

[Supporting Information]

# Synthesis of copolymerized porous organic frameworks with high gas storage properties

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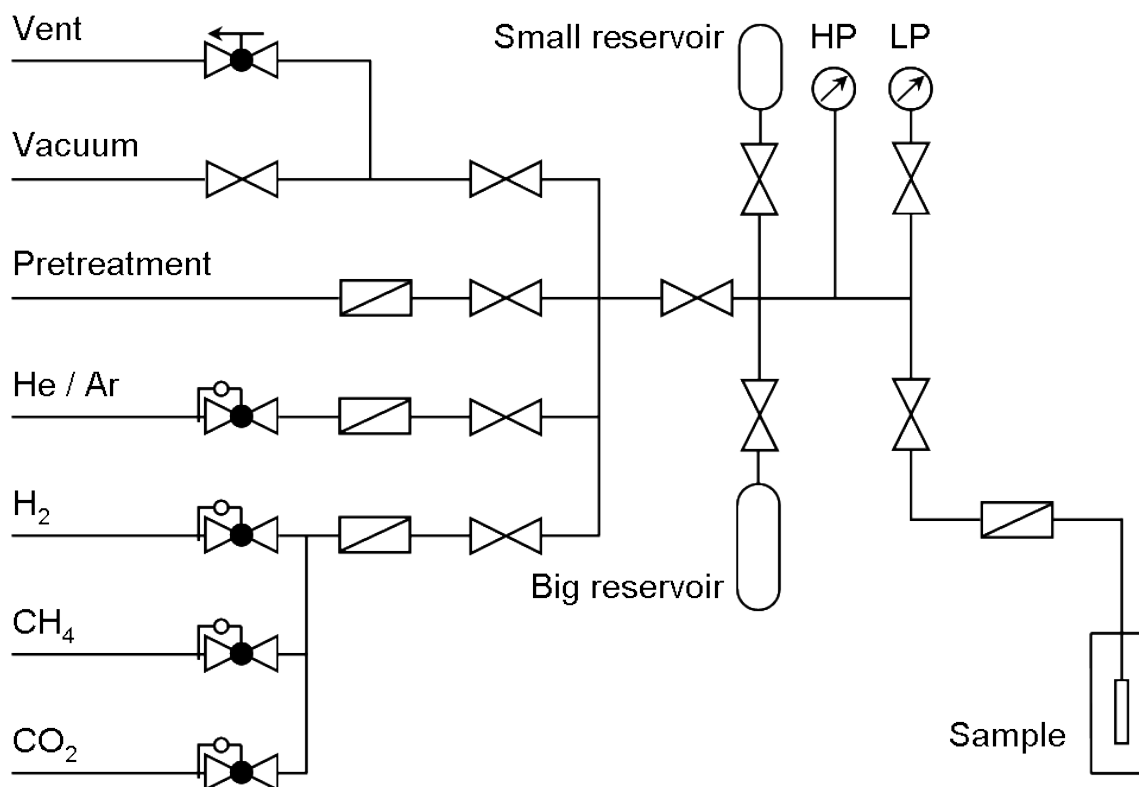
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## 1. High pressure gas storage apparatus



**Fig. S1.** Apparatus used in high pressure gas storage measurements

## **2. Instruments**

### **2-1. Low-pressure N<sub>2</sub> sorption measurements**

The N<sub>2</sub> sorption isotherm measurements were performed on a Micromeritics Tristar II 3020 surface area and pore size analyzer. After the removal of volatile entities by decanting, the samples were activated in a dynamic vacuum at 200 °C overnight. Before measurement, the samples were degassed using the “degas” function of the surface area analyzer at 200 °C for 12 h. A sample of 50 mg and a UHP-grade nitrogen (99.999 %) gas source were used in the nitrogen sorption measurements at 77 K and were maintained as liquid nitrogen throughout the whole measurement. Oil-free vacuum pumps and oil-free pressure regulators were used for the measurements to prevent the contamination of the samples during the degassing process and isotherm measurements.

### **2-2. PXRD measurements**

The PXRD measurements were performed using a SHIMADZU XRD-6000 X-ray diffractometer with Cu-K $\alpha$  radiation, 40 kV, 30 mA, and a scanning rate of 2 ° min<sup>-1</sup> (2 $\theta$ ). The sample holder is made with Al.

### **2-3. NMR experiments**

The NMR experiments were performed on a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T. The resonance frequencies at this field

strength were 100.6 MHz for  $^{13}\text{C}$ . A Chemagnetics 5 mm triple-resonance MAS probe was used to acquire the  $^{13}\text{C}$  NMR spectra with a spinning rate of 8 kHz. The chemical shift of  $^{13}\text{C}$  was externally referenced to hexamethylbenzene.

#### **2-4. TGA and FTIR measurements**

The thermogravimetric analyses (TGA) were performed using a SHIMADZU DTG-60 thermal analyzer at a heating rate of  $5\text{ }^{\circ}\text{C min}^{-1}$  in a dry air atmosphere. The FTIR spectra (KBr) were measured using a SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer.

#### **2-5. Low-pressure gas adsorption measurements**

Samples of a known weight (50 mg) were loaded into preweighed sample tubes that were then sealed to prevent exposure to air and atmospheric moisture during the transfer and weighing. To remove adsorbed materials from the surface, the samples were first heated in the sample tubes in a vacuum until the pressure in the manifold reached 100 mtorr or less, and were then kept at  $200\text{ }^{\circ}\text{C}$  under a dynamic vacuum of less than 50 mtorr for at least 10 h. The low-pressure  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{CO}_2$  adsorption measurements (up to 1 bar) were performed on a Micromeritics Tristar II 3020 surface area and pore size analyzer. After evacuation, the tubes containing the degassed samples were precisely weighed again to obtain the mass of the evacuated samples. Ultra-high-purity grade  $\text{H}_2$ ,

CO<sub>2</sub> (99.999 % purity), and CH<sub>4</sub> (99.99 % purity) gases were used for the adsorption measurement. The free space was measured using He (99.999 % purity) on the assumption that the He would not be adsorbed at any of the studied temperatures. The H<sub>2</sub> isotherms at 77 K were measured in a liquid nitrogen bath, the H<sub>2</sub> isotherms at 87 K were measured in a liquid argon bath, and the CO<sub>2</sub> and CH<sub>4</sub> isotherms at 273 K were measured in an ice-water bath.

## **2-6. High-pressure gas adsorption measurements**

The high-pressure H<sub>2</sub>, CO<sub>2</sub>, and CH<sub>4</sub> adsorption isothermal measurements were performed using home-made equipment according to Zhou's method.<sup>[1]</sup> Scientific research-grade gases were used with a purity of 99.999 %. Before measurement, the samples were fully degassed at 200 °C for at least 10 hours. About 350 mg of sample was used in each case. The CO<sub>2</sub> and CH<sub>4</sub> uptake was measured at 298 K and the H<sub>2</sub> uptake was measured at 77 K.

## **3. Materials**

Tris(4-bromophenyl)amine, bis(1,5-cyclooctadiene)nickel (0) (Ni(cod)<sub>2</sub>), 1,5-cyclooctadiene (cod), N, N-dimethylformamide (DMF), and 2,2'-bipyridyl were purchased from Sigma-Aldrich and used as received. Tetrakis(4-bromophenyl)methane was synthesized according to a previously reported procedure<sup>[2]</sup>.

#### 4. Experimental section

##### General C-POFs synthesis

Tetrakis(4-bromophenyl)methane and tris(4-bromophenyl)amine (4:1, 3:2, 2:3, 1:4, mol/mol, respectively) were dissolved in dehydrated DMF (0.01 M) to prepare the monomer mixture solution. Cod (2.0 mL, 16.1 mmol, dried over CaH<sub>2</sub>) was added to a solution of Ni(cod)<sub>2</sub> (4.41 g, 16.1 mmol) and 2,2'-bipyridyl (2.51 g, 16.1 mmol) in cold dehydrated DMF (50 mL), and the mixture was heated at 80 °C for 1 h. The monomer mixture solution was added to the resulting solution at 80 °C, and the mixture was stirred at that temperature overnight to obtain a deep purple suspension. After cooling to room temperature, concentrated HCl was added to the mixture until it turned into a green suspension. After filtration, the residue was washed with H<sub>2</sub>O, EtOH (5 × 30 mL), and CHCl<sub>3</sub> (5 × 30 mL) and dried in a vacuum to achieve the copolymer in the form of an off-white powder (94 % - 98 % yield). Elemental analysis calcd (%) for JUC-Z7 (C<sub>23.6</sub>H<sub>15.2</sub>N<sub>0.2</sub>)<sub>n</sub>, C 93.80, H 5.05, N 1.16; Found, C 93.13, H 5.41, N 1.45; FTIR (KBr):  $\nu$  = 3026, 1595, 1491, 1253, 994, 796, 754, 516; JUC-Z8 (C<sub>22.2</sub>H<sub>14.4</sub>N<sub>0.4</sub>)<sub>n</sub>, C 92.66, H 5.03, N 2.31; Found, C 92.40, H 5.36, N 2.24; FTIR (KBr):  $\nu$  = 3026, 1595, 1484, 1273, 1004, 806, 734, 537; JUC-Z9(C<sub>20.8</sub>H<sub>13.6</sub>N<sub>0.6</sub>)<sub>n</sub>, C 91.51, H 5.02, N 3.47; Found, C 91.19, H 5.33, N 3.49; FTIR (KBr):  $\nu$  = 3036, 1595, 1491, 1275, 993, 806, 745, 526; JUC-Z10

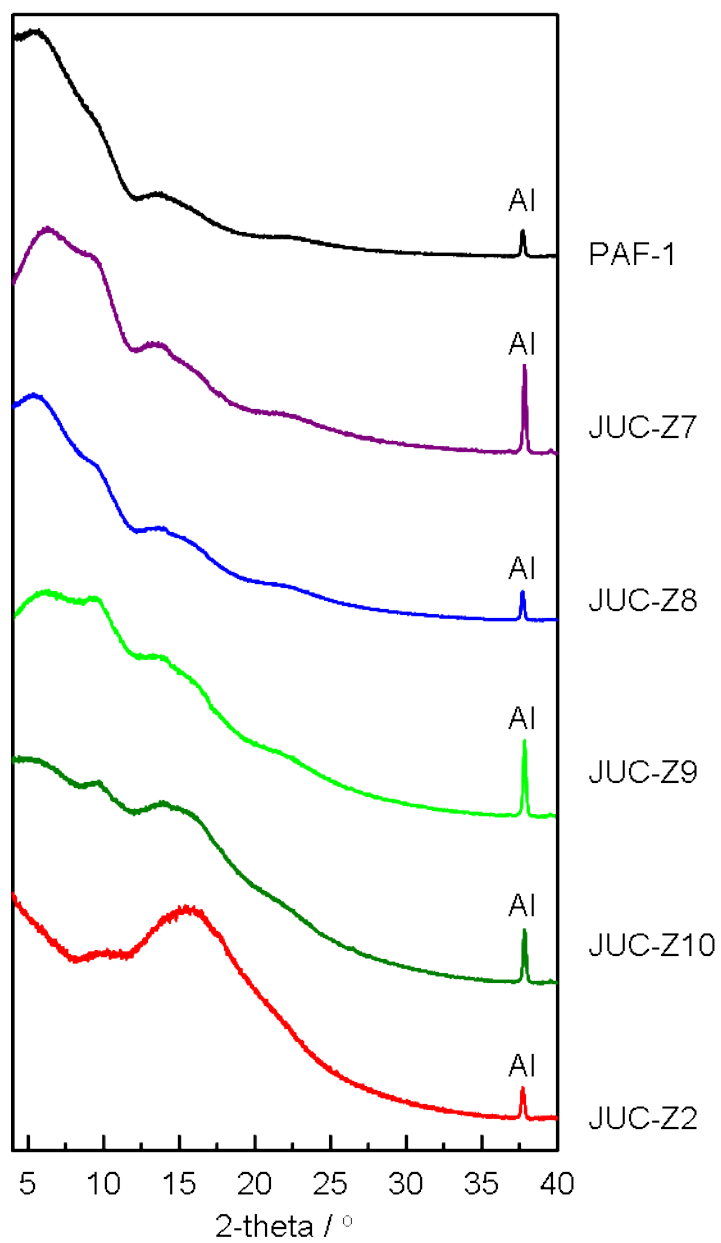
$(C_{19.4}H_{12.8}N_{0.8})_n$ , C 90.37, H 5.00, N 4.62, Found, C 90.61, H 5.17, N 4.21; FTIR (KBr):

$\nu = 3026, 1595, 1481, 1273, 993, 817, 734, 516$ .



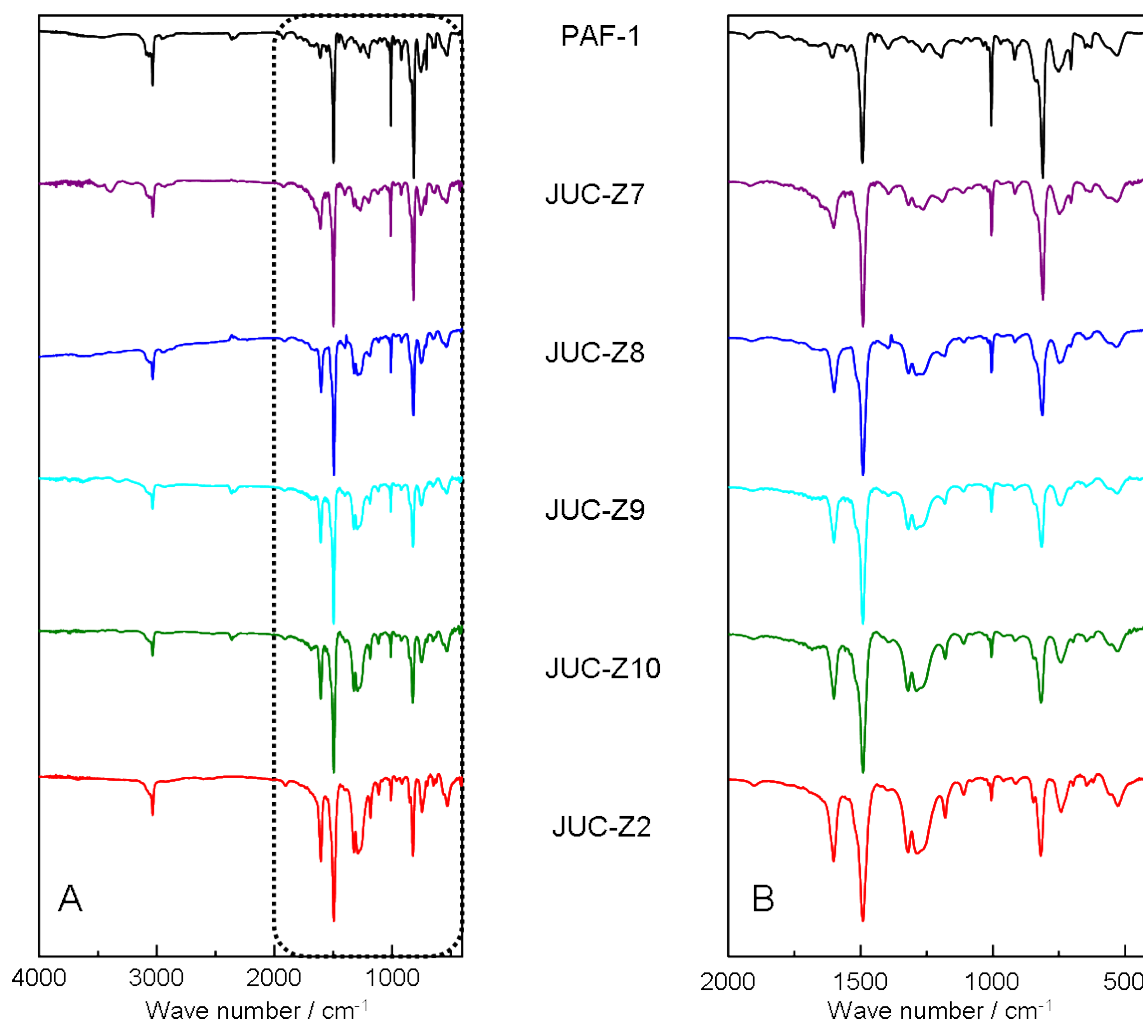
## 5. Investigation of topology structure of C-POFs

### 5-1. PXRD of PAF-1, JUC-Z2 and C-POFs



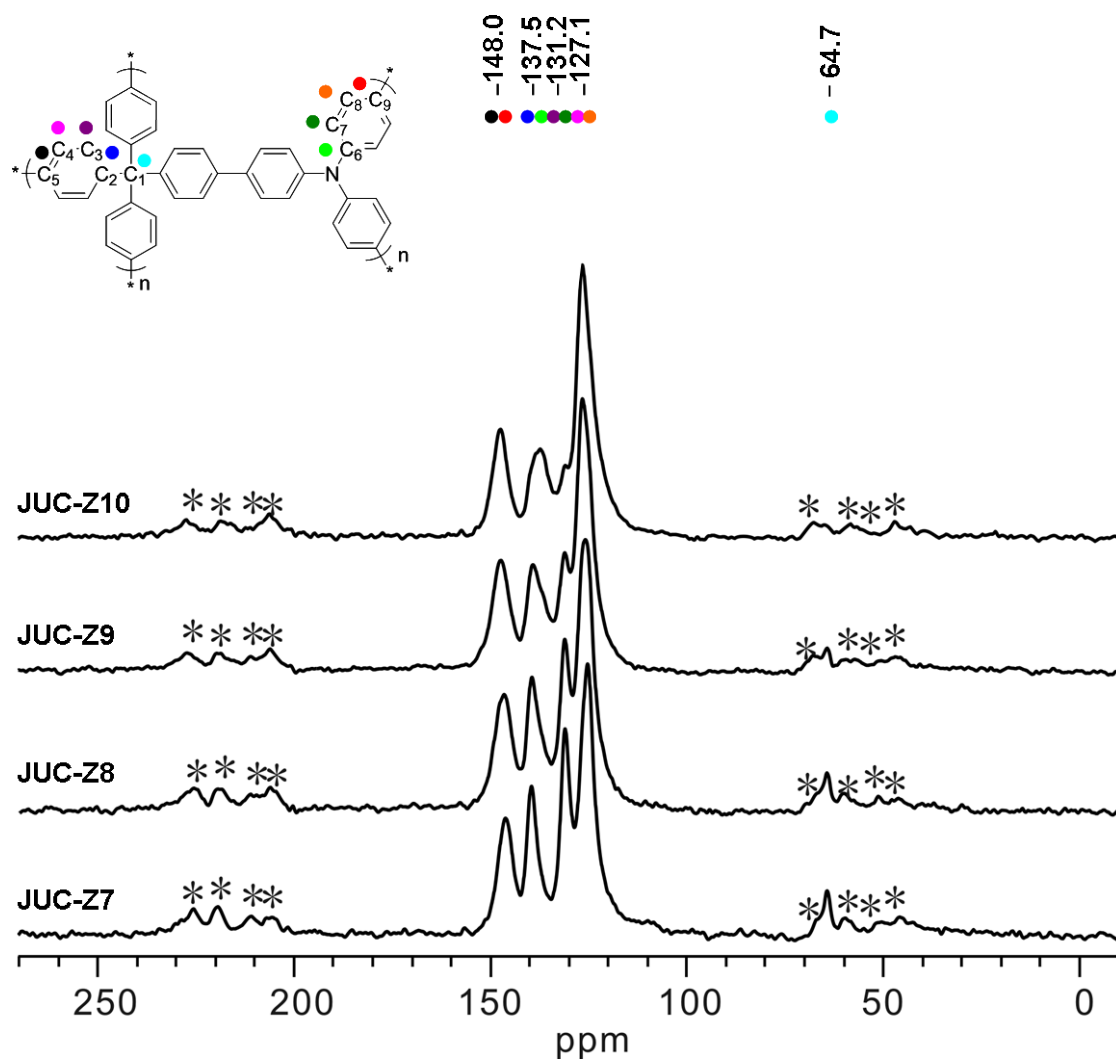
**Fig. S1.** The observed PXRD pattern of activated PAF-1, JUC-Z2 and C-POFs

## 5-2. FTIR of PAF-1, JUC-Z2 and C-POFs



**Fig. S2.** FTIR spectra of PAF-1 (black), JUC-Z2 (red), and the C-POFs (JUC-Z7 in purple, JUC-Z8 in blue, JUC-Z9 in cyan, JUC-Z10 in olive) from 400-4000 cm<sup>-1</sup> (A) and 400-2000 cm<sup>-1</sup> (B)

### 5-3. $^{13}\text{C}$ CP/MAS NMR spectra of C-POFs



**Fig. S3.**  $^{13}\text{C}$  CP/MAS NMR spectra of the C-POFs, Asterisks indicate spinning side-band peaks

#### 5-4. PSD of PAF-1, JUC-Z2 and C-POFs

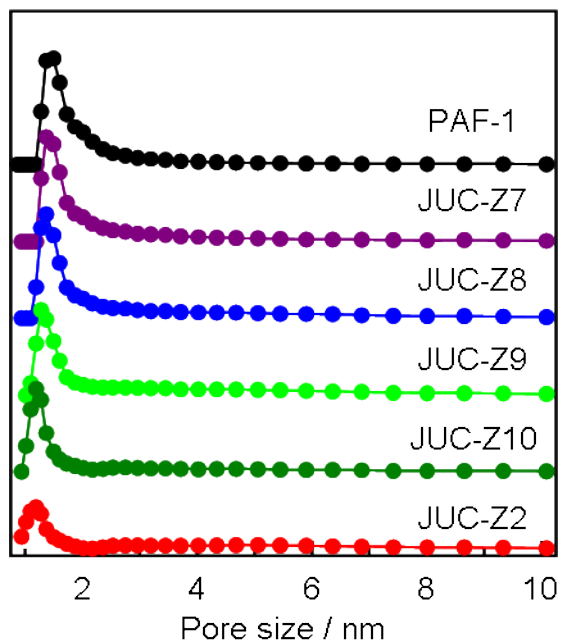


Fig. S4. PSD of PAF-1, JUC-Z2, and the C-POFs

#### 5-5. Cumulative pore volume of PAF-1, JUC-Z2 and C-POFs

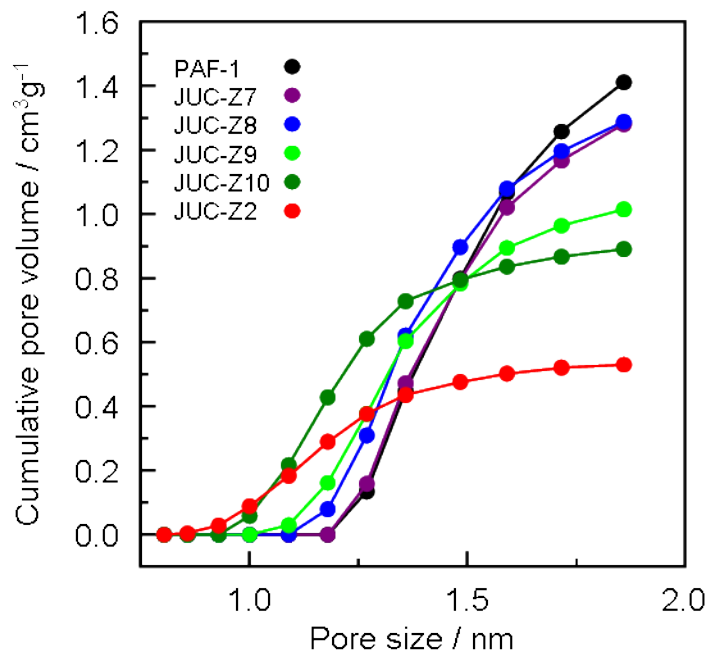
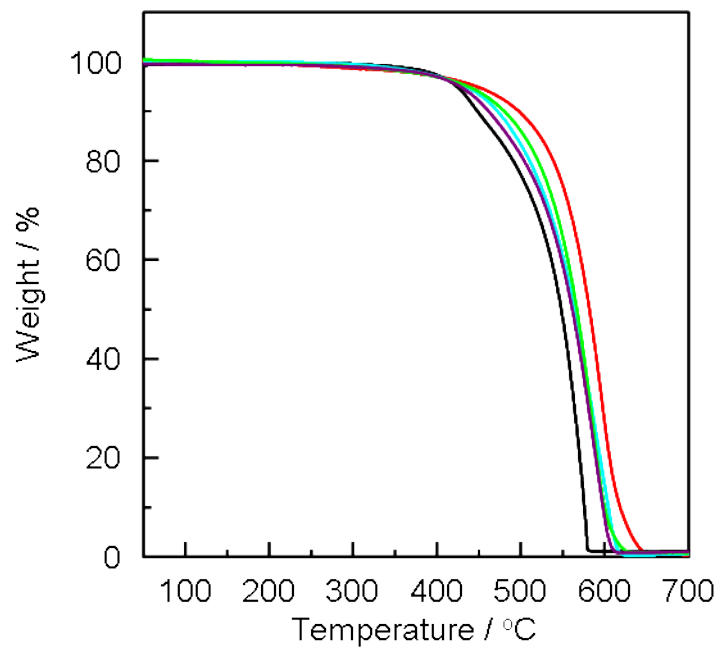


Fig. S5. Cumulative pore volume of PAF-1, JUC-Z2, and the C-POFs

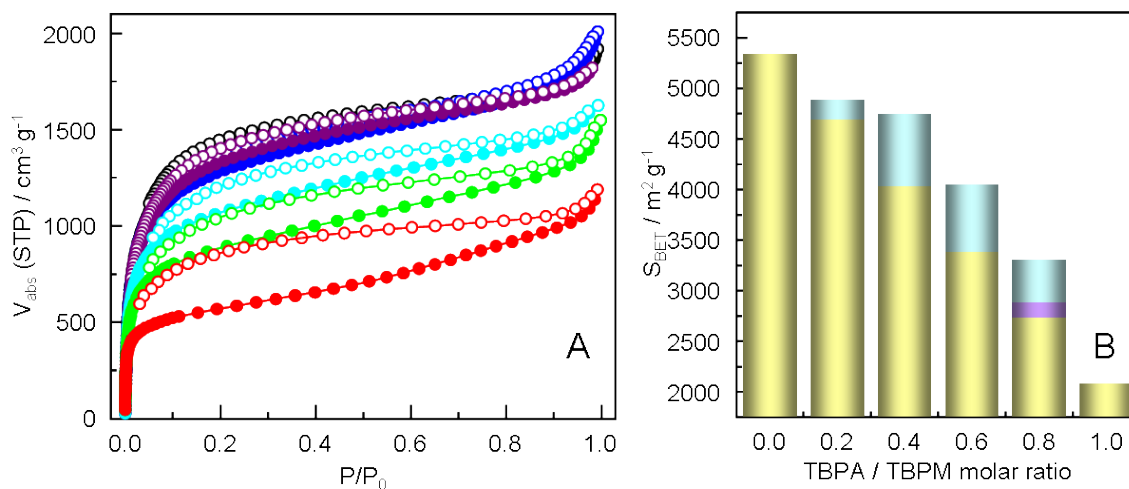
## 6. Investigation of stability

### 6-1. TGA experiment of PAF-1, JUC-Z2 and C-POFs



**Fig. S6.** TGA plot of PAF-1 (black), JUC-Z7 (purple), JUC-Z8 (blue), JUC-Z9 (cyan), JUC-Z10 (green), and JUC-Z2 (red) in dry air at a rate of 10 °C min<sup>-1</sup>

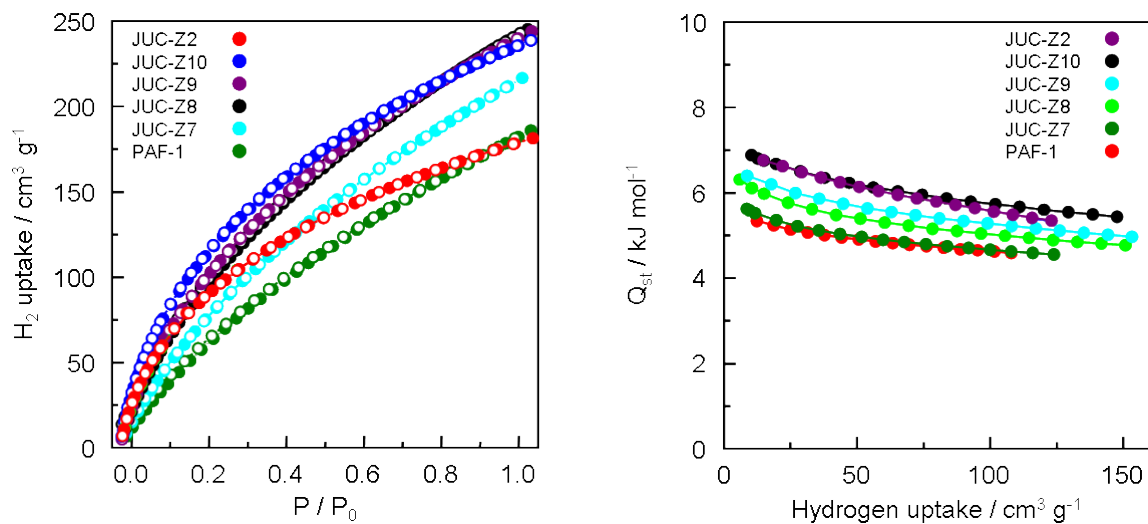
## 7. N<sub>2</sub> sorption measurements



**Fig. S7.** (A) N<sub>2</sub> sorption isotherms of PAF-1 (black), JUC-Z7 (purple), JUC-Z8 (blue), JUC-Z9 (cyan), JUC-Z10 (green), and JUC-Z2 (red): (solid symbols, adsorption; open symbols, desorption); (B)  $S_{\text{BET}}$  of PAF-1, JUC-Z2 and C-POFs (the experimental data are in blue, the calculated physical mixture data are in yellow, and the JUC-Z10-Mix is in purple)

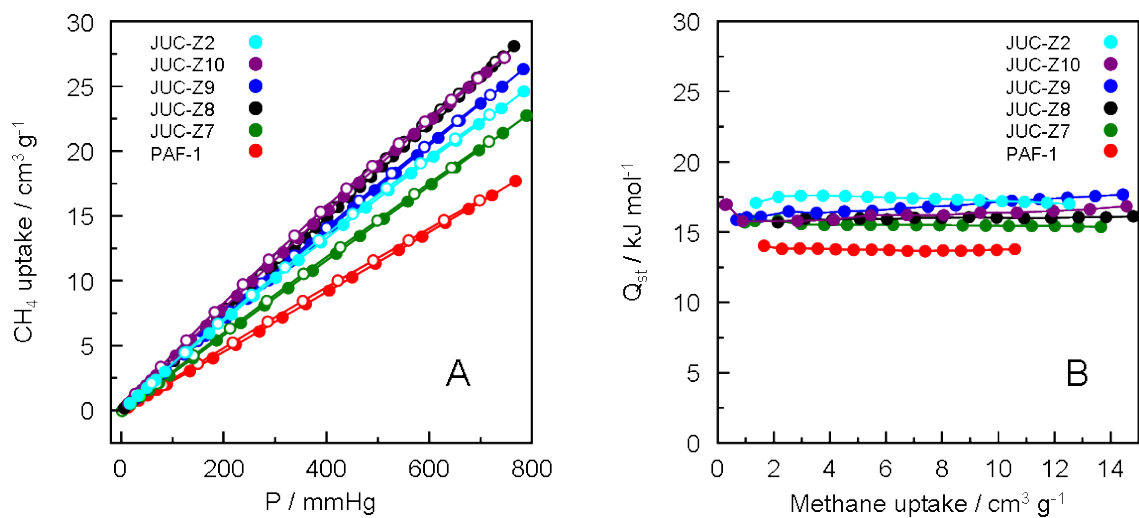
## 8. Low-pressure gas storage measurements

### 8-1. Low-pressure hydrogen uptake and $Q_{stH_2}$



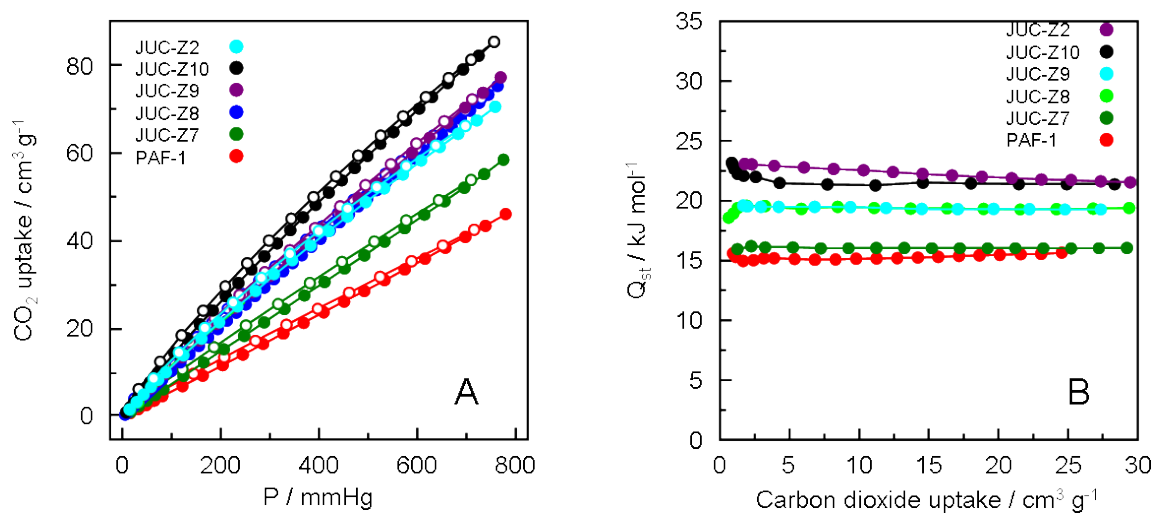
**Fig. S8.** (A) Hydrogen adsorption (filled symbols) and desorption (empty symbols) isotherms of PAF-1, C-POFs and JUC-Z2 at 77 K; (B)  $Q_{st}$  for  $\text{H}_2$  of PAF-1, C-POFs and JUC-Z2.

### 8-2. Low-pressure methane uptake and $Q_{stCH_4}$



**Fig. S9.** (A) Methane adsorption (filled symbols) and desorption (empty symbols) isotherms of PAF-1, C-POFs and JUC-Z2 at 273 K; (B)  $Q_{st}$  for CH<sub>4</sub> of PAF-1, C-POFs and JUC-Z2

### 8-3. Low-pressure carbon dioxide uptake and $Q_{stCO_2}$

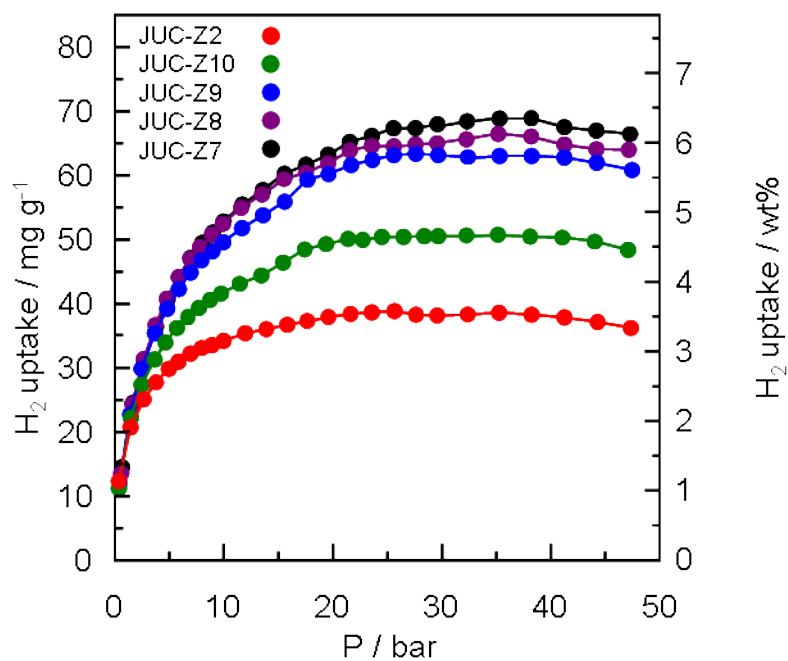




**Fig. S10.** (A) Carbon dioxide adsorption (filled symbols) and desorption (empty symbols) isotherms of PAF-1, C-POFs and JUC-Z2 at 273 K; (B)  $Q_{st}$  for CO<sub>2</sub> of PAF-1, C-POFs and JUC-Z2.

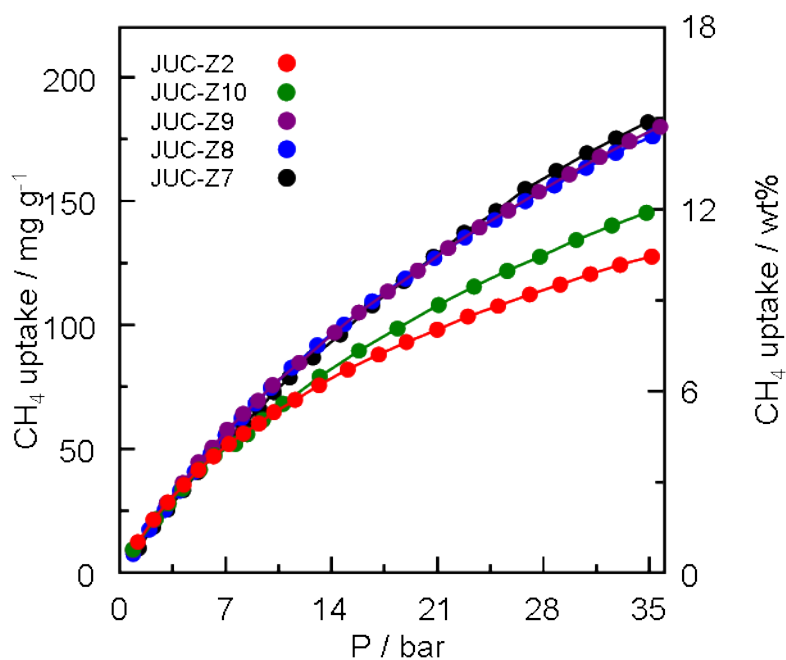
## 9. High-pressure gas storage measurements

### 9-1. High-pressure hydrogen uptake



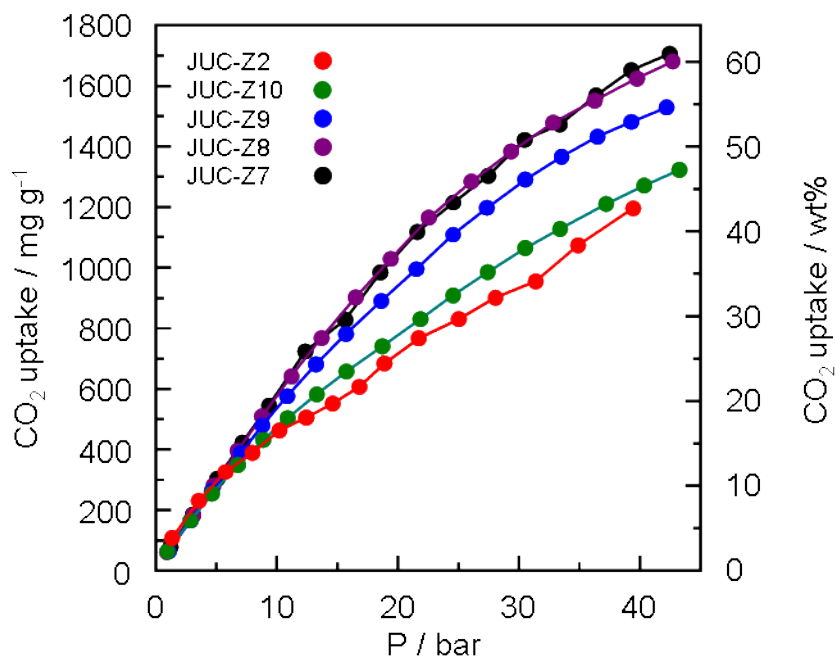
**Fig. S11.** Excess H<sub>2</sub> uptake of JUC-Z7 (black), JUC-Z8 (purple), JUC-Z9 (blue), JUC-Z10 (olive) and JUC-Z2 (red) at 77 K.

## 9-2. High-pressure methane uptake



**Fig. S12.** Excess CH<sub>4</sub> uptake of JUC-Z7 (black), JUC-Z8 (blue), JUC-Z9 (purple), JUC-Z10 (olive) and JUC-Z2 (red) at 298 K.

## 9-3. High-pressure carbon dioxide uptake



**Fig. S13.** Excess CO<sub>2</sub> uptake of JUC-Z7 (black), JUC-Z8 (purple), JUC-Z9 (blue), JUC-Z10 (olive) and JUC-Z2 (red) at 298 K.

#### **10. Reference**

1. W. Zhou, H. Wu, M. R. Hartman and T. Tildirim, *J. Phys. Chem. C.*, 2007, **111**, 16131.
2. M. Grimm, B. Kirste and H. Kurreck, *Angew. Chem.*, 1986, **98**, 1095; *Angew. Chem. Int. Ed.*, 1986, **25**, 1097.