

## Electronic Supporting Information (ESI)

### Porous Carbon Materials with Controllable Surface Area Synthesized from Metal-Organic Frameworks

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#### General methods

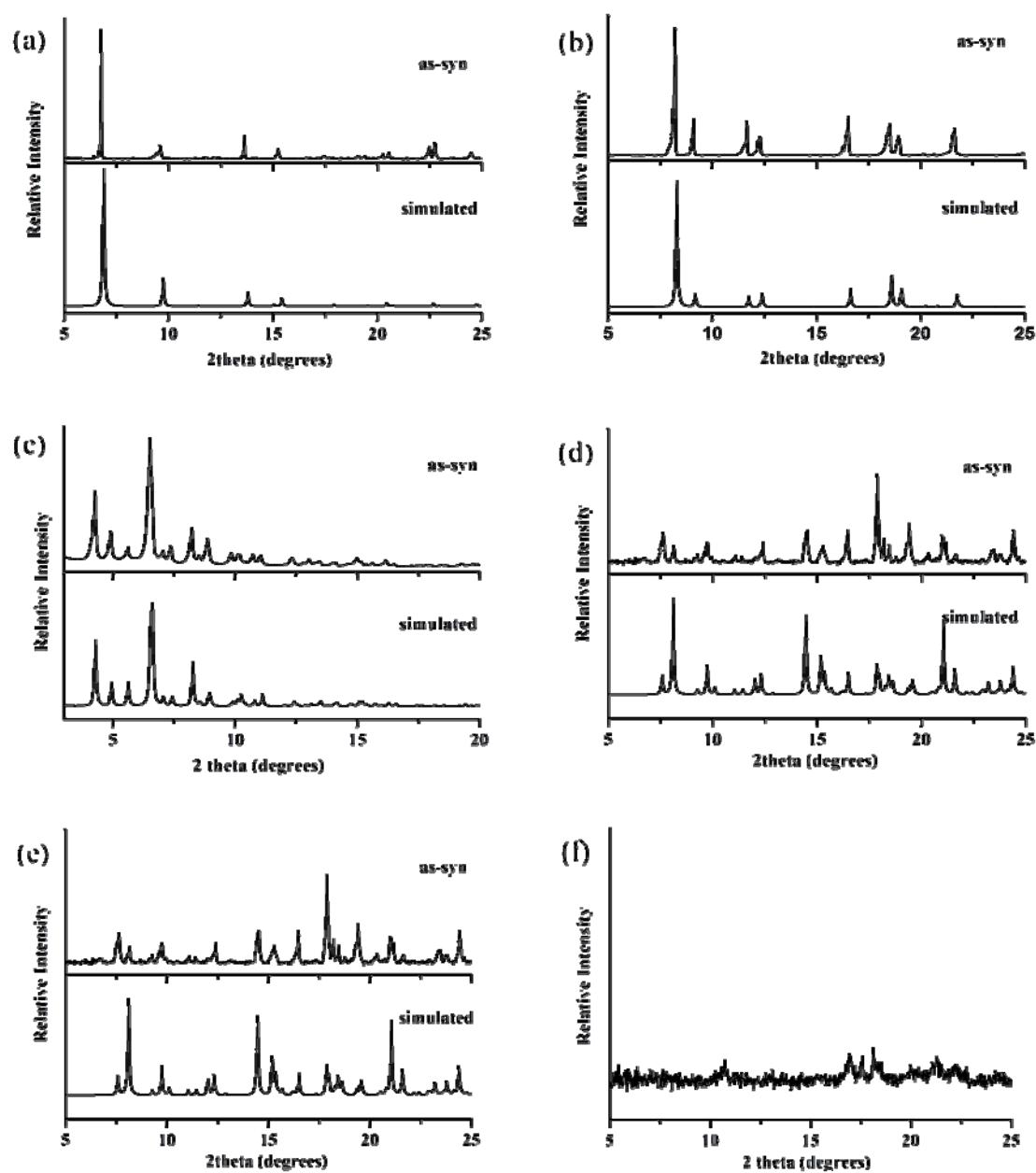
All the reagents and solvents employed were commercially available and used as supplied without further purification. A tube furnace (MTI GSL-1600X50) was used for carbonization. Raman data was obtained on a Horiba Jobin-Yvon LabRam HR spectrometer. The powder XRD diffractograms were obtained on a Bruker D8 Advance system equipped with a Cu sealed tube ( $\lambda = 1.54178 \text{ \AA}$ ). Following conditions were used: 40 kV, 40 mA, increment = 0.05°, scan speed = 3 deg/min. Gas sorption isotherms were recorded volumetrically with an automatic adsorption apparatus, Quantachrome Autosorb 1MP and BELSORP-max (BEL Japan). All gas sorption experiment was performed with high purity gases ( $\text{N}_2$ : 99.999%, Linde Korea). C, H, N, S elemental analyses data were obtained using a VarioMICRO elemental analyzer. SEM images and energy dispersive X-ray spectroscopy (EDX) data were acquired on a JEOL JSM-6610 and QUANTAX 200, respectively. High-resolution TEM images were recorded on a JEOL-2200FS electron microscope operating at 200 kV.

#### Synthesis of MOF precursors (1 – 6)

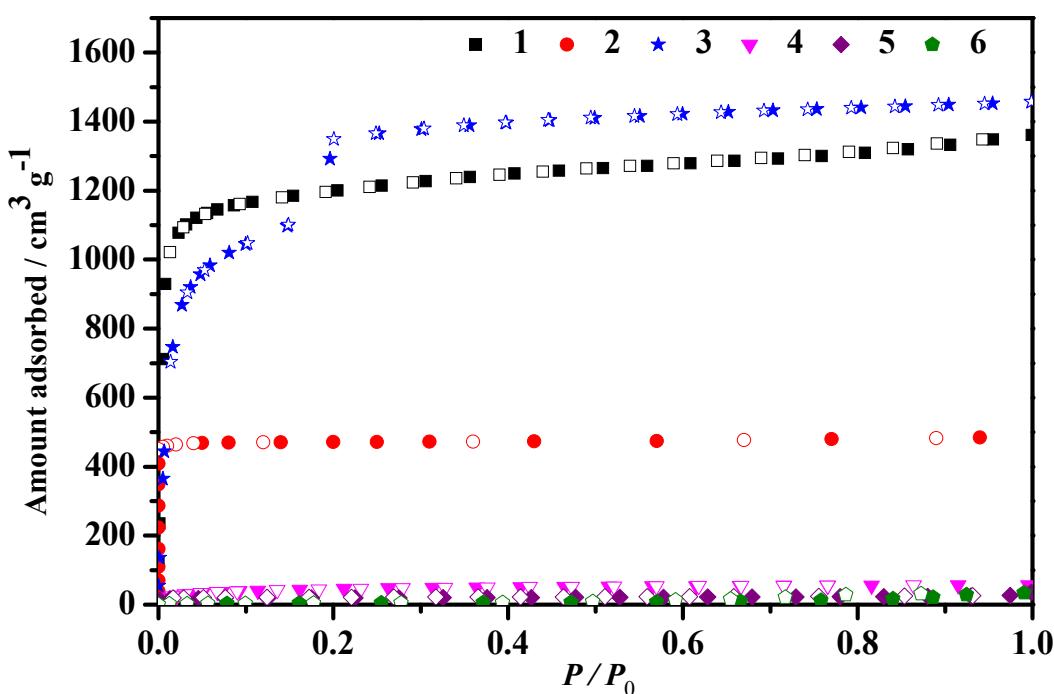
Starting MOFs  $[\text{Zn}_4\text{O}(\text{bdc})_3]$  (1)<sup>[S1]</sup>,  $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]$  (2)<sup>[S2]</sup>,  $[(\text{Zn}_4\text{O})_3(\text{bdc})_3(\text{btb})_4]$  (3)<sup>[S3]</sup> and  $[\text{Zn}_2(\text{bdc})(\text{L-lac})(\text{dmf})]$  (4)<sup>[S4]</sup> were prepared according to the literature.

The synthetic conditions of  $[\text{Zn}_3(\text{bpdc})_3(\text{dmf})_2]$  (5) were modified from the literature procedure.<sup>[S5]</sup> A mixture of  $\text{H}_2\text{bpdc}$ (1.92 g, 7.93 mmol) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (2.4 g, 8.1 mmol) was suspended in DMF (100 mL), and sonicated while heating to produce a clear solution, which was divided into 10.0 mL portions, and transferred to 10 scintillation vials. The reaction vial was then placed in an oven at 100 °C for 1 day. Product 5 was isolated as large polyhedral colorless crystals.

$[\text{Zn}_3(\text{fumarate})_3(\text{dmf})_2]$  (6) was produced as a white powder upon heating a mixture of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1.0 g, 3.3 mmol) and fumaric acid (0.39 g, 3.4 mmol) in DMF (40 mL) at 100 °C for 1 day. The resulting material was thoroughly washed with DMF and dried in air. Although the resulting material was non-crystalline, its chemical composition and formula based on TG and EA data are consistent with the reported formula. Elemental analysis data for 6: Found: C, 31.0; H, 2.8; N, 3.9. Calc. for  $\text{C}_{18}\text{H}_{22}\text{NO}_{15}\text{Zn}_3$ : C, 30.8; H, 3.2; N, 4.0%. A portion of solid sample 6 (245.5 mg) was calcinated in the air. The weight of the solid residue was found to be 92.9 mg (37.8%), calculated for  $\text{ZnO}$ : 35.7%.



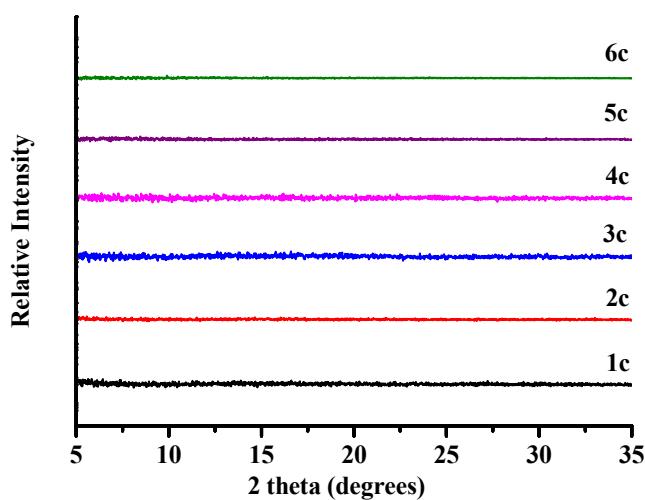
**Fig. S1** Simulated and experimental PXRD profiles of MOF precursors (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.



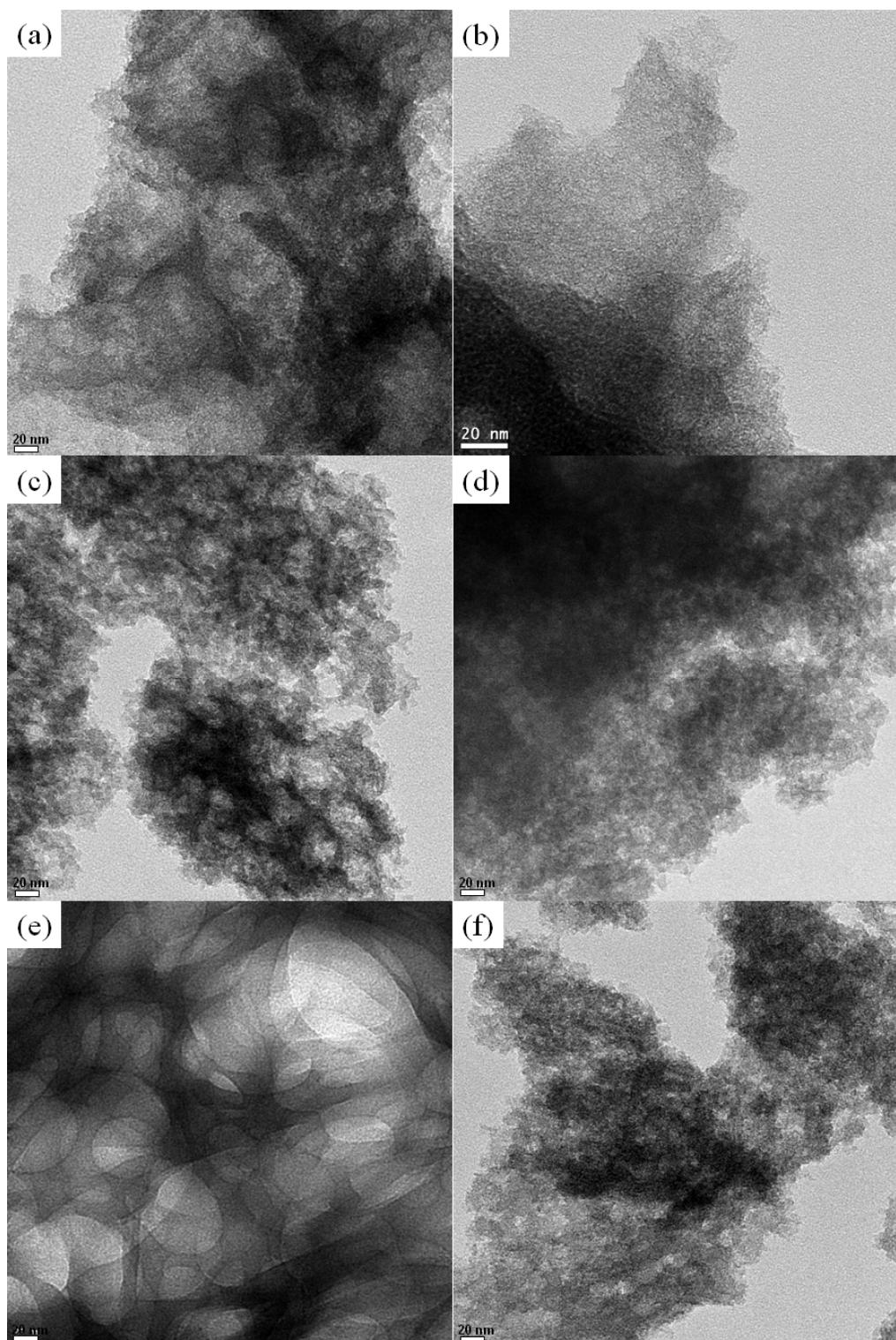
**Fig. S2** N<sub>2</sub> gas adsorption (filled symbol) and desorption (open symbol) isotherms for **1** (square), **2** (circle), **3** (star), **5** (diamond), **6** (pentagon) at 77K and CO<sub>2</sub> gas adsorption and desorption of **4** (triangle) at 197K.

#### Synthesis of carbon materials (1c – 6c)

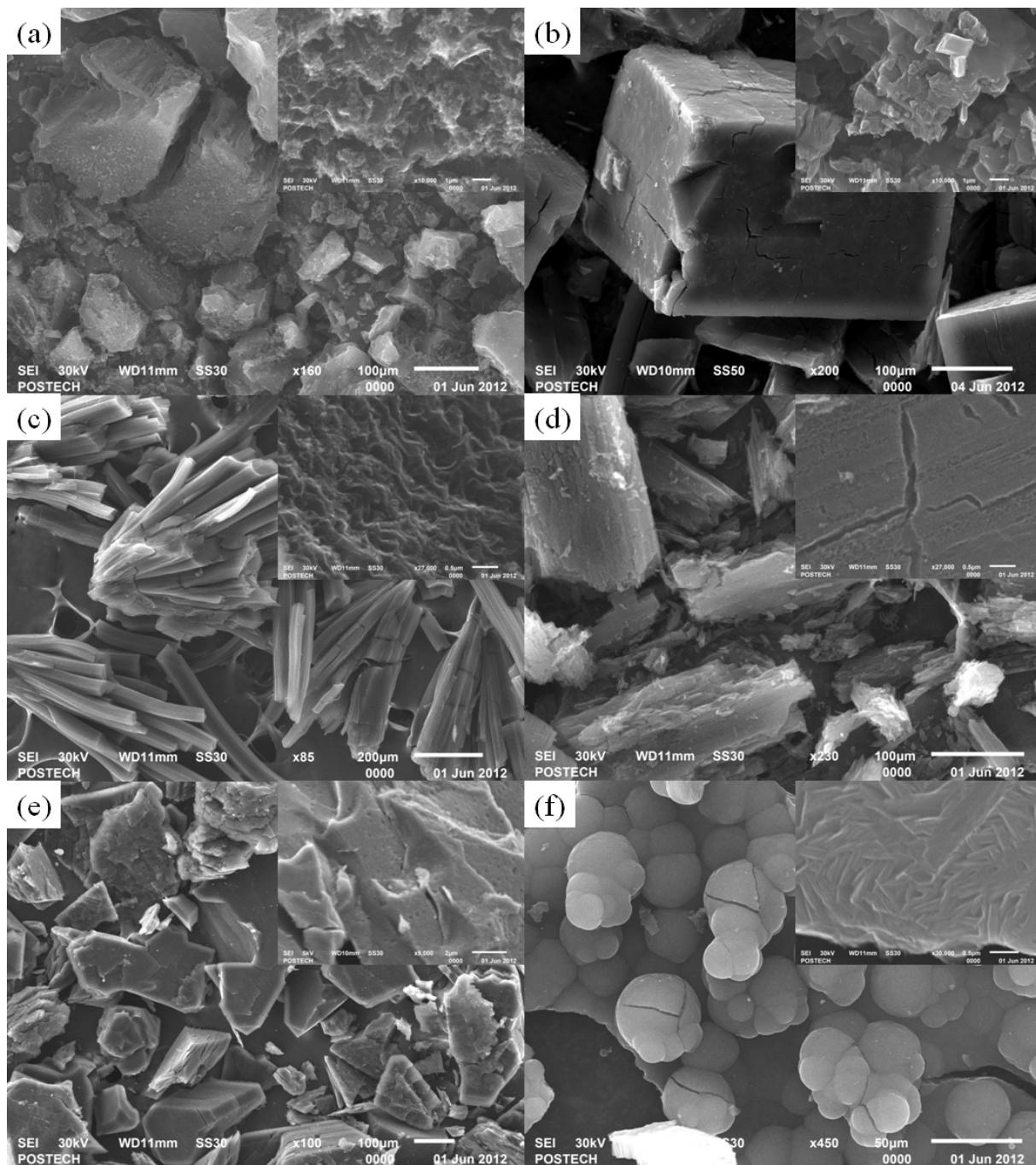
The MOF precursors **1** – **6** were heated to 1100 °C in a quartz tube furnace (diameter = 27 mm) with a heating rate of 10 °C·min<sup>-1</sup> under Ar flow (flow rate = 200 mL·min<sup>-1</sup>), carbonized for 8 h and naturally cooled down to room temperature. The resulting black powders (**1c** – **6c**, respectively) were collected.



**Fig. S3** PXRD of carbon materials **1c** (black), **2c** (red), **3c** (blue), **4c** (pink), **5c** (violet) and **6c** (olive).



**Fig. S4** TEM images of carbon materials (a) **1c**, (b) **2c**, (c) **3c**, (d) **4c**, (e) **5c**, and (f) **6c**.



**Fig. S5** SEM images of carbon materials (a) **1c**, (b) **2c**, (c) **3c**, (d) **4c**, (e) **5c**, and (f) **6c** (inset: high magnification images).

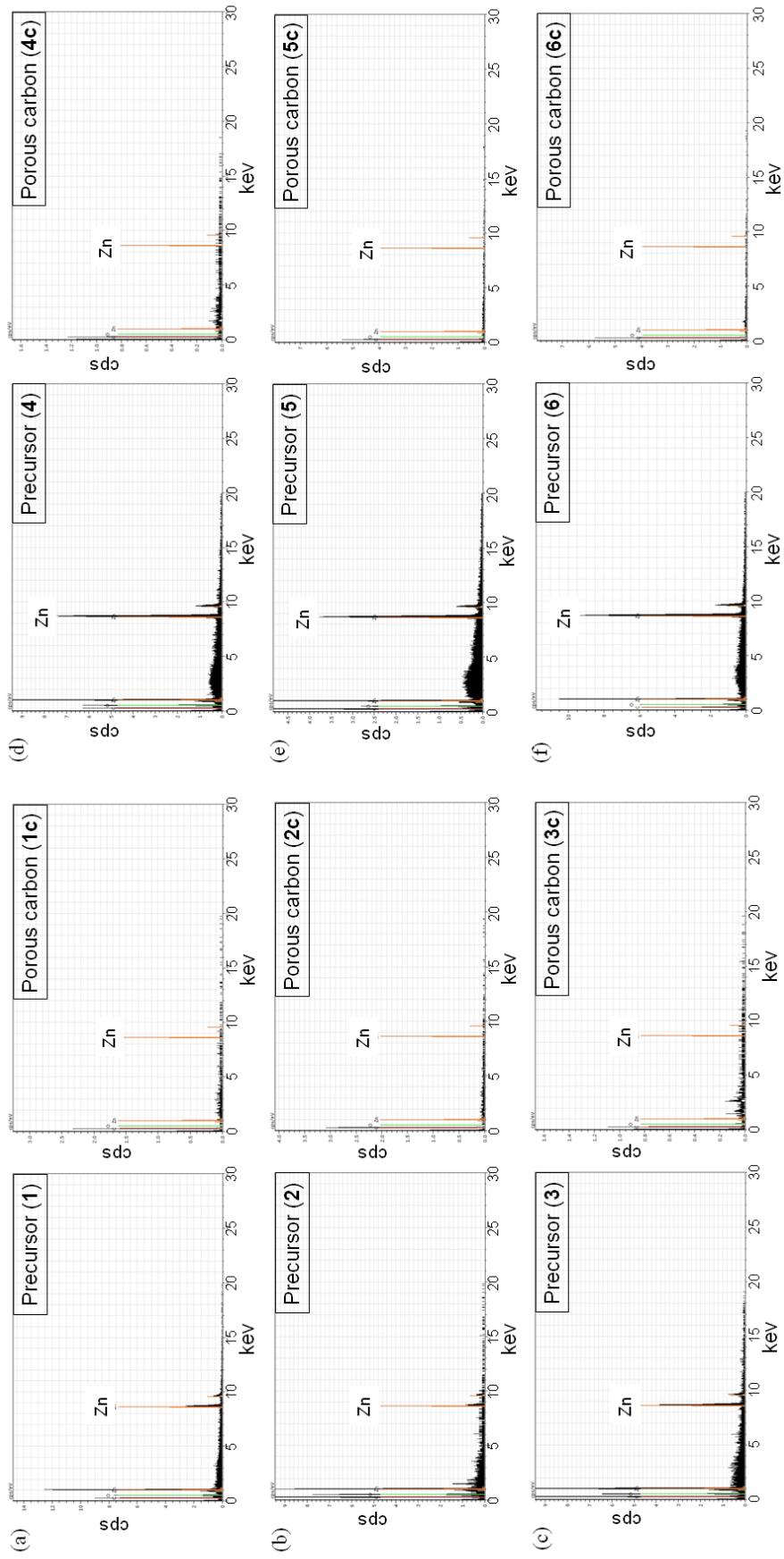
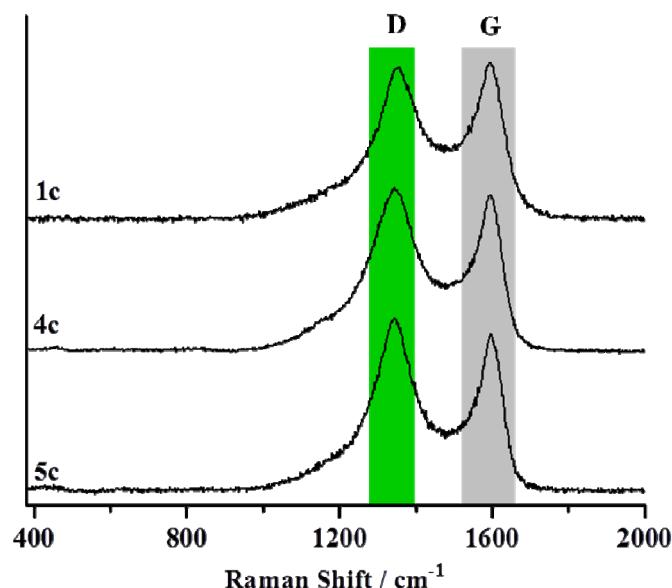


Fig. S6 EDX spectra of the materials (a) 1 and 1c (b) 2 and 2c, (c) 3 and 3c, (d) 4 and 4c, (e) 5 and 5c, and (f) 6 and 6c (black line: experimental, orange line: expected). EDX spectra were obtained using 30 kV acceleration voltage. The EDX spectra demonstrated the absence of Zn metals in the porous carbon materials.

### Raman spectra

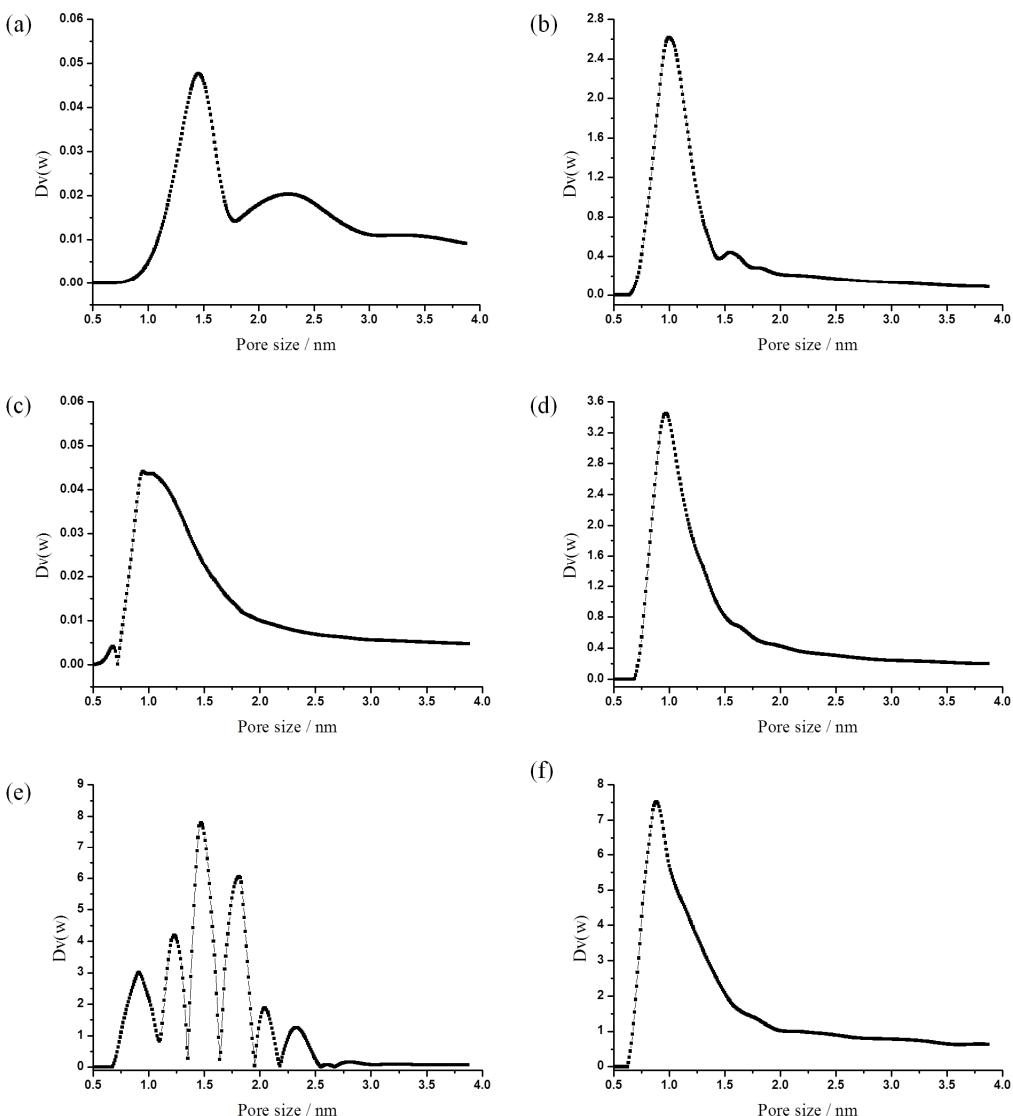
Raman spectra were measured in backscattering geometry with a JY LabRam HR fitted with a liquid-nitrogen cooled CCD detector. The spectra were collected under ambient conditions using the 514.5 nm line of an argon-ion laser (**Fig. S7**).



**Fig. S7** Raman spectra of carbon materials **1c**, **4c**, and **5c**. Green and gray lines highlight the D and G bands, respectively, due to  $sp^2$  carbon atoms.<sup>[S6]</sup>

### Gas sorption experiments

About 50 mg of samples were loaded in glass cell and activated at 120 °C under dynamic vacuum ( $10^{-4}$  bar) overnight before measurement. Nitrogen sorption isotherms were recorded in the pressure range up to  $10^{-3}$  – 100 kPa at 77 K.

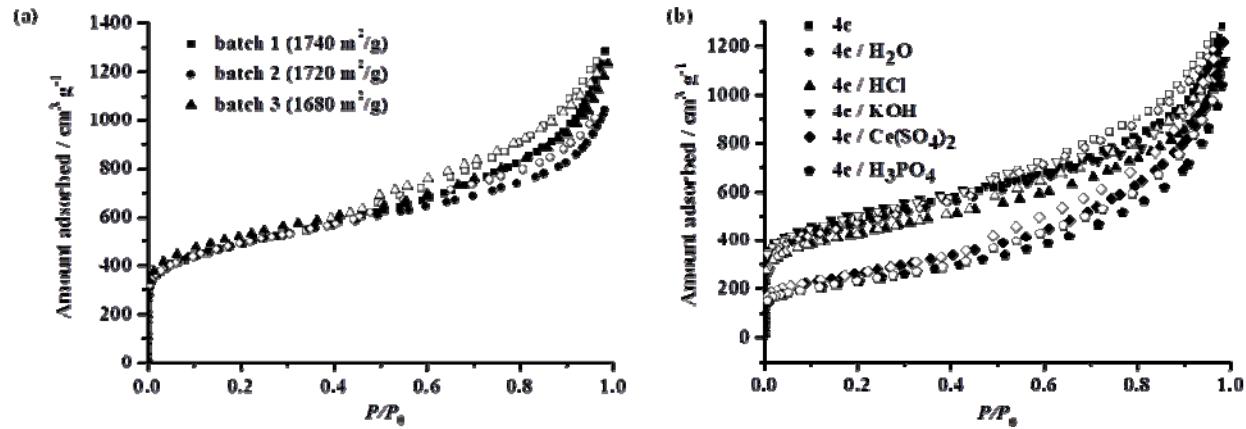


**Fig. S8** Pore-size distribution curves with adsorption volume  $V$  and pore diameter  $D$  of (a) **1c**, (b) **2c**, (c) **3c**, (d) **4c**, (e) **5c**, and (f) **6c** calculated by the SF method<sup>[S7]</sup> from  $N_2$  adsorption isotherms.

#### Reproducibility and stability study of a carbon material, **4c**.

For reproducibility test, porous carbon material **4c** was prepared three times independently from different batches of precursor **4**.  $N_2$  gas sorption isotherms were measured for each batch. The isotherm data are summarized in Fig. S9a.

The porous carbon **4c** samples were immersed in  $H_2O$ ,  $HCl$  (0.1 M),  $KOH$  (0.1 M),  $Ce(SO_4)_2$  (0.01 M water solution with several drops of  $H_2SO_4$ ) and  $H_3PO_4$  (0.01 M) for 1 day. After that thoroughly washed of the samples with distilled water (the absence of Cl, K, Ce, S or P in the corresponding carbon samples were analyzed by EDX spectra). The resulting samples were dried, activated at 120 °C under dynamic vacuum ( $10^{-4}$  bar) overnight. The  $N_2$  gas absorption isotherms are shown in Fig. S9b. The BET surface area of the resulting samples is provided in the Table S1.



**Fig. S9** Reproducibility (a) and stability (b) test for **4c** as indicated by N<sub>2</sub> sorption isotherm data at 77K. Adsorption (desorption) data are marked by filled (open) symbols, respectively.

**Table S1.** BET surface areas of **4c** treated with various chemicals.

	S <sub>BET</sub> (m <sup>2</sup> ·g <sup>-1</sup> )
no treatment	1700
H <sub>2</sub> O	1670
KOH (base)	1720
HCl (acid)	1500
H <sub>3</sub> PO <sub>4</sub> (strong oxidizing agent)	800
Ce(SO <sub>4</sub> ) <sub>2</sub> (strong oxidizing agent)	930

## References

- S1. H. Li, M. Eddaoudi, M. O'Keeffe and O. M. Yaghi, *Nature*, **1999**, *402*, 276.
- S2. D. N. Dybtsev, H. Chun and K. Kim, *Angew. Chem., Int. Ed.*, **2004**, *43*, 5033.
- S3. K. Koh, A. G. Wong-Foy and A. J. Matzger, *Angew. Chem., Int. Ed.*, **2008**, *47*, 677.
- S4. D. N. Dybtsev, A. L. Nuzhdin, H. Chun,; K. P. Bryliakov, E. P. Talsi, V. P. Fedin and K. Kim, *Angew. Chem., Int. Ed.*, **2006**, *45*, 916.
- S5. S. M. Hawxwell, H. Adams and L. Brammer, *Acta Crystallogr., Sect. B: Struct. Sci.*, **2006**, *62*, 808.
- S6. A. C. Ferrari, J. Robertson *Phil. Trans. R. Soc. Lond. A*, **2004**, *362*, 2477.
- S7. A. Saito, H. C. Foley *AIChE J.*, **1991**, *37*, 429.