Supporting Information


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Experimental Section

General Methods. All chemicals and solvents used in the syntheses were of reagents grade and used without further purification. Elemental analyses were performed with a Perkin-Elmer 2400 Series II CHN analyzer. Thermogravimetric analyses (TGA) were performed under N\textsubscript{2} atmosphere at a scan rate of 5 °C/min using TGA Q50 of TA instruments. Powder X-ray powder diffraction (PXRD) data were recorded on a Bruker D5005 diffractometer at 40 kV and 40 mA for Cu K\alpha (\(\lambda = 1.54050 \text{ Å}\)) with a scan speed of 5 °/min and a step size of 0.02 ° in 2\(\theta\).

Preparation of \([\text{Cu}_2(\text{BPnDC})_2(\text{bpy})]\)\(_n\) (SNU-6). The guest molecules in \([\text{Cu}_2(\text{BPnDC})_2(\text{bpy})]\)\(_n\cdot8\text{DMF}\cdot6\text{H}_2\text{O}\) \(_n\) (1)\(_n\) were exchanged with acetone by immersing the crystals of 1 in dried acetone for 24 h, during which time the solution was replenished with fresh acetone twice. The guest exchanged crystals were desolvated by heating at 60 °C under vacuum for 2 h in a Schlenk tube. FT-IR (Nujol): \(\nu = 1668, 1631 (\text{C=O}), \nu = 1606, 1561 (\text{O-C=O(carboxylate)}) \text{ cm}^{-1}\); UV/vis (Diffuse reflectance, \(\lambda_{max}\)): 272, 735 nm; elemental analysis calcd (%) for Cu\(_2\)C\(_{40}\)H\(_{24}\)O\(_{10}\)N\(_2\): C 58.61, H 2.95, N 3.42; found: C 57.48, H 2.87, N 3.20.

Preparation of \(n\text{(crown ether)}@[\text{Cu}_2(\text{BPnDC})_2(\text{bpy})]\)\(_n\). The desolvated SNU-6 (0.1 mmol) was immersed for 7 days in the acetone solutions of crown ether, 18-crown-6, or 15-crown-5, having various initial concentrations, \([G]_0 = 0.192 \text{ M} \sim 3.04 \text{ M}\) for 18-crown-6 and 0.0979 M \sim 2.50 M for 15-crown-5.

Low-Pressure Gas Sorption Measurements: The gas adsorption–desorption experiments were performed using an automated micropore gas analyzer Autosorb-3B (Quantochrome Instruments). All gases used were of 99.999% purity. The N\textsubscript{2} sorption isotherms were measured at 77 K. The H\textsubscript{2} sorption isotherms were monitored at 77 K and 87 K at each equilibrium pressure by the static volumetric method. The outgassing process was carried out by evacuating at room temperature for 6 h, and repeated between every experiment. After the gas sorption measurement was finished, weight of the sample was measured precisely. Surface area was determined from N\textsubscript{2} adsorption isotherm at 77 K by
using the Brunauer-Emmett-Teller (BET) and the Langmuir models, taking the data in the range $P/P_0 = 0.01 – 0.1$. Pore volume was determined by using the Dubinin-Radushkevich (DR) equation.

**Estimation of Isosteric Heat of the H$_2$ Adsorption:** The isosteric heats of H$_2$ adsorption were estimated for $n$(crown-ether)@[Cu$_2$(BPnDC)$_2$(bpy)]$n$ from the H$_2$ sorption data measured at 77 K and 87 K. A virial-type expression was used (eq 1), which is composed of parameters $a_i$ and $b_i$ that are independent of temperature.$^{2}$ In eq 1, $P$ is pressure (atm), $N$ is the amount adsorbed H$_2$ gas (mg g$^{-1}$), $T$ is temperature (K), and $m$ and $n$ represent the number of coefficients required to adequately describe the isotherms. An equation was fit using the R statistical software package.$^{3}$

$$\ln P = \ln N + \frac{1}{T} \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \quad (1)$$

To estimate the values of the isosteric heat of H$_2$ adsorption, eq 2 was applied, where $R$ is the universal gas constant.

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \quad (2)$$

**High-Pressure Gas Sorption Measurements:** High pressure gas sorption isotherms were measured by the gravimetric method using a Rubotherm MSB (magnetic suspension balance) apparatus. The H$_2$ sorption isotherms were measured at 298 K. All gases used were of 99.999 % purity and the trace of moisture was removed by a drying trap filled with 5 Å molecular sieves, which was purchased from the Chromatography Research Supplies (model 500). Desolvated solid (more than 200 mg) was quickly introduced to the apparatus, and then activated by evacuation at room temperature under vacuum. Prior to gas sorption measurement, He isotherm (up to 90 bar) was measured at 298 K to obtain the volume of framework skeleton. The excess sorption isotherms were measured and corrected for the buoyancy of the system and sample. The buoyancy correction of the sample was made by multiplying the volume of the framework skeleton by the density of corresponding gas at each pressure and temperature.$^{4}$
Theoretical determination of binding sites for crown ethers and H₂ gas in SNU-6: To find the preferential locations of crown ether molecules as guests within the framework, we conducted “locate simulations” by using a Sorption module of Materials Studio. The Metropolis Monte Carlo method was chosen for the calculation of the global minimum locations and optimized structures for 18C6 and 15C5 in the framework. Universal force field (UFF) was selected for the energy calculation, and the charge equilibration (QEq) method was used for the calculation of point atomic charges. For H₂ adsorption, we also performed “locate and adsorption isotherm simulations” using a Sorption module of Materials Studio. The Metropolis Monte Carlo method was chosen for the calculation of the hydrogen loading in the frameworks under a given fugacity. UFF was selected for the energy calculation. For the simulation of each framework, forty (40) fugacity steps in logarithmic scale (10⁻³ - 100 kPa) were calculated to obtain the isotherm and isosteric heat. Simulation temperature: 77 K; equilibrium steps: 500000; Production steps: 100000. These steps were chosen to assure the creation/destruction steps ratio about 1.00.

References


S3. The software package is available online at http://www.r-project.org.


**Table S1.** Experimental Data for 18-crown-6 Inclusion in SNU-6.

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<th>SNU-6 / mg</th>
<th>SNU-6 / mmol</th>
<th>$[G]_0$ / M</th>
<th>$[G]_{eq}$ / M</th>
<th>mol of crown-6/formula unit host</th>
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**Table S2.** Experimental Data for 15-crown-5 Inclusion in SNU-6.

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<th>SNU-6 / mmol</th>
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<th>$[G]_{eq}$ / M</th>
<th>mol of crown-5/formula unit host</th>
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Figure S1. TGA traces of $n$(18-crown-6)@SNU-6; $n = 0$ (black), 0.3 (red), 0.4 (green), 1.2 (blue), 1.5 (yellow), 1.7 (purple) moles of 18-crown-6 per unit formula of [Cu$_2$(BPnDC)$_2$(bpy)].
Figure S2. TGA traces for \( n(15\text{-crown}-5)@\text{SNU-6} \); \( n = 0 \) (black), 0.3 (red), 0.5 (green), 0.9 (blue), 1.3 (yellow), 1.8 (purple) moles of 15-crown-5 per unit formula of [Cu₂(BPnDC)₂(bpy)].
Figure S3. PXRD patterns for (a) as-synthesized SNU-6, (b) 1.7(18-crown-6)@SNU-6 before activation, and (c) 1.8(15-crown-5)@SNU-6 before activation.
Figure S4. The gas sorption isotherms of \( n \)(18-crown-6)@SNU-6 for (a) N\(_2\) at 77 K, (b) H\(_2\) at 77 K, and (c) H\(_2\) at 87 K, \( n = 0 \) (1, black), 0.3 (2, red), 0.4 (3, green), 1.2 (4, blue), 1.5 (5, brown) moles of 18-crown-6 per unit formula of [Cu\(_2\)(BPnDC)\(_2\)(bpy)].

Figure S5. The gas sorption isotherms of \( n \)(15-crown-5)@SNU-6 for (a) N\(_2\) at 77 K, (b) H\(_2\) at 77 K, and (c) H\(_2\) at 87 K, \( n = 0 \) (1, black), 0.3 (2, red), 0.5 (3, green), 0.9 (4, blue), 1.3 (5, brown) moles of 15-crown-5 per unit formula of [Cu\(_2\)(BPnDC)\(_2\)(bpy)].
Figure S6. The H₂ adsorption isotherms of 0.3(18-crown-6)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading (right).

Figure S7. The H₂ adsorption isotherms of 0.4(18-crown-6)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading.
**Figure S8.** The H₂ adsorption isotherms of 1.2(18-crown-6)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading (right).

**Figure S9.** The H₂ adsorption isotherms of 0.3(15-crown-5)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading (right).
**Figure S10.** The H₂ adsorption isotherms of 0.5(15-crown-5)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading (right).

**Figure S11.** The H₂ adsorption isotherms of 0.9(15-crown-5)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H₂ adsorption (right) depending on H₂ loading (right).
Figure S12. The H$_2$ adsorption isotherms of 1.3(15-crown-5)@SNU-6 measured at 77 K (red) and 87 K (blue) that are fit to virial equation (left), and the isosteric heat of H$_2$ adsorption (right) depending on H$_2$ loading (right).
Figure S13. Molecular structures and atomic point charges of (a) 18-crown-6 and (b) 15-crown-5, calculated by charge equilibration (QEq) method.
Figure S14. Binding sites of 18-crown-6 in SNU-6 calculated by “locate simulations” using a Sorption module of Materials Studio. (a) 4, (b) 8, (c) 12, and (d) 18 molecules of 18-crown-6 in a unit cell (Z = 8) of SNU-6. A unit cell contains 8 formula units of SNU-6. According to experimental results, maximum 2.40 molecules of 18C6 can be included per formula unit of SNU-6 having 2 Cu(II) ions.
Figure S15. Binding sties of 15-crown-5 in SNU-6 calculated by “locate simulations” using a Sorption module of Materials Studio. (a) 2, (b) 4, (c) 8, (d) 12, and (e) 20 molecules of 15-crown-5 in a unit cell (Z = 8) of SNU-6. A unit cell contains 8 formula units of SNU-6. According to experimental results, maximum 2.92 molecules of 15C5 can be included per formula unit of SNU-6 having 2 Cu(II) ions.
**Figure S16.** Adsorption sites of H$_2$ molecules in (a) 18-crown-6 and (b) 15-crown-5, calculated by “locate simulations” using a Sorption module of Materials Studio.
Figure S17. Theoretical H$_2$ adsorption sites in (a) SNU-6, (b) 0.5(18-crown-6)@SNU-6, (c) 1.0(18-crown-6)@SNU-6, (d) 0.5(15-crown-5)@SNU-6, and (e) 1.0(15-crown-5)@SNU-6. These are calculated by “locate simulations” using a Sorption module of Materials Studio.
Figure S18. Theoretical H₂ adsorption isotherm (open □) of SNU-6 calculated by “adsorption isotherm simulation” using a Sorption module of Materials Studio, which is compared with experimental isotherm (filled ■).
Figure S19. Theoretical H$_2$ adsorption isotherm (open □) for 0.4(18-crown-6)@SNU-6 calculated by “adsorption isotherm simulation” using a Sorption module of Materials Studio, which is compared with experimental isotherm (filled ■).
**Figure S20.** Theoretical H$_2$ adsorption isotherm (open □) for 0.3(15-crown-5)@SNU-6 calculated by “adsorption isotherm simulation” using a Sorption module of Materials Studio, which is compared with experimental isotherm (filled ■).