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Enhanced isosteric heat of H₂ adsorption by inclusion of crown ethers in a porous metal–organic framework†

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Inclusion of 18-crown-6 or 15-crown-5 in a porous MOF increased the isosteric heats of H₂ adsorption significantly, which are comparable to MOFs containing open metal sites.

Porous metal–organic frameworks (MOFs) have been attracting attention as the potential hydrogen storage materials since MOFs can store a large amount of hydrogen.¹ For example, the hydrogen storage capacities of MOF-210, NU-100, and SNU-77 are 8.6 wt% (total 16.7 wt%) at 77 K and 70 bar,² 9.95 wt% (total 16.4 wt%) at 77 K and 56 bar,³ and 8.1 wt% (total 11.0 wt%) at 77 K and 90 bar,⁴ respectively. However, the practical application of the MOFs as hydrogen storage materials has been confronted with a difficulty because their hydrogen storage capacities are very low at ambient temperature. The targets for onboard hydrogen storage systems that are established by the United States Department of Energy, which should be achieved by 2017, are 5.5 wt% at the operating temperature of –40 to 60 °C and the maximum delivery pressure of 100 atm. Among the candidate hydrogen storage materials developed so far, none is capable of reaching these targets yet.

To extend the hydrogen storage performance of MOFs at the ambient temperature, the isosteric heat (Q_{st}) of H₂ adsorption should be substantially increased.⁵ The optimum heat of H₂ adsorption for the effective ambient temperature storage and release of the gas has been estimated to be 15–20 kJ mol^{−1},^{6,7} which is still beyond the highest reported values. To improve the H₂ adsorption capacity at room temperature, the MOFs have been modified by attaching the functional groups,⁸ generating the accessible metal centers,⁹ and embedding the metal nanoparticles in the MOFs.¹⁰ In addition, alkali or alkaline earth metal ions were included in the MOFs as the attempts to increase Q_{st} . However, the values of the increase were commonly very small, 0.2–1.1 kJ mol^{−1},^{11,12} and only Li-MIL-53(Al) increased Q_{st} by 5.8 kJ mol^{−1}.¹³ As for the inclusion of neutral organic molecules, there has been no report yet revealing if Q_{st} can be increased by the organic inclusions, although there exists a theoretical study predicting that impregnation

of magnesium-decorated fullerenes in IRMOF-8 might enhance Q_{st} up to 11 kJ mol^{−1}.¹⁴

We expected that inclusion of organic compounds, which can provide electrostatic field in a MOF, might enhance the binding affinity of gases including H₂ molecules. Therefore, we have chosen 18-crown-6 (18C6) and 15-crown-5 (15C5) as the guest inclusions, whose molecular sizes are 11.6 and 10.5 Å, respectively, according to our estimation by using the energy minimization function of MM2.¹⁵ We have chosen [Cu₂(BPnDC)₂bpy] (**SNU-6**)¹⁶ as a porous MOF, since it has large pores (pore size, 18.2 Å) that are enough to accommodate these crown ethers, as well as large void space (83.7% of whole framework), high pore volume (1.05 cm³ g^{−1}), and high surface area (Langmuir, 2910 m² g^{−1}; BET, 2590 m² g^{−1}). It showed high H₂ gas storage capacities, 1.68 wt% at 77 K and 1 atm; excess 4.87 wt% and total 10.0 wt% at 77 K and 70 bar.

Here we report for the first time that 18C6 and 15C5 that are included as guest molecules in **SNU-6** enhance Q_{st} of H₂ adsorption in the MOF significantly, up to 10.5 kJ mol^{−1} that is 2.8 kJ mol^{−1} higher than that (7.74 kJ mol^{−1}) of pristine **SNU-6**. The enhancement is much higher than those occurred as a result of the inclusion of alkali or alkaline-earth metal ions and comparable to those by the open metal sites in a MOF.

In the experiments, the desolvated **SNU-6** was immersed for 7 days in the acetone solutions of crown ethers, which have various initial concentrations ([G]₀). The amounts of crown ether included in the pores of **SNU-6** under the equilibrium conditions, which depend on [G]₀, were estimated from the elemental analysis (EA) and thermogravimetric analysis (TGA) data obtained for the samples that were dried at room temperature under vacuum for 6 h. The concentration of these crown ethers in the solution could not be measured by gas chromatography or spectrophotometry because they have very high boiling points (116 °C at 0.2 Torr for 18C6; 93–96 °C at 0.05 Torr for 15C5) and did not absorb light in the wavelength region that is higher than 330 nm (cut-off point of acetone). The amounts of crown ether included in the MOF were plotted against the equilibrium concentration of the crown ether (Fig. 1), and the data were fitted to eqn (1)¹⁷ to obtain the formation constant (K_f) of crown-ether@MOF, and the maximum amount (mole) of crown ether ([BS]_{0/ω}) that can be included in the formula unit of **SNU-6** containing two Cu(II) ions. Analysis of the data provides $K_f = 0.832$ and [BS]_{0/ω} = 2.40 mol for 18C6, and $K_f = 0.648$ and [BS]_{0/ω} = 2.92 mol for 15C5. These values indicate that **SNU-6**

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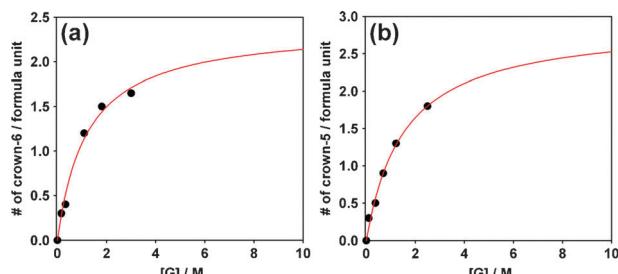


Fig. 1 Binding of **SNU-6** with (a) 18C6 and (b) 15C5 in acetone. The solid line indicates the best fit curve to eqn (1). The equilibrium concentrations of 18C6 and 15C5 were calculated from $[G]_0$ value, TGA data, and the EA data that were obtained for crown ether@**SNU-6** dried at room temperature under vacuum for 6 h.

has higher binding affinity for 18C6 than for 15C5, but slightly greater capacity for a smaller crown ether, 15C5.

$$\begin{aligned} [\text{BS} \cdot \text{G}] / \omega &= -\frac{([\text{BS}]_0 / \omega)[\text{G}]}{[\text{G}] + \frac{1}{K_f}} \\ &= \frac{([\text{BS}]_0 / \omega)([\text{G}]_0 - [\text{BS} \cdot \text{G}])}{[\text{G}]_0 - [\text{BS} \cdot \text{G}] + \frac{1}{K_f}} \end{aligned} \quad (1)$$

The powder X-ray diffraction (PXRD) patterns (see ESI†) indicate that the framework structure of **SNU-6** is retained even after inclusion of the crown ethers followed by removal of guest solvent at 25 °C under vacuum. Although **SNU-6** maintained the single crystallinity even after the immersion in highly concentrated 18C6 or pure 15C5, the 18C6 or 15C5 inclusions could not be located in the **SNU-6** by the synchrotron X-ray diffraction data collected at 100 K. Therefore, we conducted a “locate simulation” by using a sorption module of Materials Studio to find the most appropriate shape and distribution of the 18C6 and 15C5 guests within **SNU-6** (see ESI†).¹⁸ 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 (QEeq) method was used for the calculation of point atomic charges. The results indicate that at low loadings of 18C6 and 15C5 (≤ 0.5 molecules per formula unit of **SNU-6** = 4 molecules in a unit cell), 18C6 and 15C5 reside beside 4,4-bipyridine linking the Cu₂ paddlewheel of **SNU-6** (see ESI†), and stabilized by *ca.* 17 kcal mol⁻¹ for 18C6 and 14 kcal mol⁻¹ for 15C5 compared to free 18C6 and 15C5 due to van der Waals and electrostatic interactions with the MOF. At higher loading than 0.5 molecules per formula unit of **SNU-6**, additional crown ether molecules are filled from the vicinity of previously located crown ethers.

The gas sorption isotherms were measured for N₂ and H₂ for the samples including various amounts of crown ethers. As shown in Table 1 and Fig. 2, surface area, pore volume, and H₂ gas uptake capacities at 77 and 87 K decrease as the amount of 18C6 increases. When more than 1.7 moles of 18C6 were included per formula unit of **SNU-6**, the sample did not adsorb H₂ gas. However, **SNU-6** including 18C6 shows enhanced Q_{st} of H₂ adsorption: when 1.2 mol of 18C6 was included per unit formula of the host, the Q_{st} value reached 10.5 kJ mol⁻¹, which is 2.8 kJ mol⁻¹ higher than that of pristine **SNU-6**.

Table 1 Gas sorption properties of *n*(18C6)@**SNU-6**

Mol of 18C6/formula unit host (<i>n</i>)	Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	H ₂ uptake/wt%	Q_{st} of H ₂ adsorption/kJ mol ⁻¹
			77 K	87 K
0	2910	1.05	1.68	1.10
0.3	2100	0.78	1.29	0.85
0.4	1680	0.59	1.03	0.71
1.2	637	0.24	0.52	0.34
1.5	83.7	0.052	0.14	n/a ^a

^a Virial fit was unsuccessful.

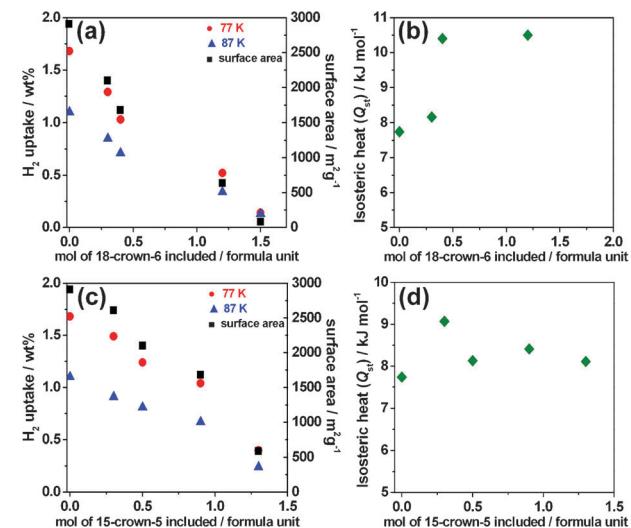


Fig. 2 Relationship of surface areas (■), H₂ uptake capacities at 77 K (●) and 87 K (▲), and Q_{st} of H₂ adsorption (◆) vs. the amount of crown ether inclusion, (a and b) for *n*(18C6)@**SNU-6** and (c and d) for *n*(15C5)@**SNU-6**.

In the case of *n*(15C5)@**SNU-6**, the surface area, pore volume, and H₂ gas uptake capacities at 77 and 87 K also decrease as the amount of 15C5 inclusion increases (Table 2 and Fig. 2). Again, Q_{st} of H₂ adsorption increases as the amount of 15C5 inclusion increases, and the Q_{st} value reaches 9.07 kJ mol⁻¹ when *n* = 0.3. In particular, 0.9(15C5)@**SNU-6** has surface area, pore volume, and H₂ gas uptake capacities that are very similar to those of 0.4(18C6)@**SNU-6**. However, 0.4(18C6)@**SNU-6** exhibits a Q_{st} value (10.4 kJ mol⁻¹) greater than that (8.41 kJ mol⁻¹) of 0.9(15C5)@**SNU-6**, indicating that the H₂ molecules interact with 18C6 more strongly than with 15C5.

At 298 K and 80 bar, the H₂ storage capacities in **SNU-6**, 0.4(18C6)@**SNU-6**, and 1.2(18C6)@**SNU-6** are 0.32, 0.30 and 0.19 wt%, respectively, indicating that crown ether inclusion decreases the H₂ uptake because of their occupancy on the MOF surface (Fig. 3a). However, considering the H₂ uptake

Table 2 Gas sorption properties of *n*(15C5)@**SNU-6**

Mol of 15-crown-5/host	Surface area/m ² g ⁻¹	Pore volume/cm ³ g ⁻¹	H ₂ uptake capacity/wt%	Q_{st} of H ₂ adsorption/kJ mol ⁻¹
			77 K	87 K
0	2910	1.05	1.68	1.10
0.3	2610	0.96	1.49	0.91
0.5	2100	0.78	1.24	0.81
0.9	1680	0.63	1.04	0.67
1.3	589	0.23	0.40	0.24

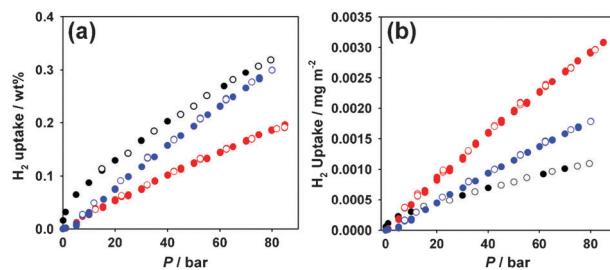


Fig. 3 The H₂ adsorption/desorption: (a) high pressure H₂ adsorption/desorption isotherms at 298 K, and (b) high pressure H₂ uptake at 298 K per unit surface area, for SNU-6 (black), 0.4(18C6)@SNU-6 (blue), and 1.2(18C6)@SNU-6 (red). Filled and open symbols represent adsorption and desorption data, respectively.

capacities per unit surface area (Fig. 3b), which are 0.0011 mg m⁻² for SNU-6, 0.0018 mg m⁻² for 0.4(18C6)@SNU-6, and 0.0030 mg m⁻² for 1.2(18C6)@SNU-6, it is obvious that the inclusion of crown ethers significantly enhances H₂ adsorption in the MOF at room temperature.

The role of 18C6 and 15C5 in H₂ adsorption in the MOF is to provide the electrostatic field for the stronger interaction with H₂ gas molecules. According to our theoretical calculation using the QE method, the partial atomic charges of 18C6 and 15C5 ranged from -0.471e to -0.480e for oxygen, +0.043e to +0.154e for hydrogen, and +0.039e to +0.045e for carbon (see ESI†).^{18,19} According to the measured Q_{st} values, it appears that the strength of the electrostatic field provided by six or five ether oxygen atoms of the crown ethers is comparable to that of the vacant coordination site on the metal ion in a MOF.

We also performed Grand Canonical Monte Carlo (GCMC) calculation to locate the H₂ molecules in the materials upon H₂ adsorption (see ESI†).¹⁸ The theoretical results show that a hydrogen molecule fits in the hole of free 18C6, but it sits above the center of the free 15C5 plane due to the smaller hole size of 15C5 than 18C6 (see ESI†). In pristine SNU-6, the preferential location of H₂ is the adjacent sites to Cu₂ paddle-wheel units. However, in the presence of the crown ether inclusions, H₂ molecules locate in the neighborhood of crown ethers and Cu₂ paddle-wheel units of SNU-6. In these cases, the interaction enthalpies (non-bond energies) of H₂ with *n*(18C6)@SNU-6 and *n*(15C5)@SNU-6 become lowered by *ca.* 2 kJ mol⁻¹ and *ca.* 0.4 kJ mol⁻¹, respectively, compared with that in pristine SNU-6. The theoretical Q_{st} values derived from the simulated H₂ adsorption isotherms are 7.0–5.7, 11.9–7.2, and 7.3–6.5 kJ mol⁻¹ for SNU-6, 0.4(18C6)@SNU-6, and 0.3(15C5)@SNU-6, respectively. Even though these theoretical values differ from the experimental values by 0.7–1.7 kJ mol⁻¹, they also clearly indicate that the 18C6 guest significantly enhances the isosteric heats of the H₂ adsorption due to the electrostatic interactions between the oxygen atoms of crown ethers and the H₂ molecules.

In conclusion, we have demonstrated by the experimental and theoretical studies that the inclusion of 18C6 and 15C5 in a porous MOF that has large pores significantly increases Q_{st} of the H₂ adsorption. Compared with *ca.* 1.1 kJ mol⁻¹ increase in the Q_{st} value by the inclusion of alkali metal or alkali earth metal ions,^{11,12} the present increase of *ca.* 2.8 kJ mol⁻¹ (experimental) and *ca.* 4.9 kJ mol⁻¹ (theoretical) by the inclusion of 18C6 is remarkable. It is comparable to the effect of the accessible metal sites⁹ in

the MOF, enhancing by 2.5–5.1 kJ mol⁻¹. According to the present results, 18C6 has a greater effect than 15C5 on the enhancement of Q_{st} . We are currently developing MOFs constructed of crown ethers as a part of the building units, which we expect to provide high Q_{st} as well as high surface area and high pore volume. In addition, to test our original approach of including organic guests in suitable MOFs for the enhancement of gas adsorptions not only of H₂ gas but also of other gases, we will further conduct the experiments with other organic guests such as calixarenes²⁰ and dendrimers, employing other MOFs with appropriate pore sizes such as IRMOF-8, MOF-177, and MOF-199 (HKUST-1).

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