

Supporting Information for

Siloxane D4 Capture by Hydrophobic Microporous Materials

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Preparation of porous compounds.

[Zn₄O(bdc)(bpz)₂] (bdc = 1,4-benzenedicarboxylate, bpz = 3,3',5,5'-tetramethyl-4,4'-bipyrazolate),¹ [Al(OH)(2,6-ndc)] (2,6-ndc = 2,6-naphthalenedicarboxylate, DUT-4),² poly(4,4'-biphenylene)silane (EOF-2)³ were synthesized according to the reported procedures. Activated carbon was purchased from NACALAI TESQUE, INC. BET surface area is 1050 m² g⁻¹ and the average pore diameter is 1.8 nm. Please note that there are various activated carbon materials with different property, and the studied activated carbon in here is one of the examples to compare with the inorganic-organic microporous compounds.

Physical measurements.

Powder X-ray diffraction (PXRD) data were recorded on a Bruker AXS NEW D8 ADVANCE and scanning step of 0.05 °. Thermogravimetric analysis (TGA) data were carried out with a Bruker AXS TG-DTA 2000SR in nitrogen atmosphere and at a heating rate of 10 °C min⁻¹. Adsorption isotherms (N₂ at 77 K, CO₂ at 298 K, CH₄ at 298 K) were measured on the BELSORP mini (BEL Japan, Inc.). Before the measurement, the samples were activated by heating at 393 K under vacuum for more than 12 hours. Solid state NMR measurements were carried out on a 9.4 T Bruker solid-state NMR instrument with an ADVANCE III 400 MHz spectrometer. ²⁹Si cross-polarization magic angle spinning (CPMAS) spectra were obtained using a double resonance 7 mm magic angle spinning (MAS) probe. A recycle delay and spinning rate are 3s and 7 kHz, respectively. ²⁹Si chemical shifts were referenced to tetramethylsilane at 0 ppm. Siloxane D4 adsorption measurement under kinetic condition were carried out under the following conditions; flow gas composition was siloxane D4 (5 ppm) in the air with 50% relative humidity and at 298 K. Flow rate was 0.5 L min⁻¹ and space velocity was 100,000 hour⁻¹. Diameter of the sample column was 26 mm, and we used approximately 100 mg of each sample.

Molecular mechanics calculation.

The geometry of isolated siloxane is optimized by molecular mechanics (MM) calculation. The structure is shown in below Figure S6. Optimized siloxane D4 was introduced into the DUT-4 pore which was constructed from the crystal structure with added hydrogen atoms. The siloxane D4 was

put with various orientations as an initial structure. We exhibited the some representative initial structures and optimized structures as in Figure S7. All calculations were carried out using Forcite module implemented in Material Studio 6.0 Package (Accelrys Inc., San Diego, CA). Universal Force Field was employed. The cell parameters of DUT-4 framework were kept constant same as the reported crystal structure, because less structural flexibility of the framework are revealed in previous work. Introduced siloxane D4 and components of framework are freely optimized under constant cell parameters. Energy and force threshold of convergence tolerance is $0.001 \text{ kcal}\cdot\text{mol}^{-1}$, and $0.5 \text{ kcal}\cdot\text{mol}^{-1}\cdot\text{\AA}^{-1}$, respectively. Siloxane D4 molecule is rectangular shape and methyl groups direct to the corner in optimized structures whenever we start from various initial orientation of siloxane D4.

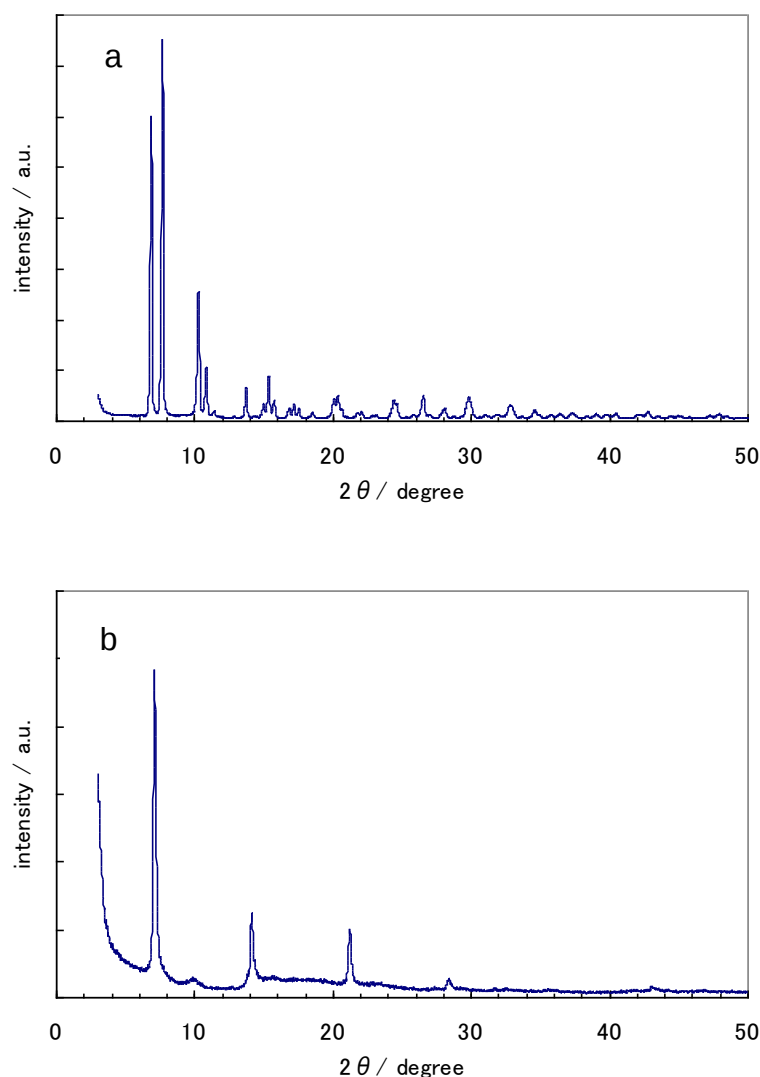


Figure S1. PXRD patterns of (a) $[\text{Zn}_4\text{O}(\text{bdc})(\text{bpz})_2]$ and (b) DUT-4.

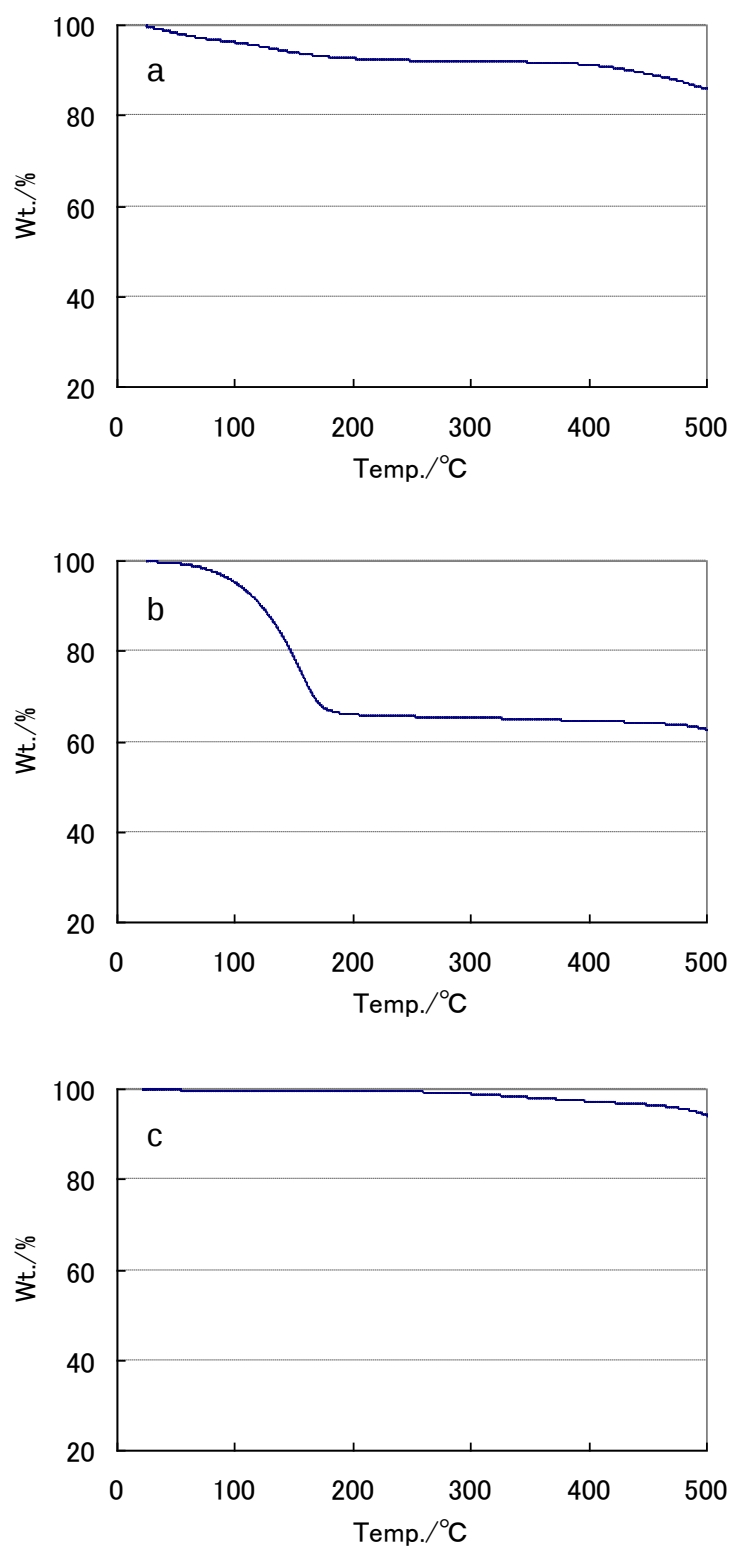
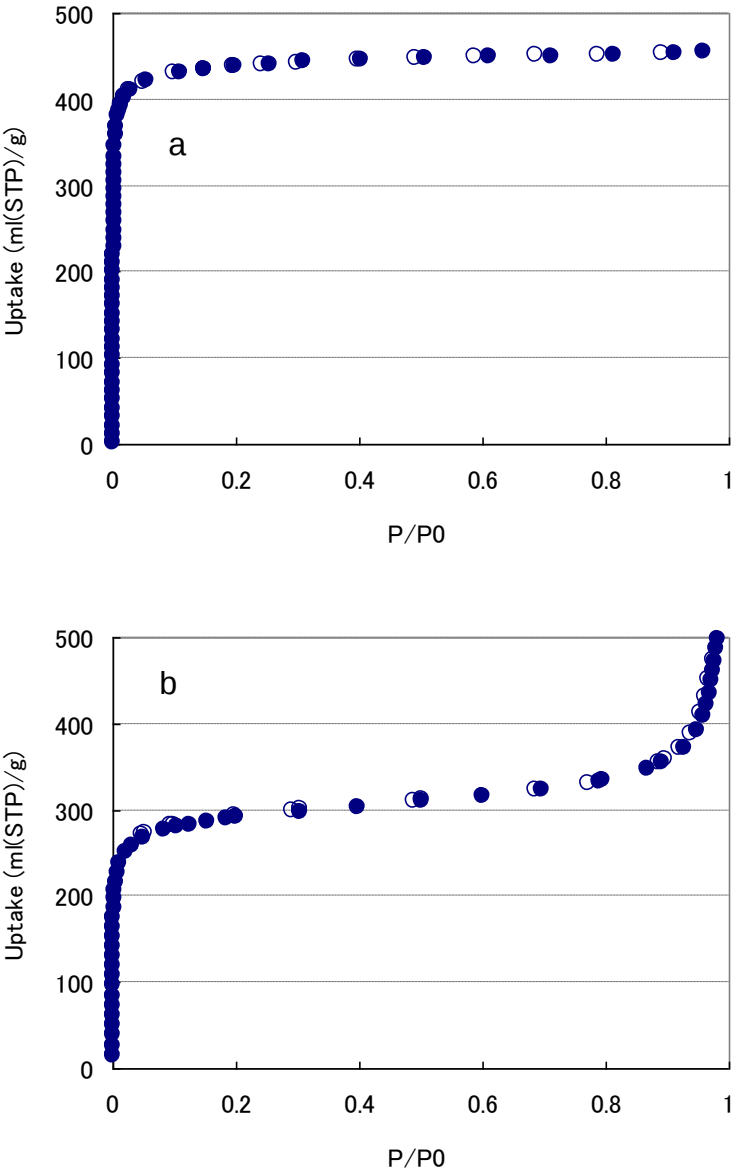


Figure S2. TGA profiles of as-synthesized states of (a) $[\text{Zn}_4\text{O}(\text{bdc})(\text{bpz})_2]$, (b) DUT-4, and (c)

EOF-2 from 25 to 500 °C.



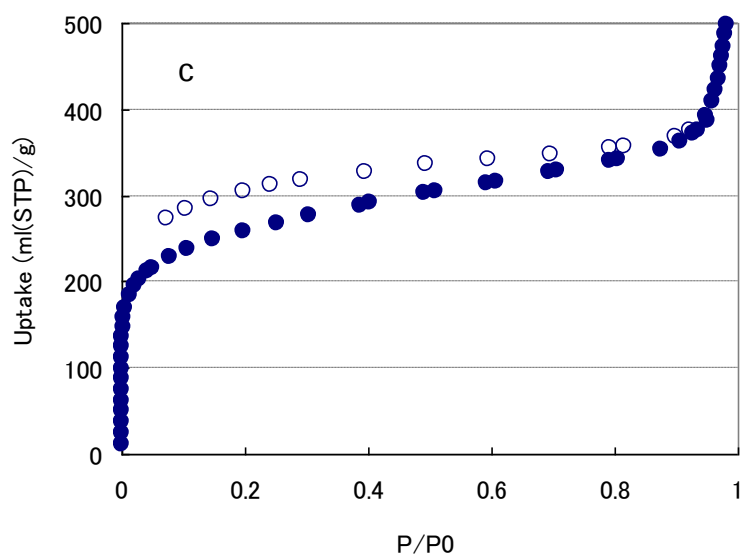


Figure S3. N₂ adsorption and desorption isotherms at 77 K for (a) [Zn₄O(bdc)(bpz)₂], (b) DUT-4, (c) EOF-2 (adsorption: solid circle, desorption: open circle).

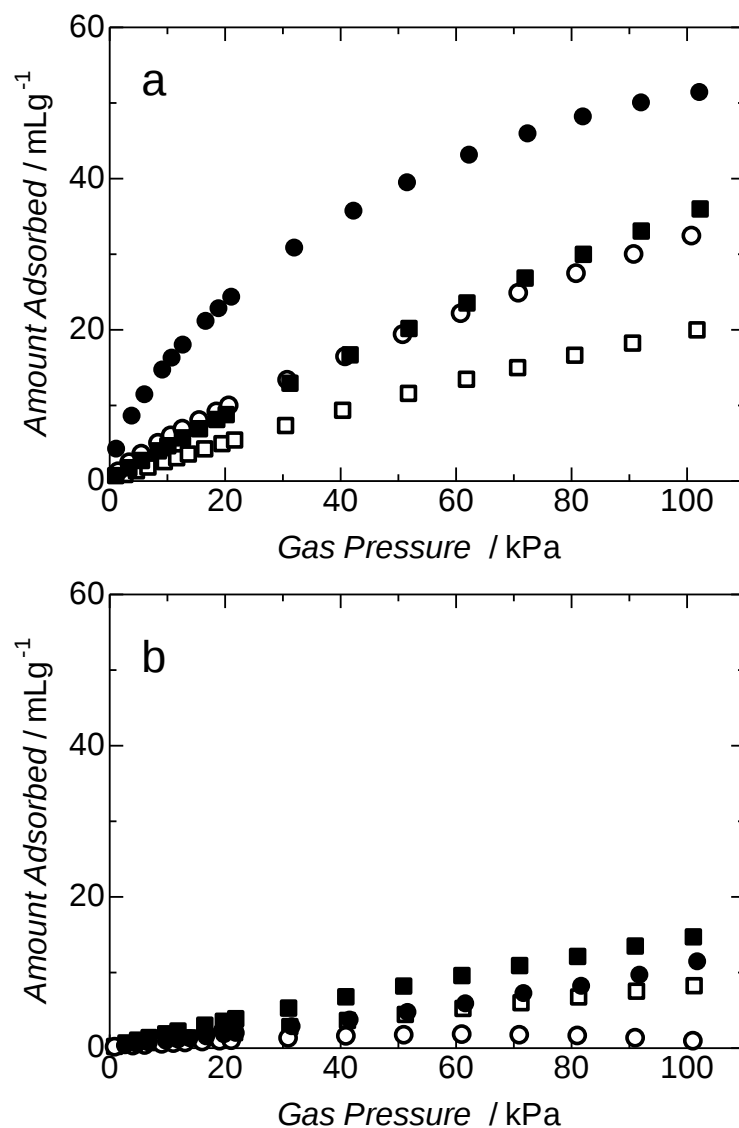


Figure S4. (a) CO₂ and (b) CH₄ adsorption isotherms of [Zn₄O(bdc)(bpz)₂] (■), DUT-4 (○), EOF-2 (□), activated carbon (●) at 298 K, respectively.

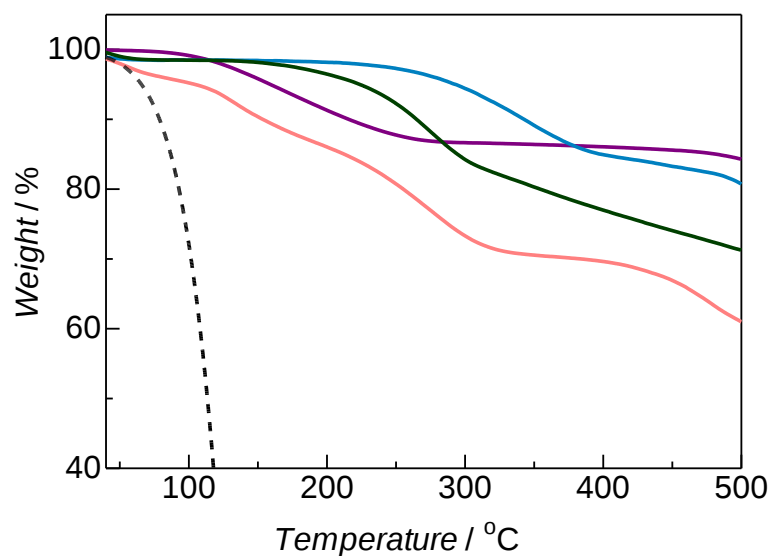


Figure S5. TGA profiles of samples which fully adsorb siloxane D4. [Zn₄O(bdc)(bpz)₂] (pink), DUT-4 (blue), EOF-2 (purple), activated carbon (deep green). Dot black line is the profile of pure siloxane D4.

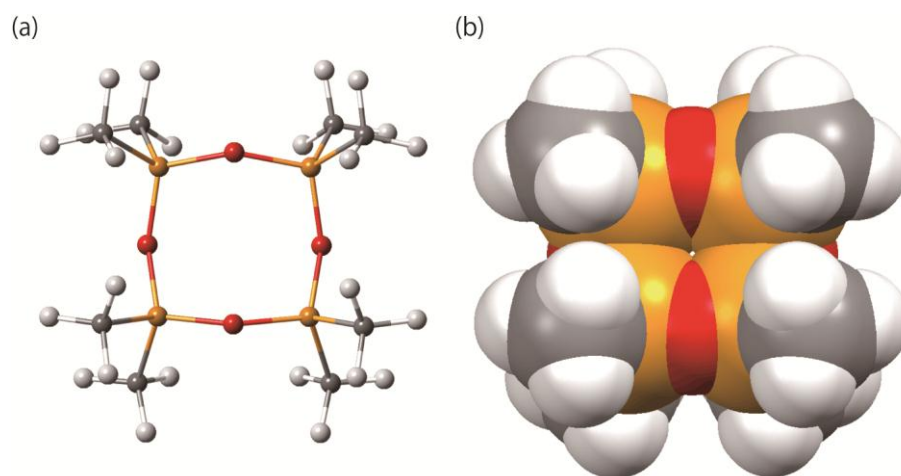


Figure S6. (a) Rectangular optimized structure of siloxane D4 and (b) CPK model. Orange, gray, red, and white show silicon, carbon, oxygen, and hydrogen, respectively.

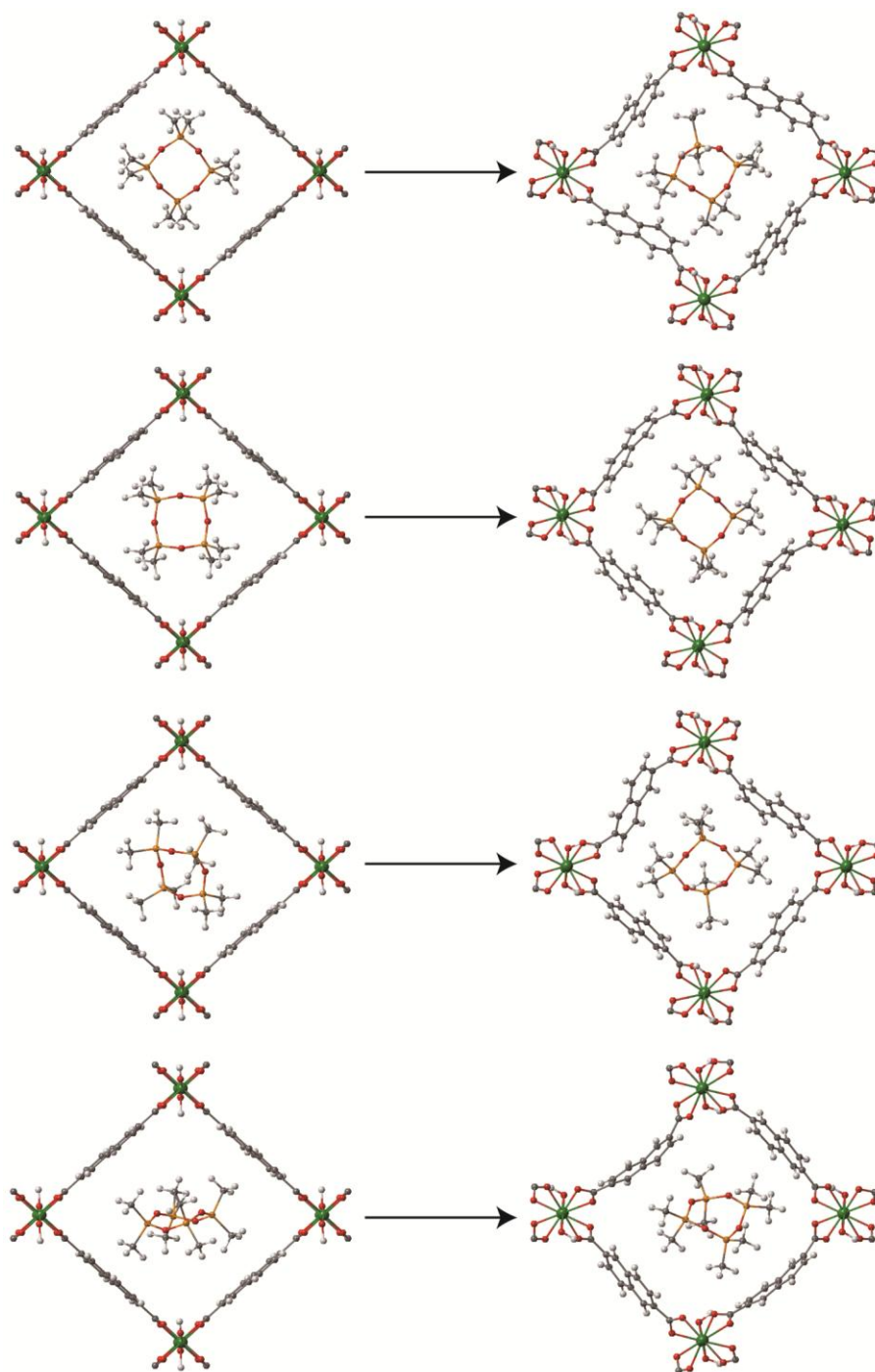


Figure S7. Various initial structures of DUT-4 with siloxane D4 molecule in left side, and geometry optimized structures in right side by molecular mechanics calculation. Green orange, gray, red, and white show aluminum, silicon, carbon, oxygen, and hydrogen, respectively.

References

- (1) Hou, L.; Lin, Y. Y.; Chen, X. M. *Inorg. Chem.* **2008**, *47*, 1346.
- (2) Senkovska, I.; Hoffmann, F.; Froba, M.; Getzschmann, J.; Bohlmann, W.; Kaskel, S. *Micropor. Mesopor. Mater.* **2009**, *122*, 93.
- (3) Rose, M.; Bohlmann, W.; Sabo, M.; Kaskel, S. *Chem. Commun.* **2008**, 2462.