Engineering a pillar[5]arene-based supramolecular organic framework by co-crystallization method

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General Methods: Unless otherwise noted, all commercial reagents and solvents were used without purification. Separation by flash column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR spectra were recorded on a 500 MHz spectrometer with TMS as the reference. Single crystal X-ray diffraction data were collected on a SMART APEX 2 X-ray diffractometer equipped with a normal focus Mo-target X-ray tube (λ = 0.71073 Å) and data reduction included absorption corrections by the multi-scan method. The structures were solved by direct methods and refined by full-matrix least-squares using SHELXS-97. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were added at their geometrically ideal positions and refined isotropically. Thermogravimetric analysis (TGA) was performed on a SDT Q600 thermogravimetric analyzer, and the samples were heated to 800 °C at a rate of 10 °C min^{-1} under a nitrogen atmosphere. Powder X-ray diffraction (XRD) measurements were conducted using a Bruker AXS D8 ADVANCE X-ray diffractometer with a Cu K_α (λ = 1.5418 Å) radiation source operated at 40 kV and 40 mA. Diffraction patterns were collected at a scanning rate of 2° per min with a step size of 0.02°. The samples were degassed at 80 °C for 12 h under vacuum before gas adsorption studies. Nitrogen adsorption/desorption isotherms were measured by a JW-BK122W. Carbon dioxide adsorption/desorption isotherms were measured by a ASAP 2460. Pore size distribution was calculated by NLDFT method from CO_2 sorption isotherms at 273K.

Crystallographic Data of P5-Bpy-SOF: [C55 H46 N4 O10]; Mr = 922.96; T = 173 (2) K; triclinic; space group $P\bar{1}$; a = 15.3667(9); b = 15.6328(9); c = 15.7002(9) Å; α = 67.764(2); β = 67.426(2); γ = 73.049(2); V = 3176.1(3) Å^3; Z = 2; ρ_{calcd} = 0.965 g/cm^3; crystal size = 0.44x 0.36 x 0.26 mm; μ = 0.067 mm^{-1}; reflections collected 37462; unique reflections 11130; data/restraints/parameters 11130 /0/ 626; GOF on F^2 0.996; R_{int} for independent data 0.0561; final R_1 = 0.0700, wR_2 = 0.1988; R indices (all data) R_1 = 0.1085, wR_2 = 0.2188; largest diff. peak and hole: 0.692 and -0.426 eÅ^{-3}.

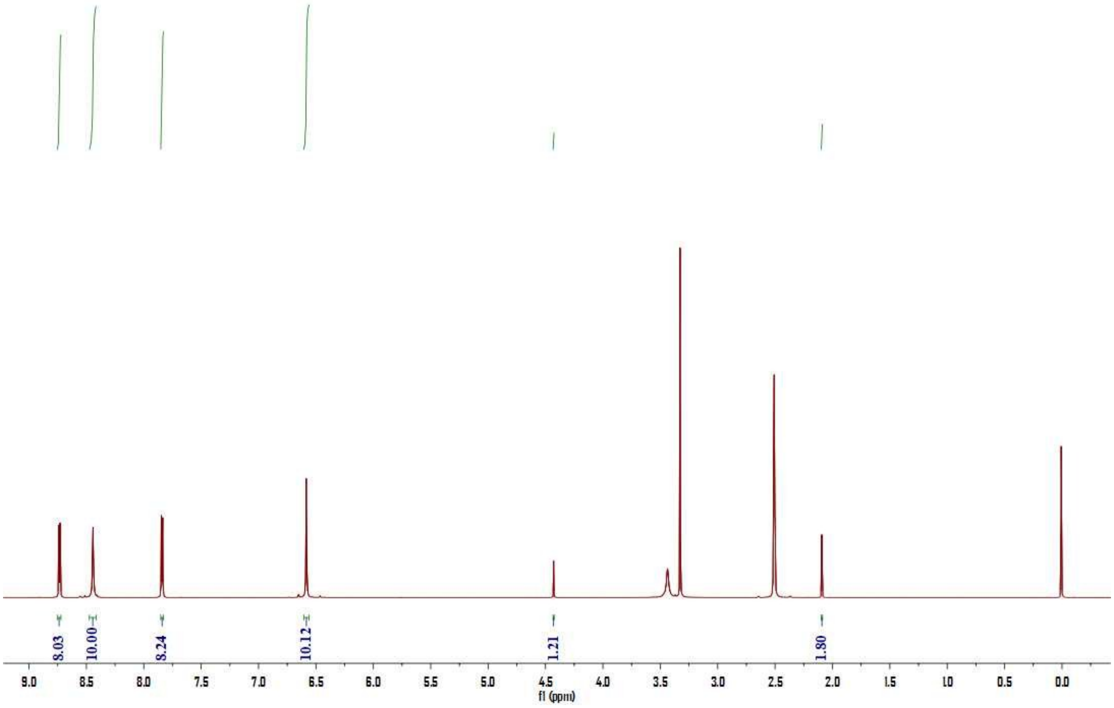

Fig. S1. ^{1}H NMR spectrum of as-prepared **P5-bpy-SOF** in DMSO-d_6.

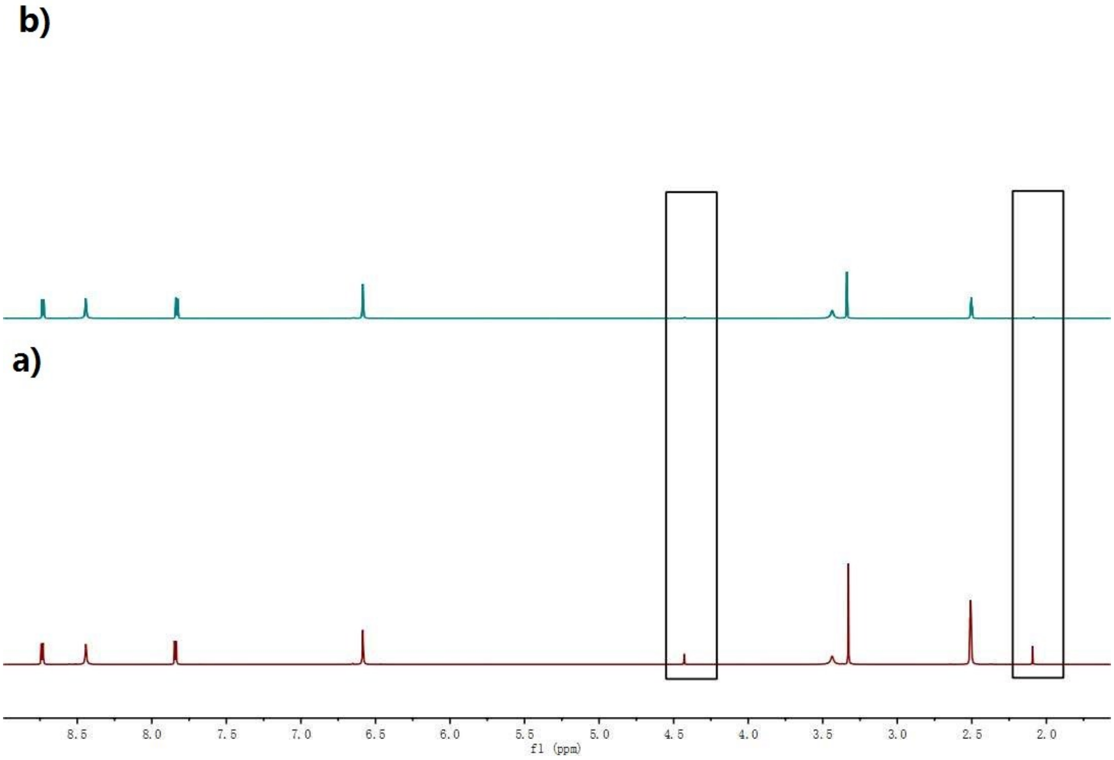

Fig. S2. ^{1}H NMR spectra of **P5-bpy-SOF** in DMSO-d_6: a) freshly prepared **P5-bpy-SOF**; b) after vacuum drying at 80°C for 12h.

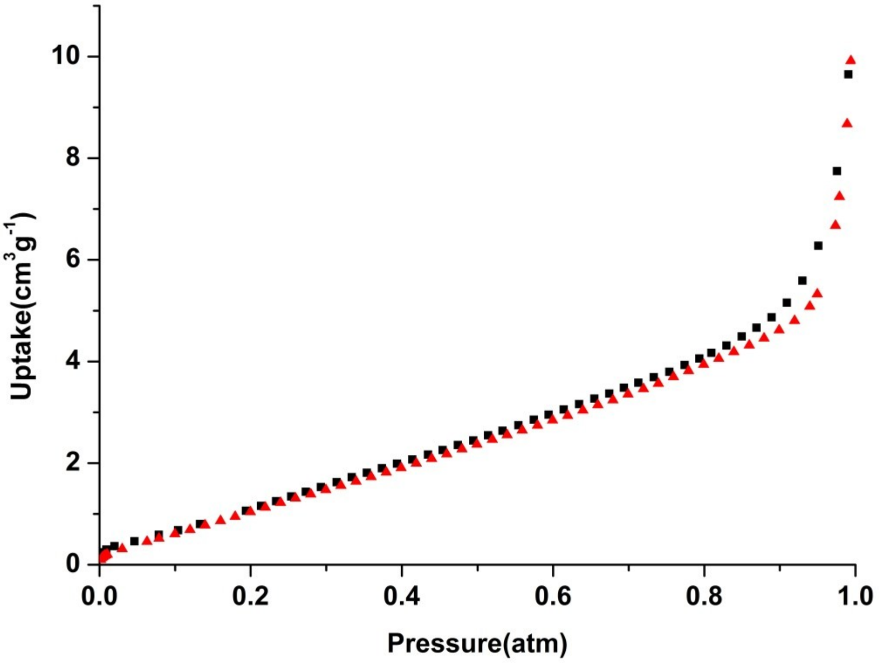

Fig. S3. N_2 adsorption (red) and desorption (black) isotherms for activated **P5-bpy-SOF** at 77 K.

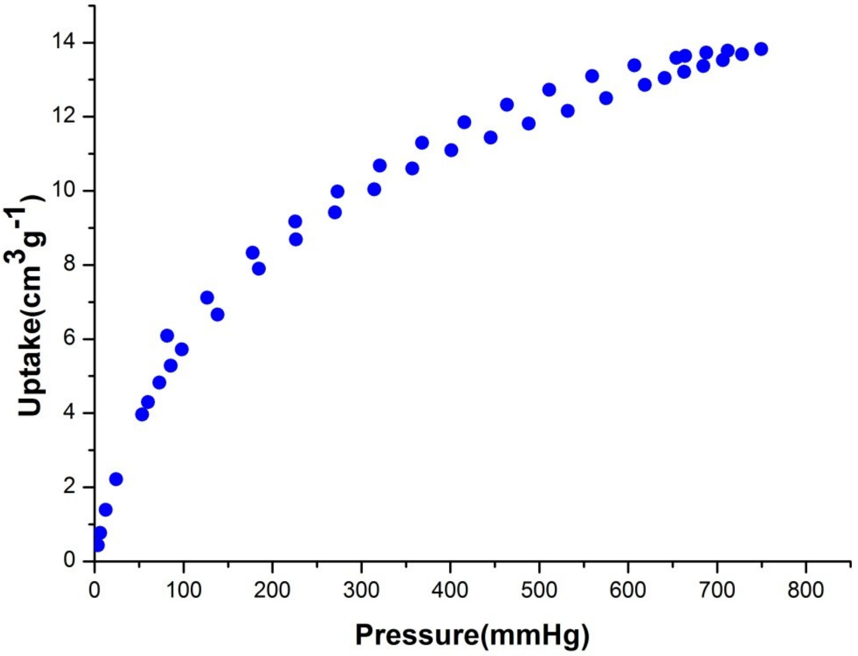

Fig. S4. CO_2 sorption isotherms for activated **P5-bpy-SOF** at 273 K

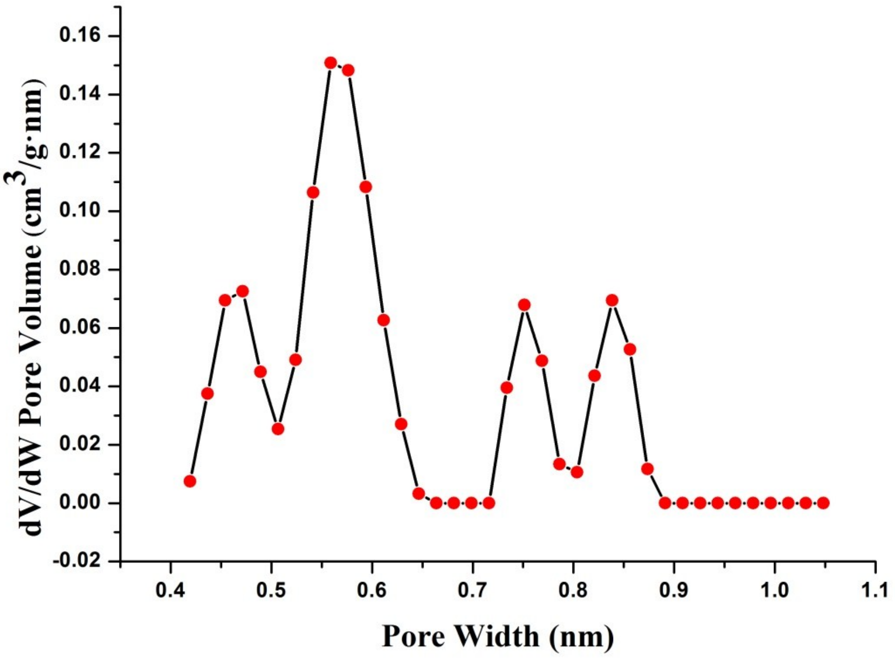

Fig. S5. Pore size distribution calculated by NLDFT method from CO_2 sorption isotherms for activated **P5-bpy-SOF** at 273K. It shows four main sharp peaks at about 0.45nm, 0.55 nm, 0.75 nm and 0.85 nm.

Isosteric Heat of Adsorption (Qst) Calculations

A virial-type[1-2]expression comprising the temperature-independent parameters a_i and b_j was employed to calculate the enthalpies of adsorption for CO_2 (at 273 and 298K) on **P5-bpy-SOF**. In the case, the data were fitted using the equation:

$$LnP = LnN + 1/T\sum_{i=0}^{m} a_i N^i + \sum_{j=0}^{n} b_j N^j$$

P is the pressure expressed in Torr, N is the amount adsorbed in mmol g^{-1}, T is the temperature in K, a_i and b_j are virial coefficients, and m, n represent the number of coefficients required to adequately describe the isotherms (m and n were gradually increased until the contribution of extra added a and b coefficients was deemed to be statistically insignificant towards the overall fit, and the average value of the squared deviations from the experimental values was minimized). The values of the virial coefficients a_0 through a_m were then used to calculate the isosteric heat of adsorption using the following expression:

$$Q_{st} =- R\sum_{i=0}^{i} a_i N^i$$

Q_{st} is the coverage-dependent isosteric heat of adsorption and R is the universal gas constant. The heat of CO_2 sorption for **P5-bpy-SOF** in this manuscript is determined by using the excess sorption data measured in the pressure range from 0−800 mmHg (273 and 298 K), which is fitted by the virial-equation very well ($R^2>0.996$).

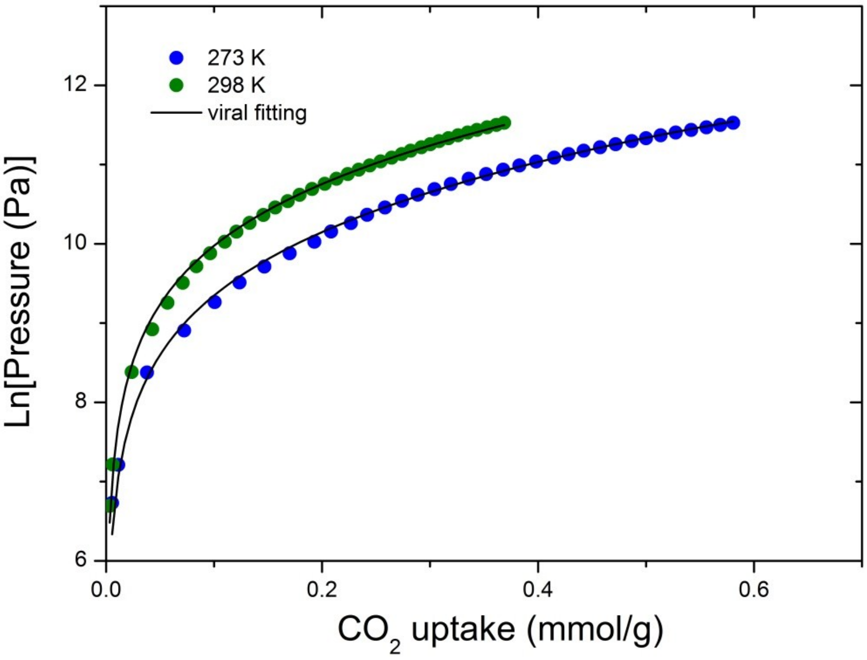

Fig. S6. The virial fitting curve.

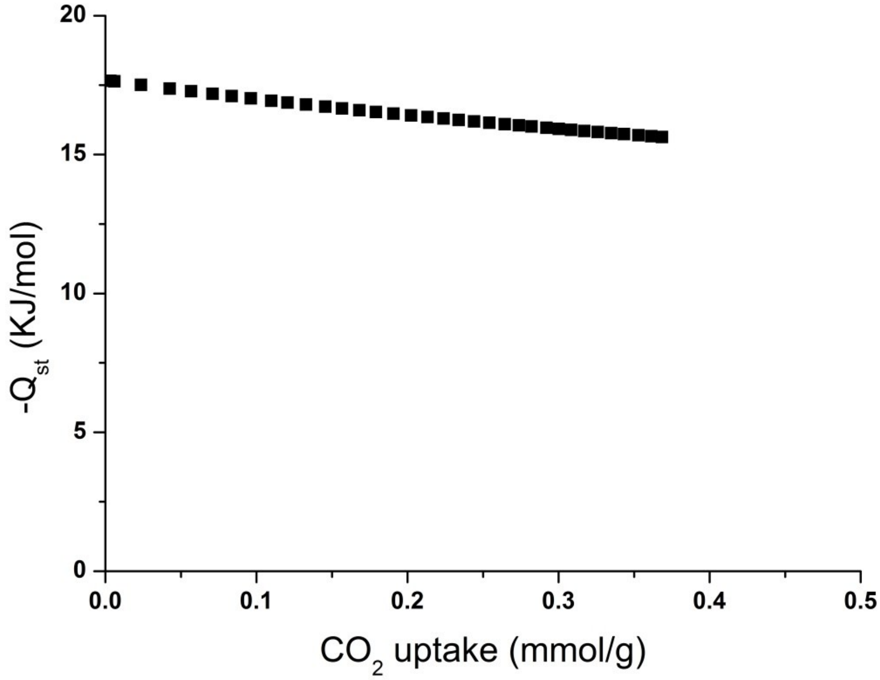

Fig. S7. The CO_2 adsorption enthalpy.

Large-Scale Preparation of P5-bpy-SOF

To a solution of **P5** (610 mg, 1.0 mmol) in acetone (400 mL) was added a solution of **bpy** (780 mg, 5.00 mmol) in nitromethane (200 mL) to result in a pale yellow transparent solution which was kept at room temperature for 24 h. The crystals formed were collected by filtration, and dried to afford **P5-bpy-SOF** (480 mg, 52%yield).

References

1. J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.*, 2006, **128**, 1304-1315
2. B. X. Dong, S. Y. Zhang, W. L. Liu, Y. C. Wu, J. Ge, L. Song and Y. L. Teng, *Chem. Commun.*, 2015, **51**, 5691-5694