

Supporting Information

π -Conjugation-directed highly selective adsorption of benzene over cyclohexane

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1. Experimental

Materials and instruments

All reagents were purchased from commercial sources and used as received. The ligand HBCbpyCl and HBCbpeCl were synthesized by the method reported in our previous papers (Published in *CrystEngComm*, 2008, 10, 1299; *Angew. Chem. Int. Ed.*, 2013, 52, 1.). Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851^e thermal analyzer under an atmosphere of flowing air, at a heating rate of 10 °C min⁻¹ from 30–800 °C. The elemental analysis (C, H, N) was performed using a Vario EL III CHNOS elemental analyzer. The IR (KBr pellet) spectra were recorded (400–4000 cm⁻¹ region) on a Bomem MB-102 IR spectrometer. Powder X-ray diffraction (PXRD) patterns were recorded on a MiniFlex diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range 5–50° with a scan speed of 3° min⁻¹. Vapor-phase adsorption isotherms were measured with an Intelligent Gravimetric Sorption Analyser IGA100B from the Hiden Corporation. The ASAP 2020 surface-area analyzer was used to measure the CO₂, N₂ and H₂ isotherms; the samples were evacuated under high vacuum at room temperature for 5 h prior to the measurements being taken.

Synthesis of 1-bpy and 2-bpe

1-bpy: HBCbpyCl (0.033 g, 0.11 mmol), H₄PMA (0.013 g, 0.05 mmol) and Zn(NO₃)₂·6H₂O (0.060 g, 0.20 mmol) were dissolved in 1 mL H₂O and 2 mL DMF. The mixture was stirred for a further 5 minutes and then filtered. The resulting solution was left for slow evaporation at room temperature. After one week bulk colorless crystals were obtained (yield: 37%).

Elemental analysis for [Zn(BCbpy)(PMA)_{0.5}]·7H₂O·DMF: C₂₆H₃₆N₃O₁₄Zn (*Mr* = 679.96) Calcd: C: 45.92, N : 6.18, H: 5.34. Found: C: 45.96, N: 6.16, H: 5.00. FT-IR (KBr, cm⁻¹): 3408(s), 1636(s), 1611(s), 1490(w), 1460(w), 1421(s), 1357 (s), 1222(m), 1160(w), 1137(w), 1076(w), 1020(m), 931(w), 869(m), 815(m), 736(w)

2-bpe: HBCbpeCl (0.035 g, 0.10 mmol), H₄PMA (0.003g, 0.01 mmol) and Zn(NO₃)₂·6H₂O (0.060 g, 0.20 mmol) were dissolved in 4 mL of DMF. The mixture was stirred for a further 5 minutes and then filtered. The resulting solution was left for slow evaporation at room temperature. After one week bulk colorless crystals were obtained (yield: 46%).

Elemental analysis for [Zn(BCbpe)(PMA)_{0.5}]·8H₂O·DMF: C₂₈H₄₀N₃O₁₅Zn (*Mr* = 724.02) Calcd: C:

46.45, N : 5.80, H: 5.57; Found: C: 46.16, N: 5.93, H: 5.49. FT-IR (KBr, cm^{-1}): 3408(s), 1658(m), 1633(m), 1613(s), 1564(m), 1512(w), 1416(m), 1362(s), 1323(m), 1254(w), 1160(w), 1098(w), 1027(w), 852(m), 818(m), 758(m).

2. X-ray crystallography

The X-ray diffraction data for compound **1-bpy** were collected at 293 K on an Agilent SuperNova X-ray diffractometer with Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). The data were collected at 293 K on Rigaku Mercury CCD diffractometers with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) for **2-bpe**. Absorption corrections were performed using a multi-scan method. The structures were solved by direct methods with SHELXS-97 and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. Because solvent molecules in the crystal were highly disordered and can not be modelled properly, their contribution to the scattering was removed with the SQUEEZE option in PLATON. The final structural model was refined without the guest molecules by using the SQUEEZE option of PLATON. The reported refinements are solvent-free structure by SQUEEZE routine. The proposed formula of **1-bpy** and **2-bpe** was determined by elemental analysis (EA) and thermal gravimetric analysis (TGA).

Crystal data for **1-bpy**: $\text{C}_{23}\text{H}_{15}\text{N}_2\text{O}_6\text{Zn}$; $M_r = 480.74$; monoclinic $P2_1/n$; $a = 16.2561(6)$, $b = 9.0343(2)$, $c = 20.6184(6)$, $\beta = 90.954(3)^\circ$, $V = 3027.65(16) \text{ \AA}^3$; $T = 293 \text{ K}$; $Z = 4$; $D_c = 1.055 \text{ g cm}^{-3}$; $\mu (\text{Cu K}\alpha) = 1.392 \text{ mm}^{-1}$; $F(000) = 980$; 11413 reflections collected, of which 5972 unique ($R_{\text{int}} = 0.0271$); $\text{GOF} = 1.066$; $R_1 = 0.0491$ and $wR_2 = 0.1501 [I > 2\sigma(I)]$. CCDC 989780

Crystal data for **2-bpe**

2-bpe $\text{C}_{25}\text{H}_{17}\text{N}_2\text{O}_6\text{Zn}$; $M_r = 506.78$; monoclinic $P2_1/n$; $a = 18.085(6)$, $b = 9.034(3)$, $c = 22.337(8)$, $\beta = 100.725(4)^\circ$, $V = 3586(2) \text{ \AA}^3$; $T = 293 \text{ K}$; $Z = 4$; $D_c = 0.939 \text{ g cm}^{-3}$; $\mu (\text{Mo K}\alpha) = 0.713 \text{ mm}^{-1}$; $F(000) = 1036$; 27597 reflections collected, of which 8155 unique ($R_{\text{int}} = 0.0489$); $\text{GOF} = 1.015$; $R_1 = 0.0572$ and $wR_2 = 0.1687 [I > 2\sigma(I)]$. CCDC 989779

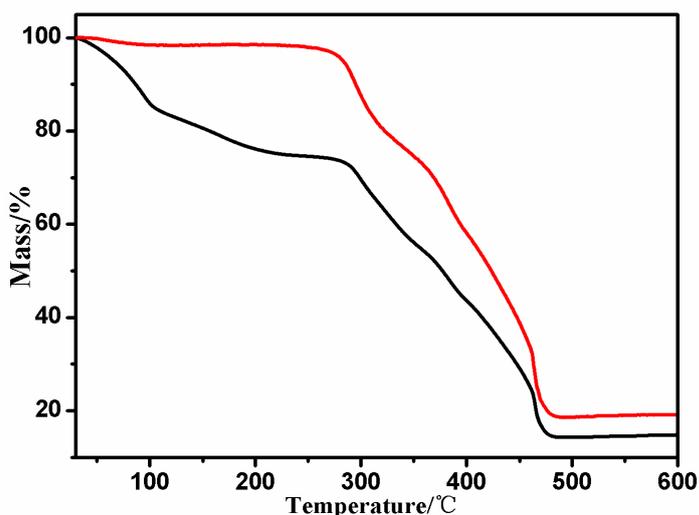


Fig. S1 The TG Plots of **1-bpy** (black) and desolvated sample **1-bpy'** (red).

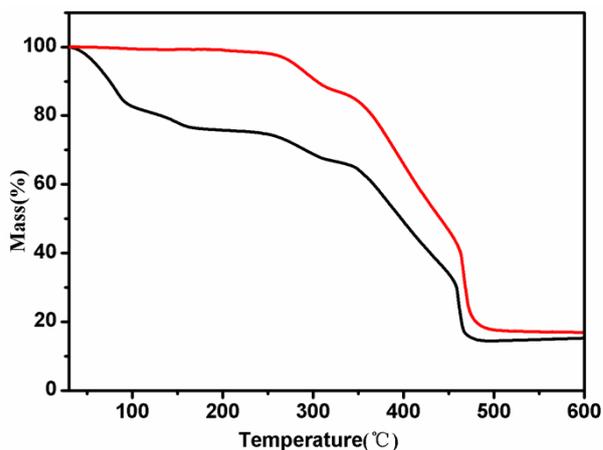


Fig. S2 The TG Plots of **2-bpe** (black) and desolvated sample **2-bpe'** (red).

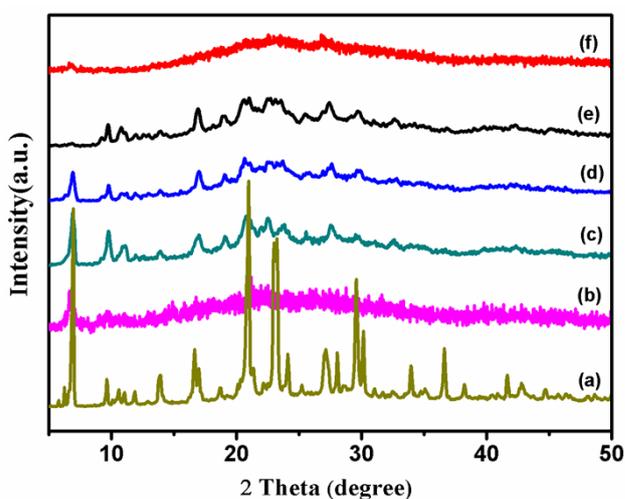


Fig. S3 X-ray powder-diffraction patterns for **1-Bpy** (a) as-synthesized; (b) desolvated sample and desolvated samples exposed to (c) water; (d) methanol; (e) ethanol; (f) benzene for 18 h, respectively.

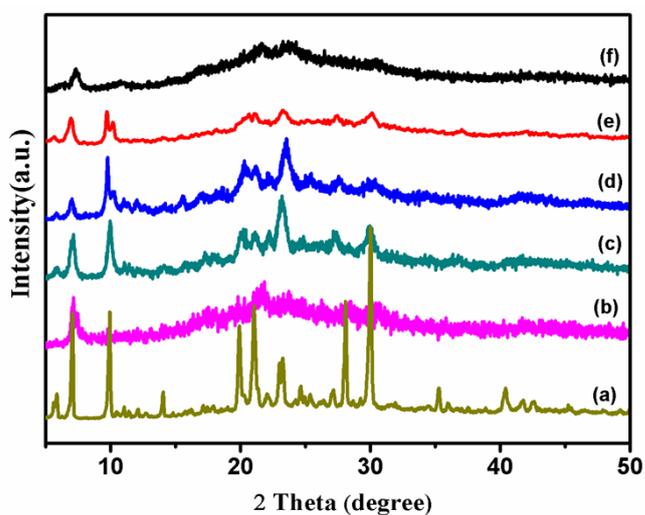


Fig. S4 X-ray powder-diffraction patterns for **2-bpe** (a) as-synthesized; (b) desolvated sample and desolvated samples exposed to (c) water; (d) methanol; (e) ethanol; (f) benzene for 18 h, respectively.

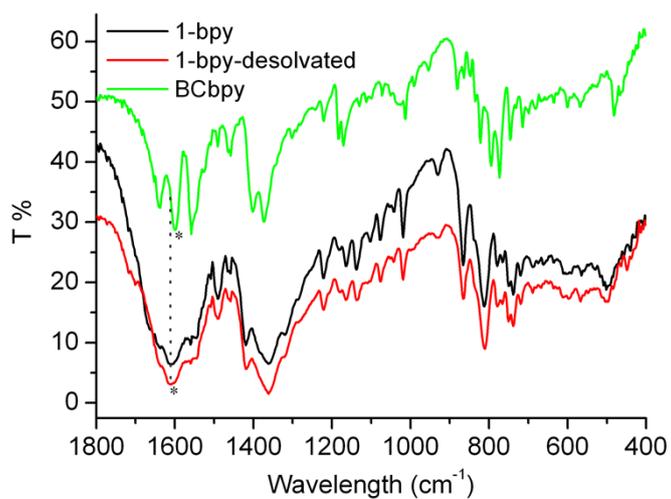


Fig.S5 IR spectra of **1-bpy** (black), desolvated sample (red) and BCbpy ligand (green).

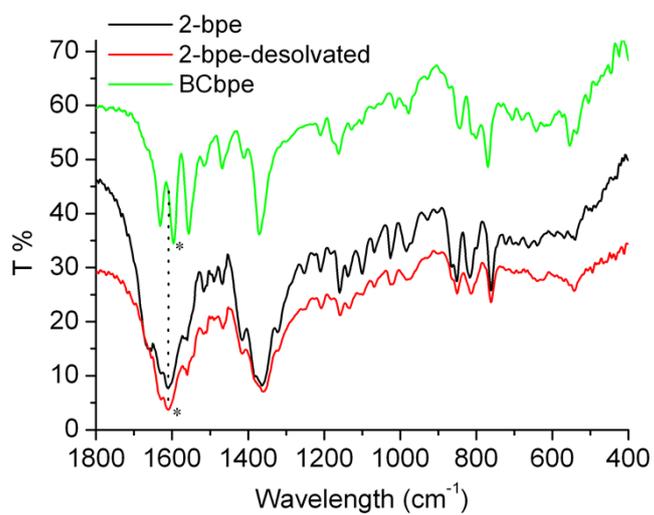


Fig.S6 IR spectra of **2-bpe** (black), desolvated sample (red) and BCbpe ligand (green).