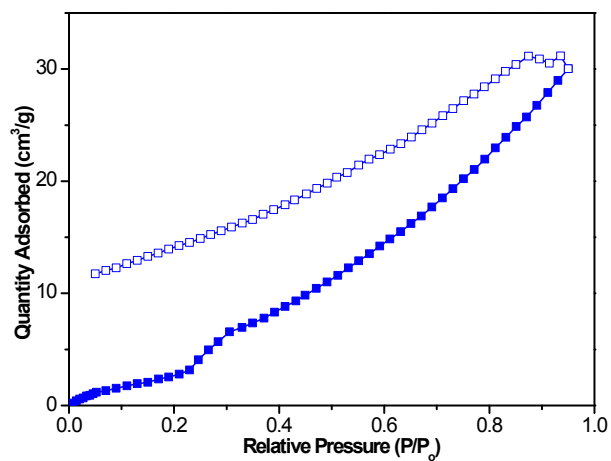
**Fig. S7** View of the 3D network compound **5** with 1D nanochannel along the *b*-axis.



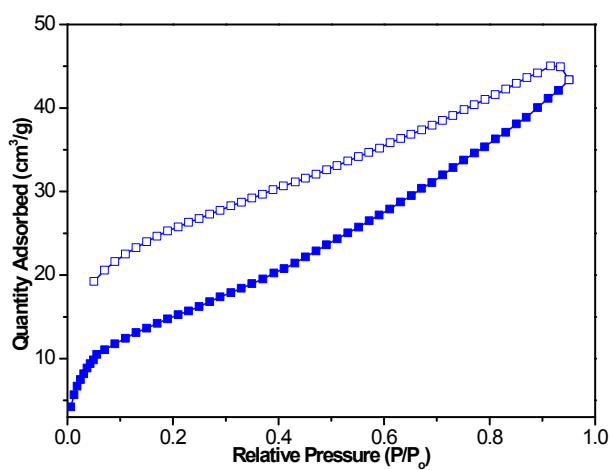
The  $\text{CuO}_4\text{N}_2$  and  $\text{PCO}_3$  polyhedra are shaded in cyan and purple, respectively. The ester groups in BPDP ligand toward the channels and isolated aqua located at the channels are omitted for clarity.



**Fig. S8** View of the 3D network compound **6** with 1D nanochannel along the  $b$ -axis. The  $\text{CuO}_4\text{N}_2$  and  $\text{PCO}_3$  polyhedra are shaded in cyan and purple, respectively. The ester groups in BPDP ligand toward the channels and isolated aqua located at the channels are omitted for clarity.

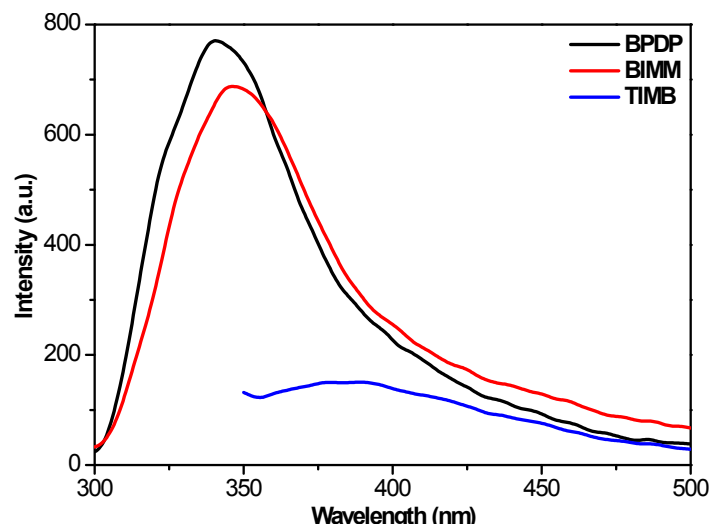


(a)



(b)

**Fig. S9** CO<sub>2</sub> adsorption-desorption curves for (a) compound **4** and (b) compound **6** at 195 K.



**Fig. S10** Solid-state emission spectra of the three ligands under  $\lambda_{\text{ex}} = 278$  nm (for BPDP and BIM) or 330 nm (for TIB) at room temperature.