Postsynthetic Exchanges of the Pillaring Ligand in Three-Dimensional Metal–Organic Frameworks

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Supporting Information

ABSTRACT: Metal–organic frameworks, [Ni(HBTC)(dabco)] (2) and [Ni2(HBTC)2(bipy)]0.6(dabco)1.4 (3) (where H3BTC is 1,3,5-benzenetricarboxylic acid, dabco is 1,4-diazabicyclo[2.2.2]octane, and bipy is 4,4′-bipyridine), were prepared via postsynthetic ligand exchanges of [Ni(HBTC)(bipy)] (1). By controlling the concentration of dabco, we could obtain not only entropically favorable 2 with completely exchanged dabco but also enthalpically favorable 3 with selectively exchanged bipy/dabco in the alternating layers.

KEYWORDS: metal–organic frameworks (MOFs), postsynthetic modification (PSM), postsynthetic ligand exchange (PSLE), enthalpically favorable exchange, entropically favorable exchange, gas sorption, adsorption enthalpy

INTRODUCTION

Postsynthetic modification (PSM) of a metal–organic framework (MOF) is a convenient synthetic approach for the preparation of new isoreticular MOFs that are difficult to obtain or cannot be attained via the conventional synthetic approaches.1 Systematic modifications of the reactive residue of an organic linker in a MOF could lead to new isoreticular MOFs with systematically varied characteristics. Recently, a new type of dative PSM, postsynthetic exchange of a structural component that was directly participating in the network connectivity, was reported.2,3 The postsynthetic ligand exchange (PSLE) led to a new isoreticular MOF with a reduced pore dimension accompanied via one-dimensional reorganization of the framework structure3b and a hybrid MOF with mixed linker ligands of the same length in a single framework without any reorganization of the framework structure.3b

Recently, there was a report about the solvothermal preparation of a three-dimensional (3D) MOF, [Ni(HBTC)-(bipy)] (1) (where H3BTC is 1,3,5-benzenetricarboxylic acid and bipy is 4,4′-bipyrindine).4 In the network structure, both NiII ion and HBTC ligand as 3-connected nodes formed two-dimensional (2D) sheets of a honeycomb (hcb) net topology, and the 2D sheets are further pillared using 2-connected bipy linkers via the metal nodes to form a 3D network structure.

Here, we report the PSLE of 1 toward new isoreticular MOFs, [Ni(HBTC)(dabco)] (2) and [Ni2(HBTC)2(bipy)]0.6(dabco)1.4 (3) (where dabco is 1,4-diazabicyclo[2.2.2]octane), that cannot be attained via the conventional one-step synthetic approach. By controlling the concentration of dabco in N,N-dimethylformamide (DMF), we could obtain not only 2 with completely exchanged pillaring layers via random exchange of a bipy linker but also 3 with alternatively exchanged pillaring layers via selective exchange. The relationship between the pore dimension and the sorption properties of the MOFs, such as adsorbate uptake amount and adsorption enthalpy, has been investigated.

EXPERIMENTAL SECTION

General Procedures. All reagents were purchased from commercial sources and used without further purification. Elemental analysis (EA) (C, H, and N) was performed at the Central Research Facilities of the Ulsan National Institute of Science & Technology. Powder X-ray diffraction (PXRD) data were recorded using a Bruker D2 Phaser automated diffractometer at room temperature, with a step size of 2θ = 0.02°. Simulated PXRD patterns were calculated using the Material Studio software package5 employing a structural model from single-crystal data.

Preparation of MOF [Ni(HBTC)(bipy)]. 1. 1 was prepared via a solvothermal reaction that was slightly modified from the reported synthetic procedures.6 A mixture of Ni(NO3)2·6H2O (37.8 mg, 0.130 mmol), H3BTC (23.2 mg, 0.110 mmol), and bipy (17.2 mg, 0.110 mmol) was dissolved in a mixed solvent of 4 mL of DMF and 4 mL of MeOH, and the solution was divided into two portions. Each portion was transferred to a 10 mL vial. The tightly sealed vial was heated at 70 °C for 2 days to form cyan hexagonal crystals. The crystals of 1 were...
harvested and washed using DMF and then air-dried at ambient temperature for a couple of hours. The activated sample, 1a, was prepared by vacuum drying overnight at 150 °C. EA was performed on the sample of 1a, which had been reexposed to air for a couple of hours. EA calcd for [Ni(HBTC)(bipy)]·2H2O (C62H12N10O8Ni, fw = 459.03 g/mol). Calcld: C, 49.71%; H, 3.51%; N, 6.10%. Found: C, 49.84%; H, 4.00%; N, 6.62.

PSLE of 1. Before ligand exchange of the MOF, the as-synthesized single crystals of 1 were soaked in DMF for a couple of days to remove any remaining reactants and side products present in the solvent cavities. After the solvent had been decanted, the crystals were air-dried at ambient temperature for a couple of hours.

[Ni(HBTC)(dabco)], 2. Approximately 10 mg of the crystals of 1 presoaked in DMF was transferred to a vial of 10 mL of a 1.0 M dabclo DMF solution and the solution in the tightly sealed vial was stored for 2 days in an oven at 100 °C. The crystals slowly changed color from cyan to pale yellow while retaining their crystallinity during the soaking. The harvested crystals were air-dried at ambient temperature for a couple of hours. The activated sample, 2a, was prepared by vacuum drying 2 at 150 °C overnight. EA was performed on the sample of 2a reexposed in air for a couple of hours. EA calcd for [Ni(HBTC)(dabco)]·2H2O (C62H12N10O8Ni, fw = 415.42 g/mol). Calcld: C, 43.41%; H, 4.86%; N, 6.75%. Found: C, 42.98%; H, 4.97%; N, 6.95%.

[Ni(HBTC)(bipy)0.6(dabco)1.4], 3. The PSLE procedure for the preparation of 3 was the same as that for 2 except for the use of a 0.05 M dabcno DMF solution for 3 days. The pale green crystals were harvested and washed using DMF and then air-dried at ambient temperature for a couple of hours. The activated sample, 3a, was prepared by vacuum drying 3 at 150 °C overnight. EA was performed on the sample of 3a that had been reexposed to air for a couple of hours. EA calcd for [Ni2(HBTC)2(bipy)0.6(dabco)1.4]·3H2O (C84H48N2012O12Ni2, fw = 874.47 g/mol). Calcld: C, 44.50%; H, 4.56%; N, 6.41%. Found: C, 44.21%; H, 4.77%; N, 6.82%.

[Ni(HBTC)(bipy)], 4. The crystals of 4 were prepared by soaking approximately 30 mg of 3 in 10 mL of a 0.1 M bipy DMF solution at ambient temperature for 7 days. EA was conducted on the activated sample that had been reexposed to air for a couple of hours, where the activated sample was prepared by soaking the crystals in fresh DMF for 2–3 days and methylene chloride for 1 day and then vacuum drying at ambient temperature overnight. EA calcd for [Ni(HBTC)(bipy)]·3.7H2O (C62H12N10O8Ni3, fw = 937.11 g/mol). Calcld: C, 43.58%; H, 4.63%; N, 5.98%. Found: C, 43.17%; H, 5.08%; N, 6.30%.

Crystallographic Data Collection and Refinement of the Structure. Crystals of 2–4 were coated with Paratone oil, and the diffraction data were measured at 173 K using Mo Kα radiation in an X-ray diffraction camera system using an imaging plate equipped with a graphite crystal incident beam monochromator. The Rapid Auto software package was used for data collection and processing. All structures were determined using direct methods employing SIR2000. The structures were refined using full-matrix least-squares calculations employing the XL program of the SHELXTL PLUS software package.

[Ni2(HBTC)2(bipy)0.6(dabco)1.4], 3. Two nickel ions, two-thirds of a BTC− ligand, and four-thirds of a H1/2BTC1.5− ligand on six diﬀerent crystallographic 3-fold symmetry sites, a pillaring dabclo ligand, and a pillaring bipy site were observed as an asymmetric unit of hexagonal space group P3. The pillaring bipy site in the asymmetric unit was statistically disordered together with two other ligated dabco sites and two lattice water sites with a total site occupancy of 1. Nickel, oxygen, and nitrogen atoms were reﬁned anisotropically, and carbon atoms were reﬁned isotropically. The hydrogen atoms were assigned isotropic displacement coeﬃcients U(H) = 1.2U(C), and their coordinates were allowed to ride on their respective atoms. The least-squares reﬁnement of the structural model was performed under geometry restraints and displacement parameter restraints, such as DFIX, DANG, EXYZ, EADP, and ISOR for the dabco and bipy molecules. The ﬁnal reﬁnement was performed with modiﬁcation of the structural factors for the electron densities of the disordered solvent region (209 Å3, 48.5% of the crystal volume) using the SQUEEZE option of the PLATON software package. Refinement of the structure converged at the following final values: R1 = 0.1172 and wR2 = 0.2531 for 3155 reflections for which I > 2σ(I), and R1 = 0.2403 and wR2 = 0.3168 for all 10006 reﬂections. The largest diﬀerence peak and hole were 1.368 and −1.25 e/Å3, respectively. The Flack parameter value (0.4 ± 0.9) that was obtained indicated that the structure is racemic twinned.

[Ni2(HBTC)2(bipy)(dabco)], 4. Two nickel ions, two-thirds of a BTC− ligand, and four-thirds of a H1/2BTC1.5− ligand on six diﬀerent crystallographic 3 sites, a pillaring dabclo ligand, and a pillaring bipy ligand were observed as an asymmetric unit of hexagonal space group P3. The pillaring bipy ligand is statistically disordered. All non-hydrogen atoms were reﬁned anisotropically. The hydrogen atoms were assigned isotropic displacement coeﬃcients U(H) = 1.2U(C), and their coordinates were allowed to ride on their respective atoms. A hydrogen atom attached to a carbonyl group of a HBTC ligand was not included in the least-squares reﬁnement of the structural model, which was performed under geometry restraints and displacement parameter restraints, such as DFIX, DANG, EXYZ, EADP, and ISOR for the disordered bipy site. The final reﬁnement was performed with modiﬁcation of the structural factors for the electron densities of the disordered solvent region (2219 Å3, 50.9% of the crystal volume) using the SQUEEZE option of the PLATON software package. Refinement of the structure converged at the following final values: R1 = 0.0945 and wR2 = 0.2337 for 5571 reﬂections for which I > 2σ(I), and R1 = 0.1403 and wR2 = 0.2700 for all 10213 reﬂections. The largest diﬀerence peak and hole were 1.631 and −0.787 e/Å3, respectively. The Flack parameter value of 0.49(3) that was obtained indicated that the structure is racemic twinned.

A summary of the crystal data for 2–4 is given in Tables S1–S3 of the Supporting Information. CCDC 894148, 893749, and 893750 contain the supplementary crystallographic data. The data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

Gas Sorption Measurements. All of the gas sorption isotherms were measured using a BELSORP-max (BEL Japan, Inc.) adsorption system employing a standard volumetric technique up to saturation pressure. The N2 (purity of 99.9999%) sorption isotherms were monitored at 77 K. The adsorption data in the pressure range of <0.1 P/P0 were ﬁtted to the Brunauer–Emmett–Teller (BET) equation to determine the BET surface area. The entire set of adsorption data was used to obtain the Langmuir speciﬁc surface area. The H2 (purity of 99.9999%) sorption isotherms were measured at 77 and 87 K, and the CO2 (purity of 99.9999%) and CH4 (purity of 99.95%) sorption isotherms were measured at 195 and 273 K.

Computations. The Vienna Ab initio Simulation Package was used to calculate the ground state of many-electron systems in the framework of density functional theory. The plane-wave basis set with an energy cutoff of 400 eV and the Perdew–Burke–Efrosz–Held-type gradient-corrected exchange-correlation potential were employed.
RESULTS AND DISCUSSION

Attempt To Synthesize the Isoreticular MOFs via the Conventional Approach. Attempts to prepare 2 and 3 via a one-pot solvothermal reaction were not successful. While the solvothermal reaction of H$_2$BTC with $\sim$1.2 equiv of Ni$^{II}$ ion in DMF at 130 °C for 3 days in the presence of an equivalent amount of bipy as a pillaring linker led to the 3D MOF, 1, with a 5,5-connected hms net topology, a similar solvothermal reaction in the presence of dabco as a potential pillaring linker produced only the reported 2D MOF, [Ni(HBTC)(DMF)$_2$] (Figure S1 of the Supporting Information), where the 2D sheet of the MOF made of Ni$^{II}$ ion and HBTC ligand is the same as that of 1, but the 3-connected nickel centers of an hcb net topology are ligated with two additional monodentate DMF (Figure S2 of the Supporting Information). While bipy was incorporated as a pillaring linker in the structure of 1, dabco was not.

PSLE of the MOF. 2 could be obtained only by soaking 1 in a dabco DMF solution via the PSLE of the structural organic linker of 1, bipy. When the cyan single crystals of 1 were soaked in a 1.0 M dabco DMF solution at 100 °C, the crystals underwent a change in color from cyan to pale yellow (Figure 1).

![Figure 1](https://dx.doi.org/10.1021/cm303624p001)

To check whether the change from the cyan crystals of 1 to the pale yellow crystals of 2 is a single-crystal-to-single-crystal (SCSC) transformation, one single crystal of 1 was selected and was soaked in the same way as for the bulk crystals. The single crystal retained its crystallinity without any indication of dissolution, and there was no hint of the formation of any additional crystals. The PXRD patterns of the crystals showed gradual intensity decreases of the $(h,k,l)$ reflections with a non-zero $l$ index while retaining the intensities of the $(h,k,0)$ reflections as the soaking proceeds (Figure 2a). Two new broad peaks at $\theta \approx 12.5^\circ$, $25^\circ$, and $38.5^\circ$, corresponding to $(0,0,1)$, $(0,0,2)$, and $(0,0,3)$ reflections, respectively, indicated that the $c$-axis dimension of the crystal decreased from $\sim$11 to $\sim$7 Å while the dimensions of the $a$–$b$ plane remained intact (Figure 2b). The longer bipy pillaring linkers between the 2D sheets were replaced by the shorter dabco linkers, and the replacement was completed within 30 h.

The complete exchange of pillaring ligand was confirmed by the X-ray diffraction analysis of a single crystal of 2 (Figure 3). The $\sim$7 Å intersheet distance caused by the dabco pillaring linker agrees well with the PXRD pattern of 2.

3 could also only be obtained by the PSLE of 1 in a DMF solution containing dabco as an additional potential pillaring ligand via partial and selective exchange of the existing pillaring ligand, bipy. Soaking the crystals of 1 in a 0.05 M dabco DMF solution at 100 °C showed a change in the color of the crystals from cyan to pale green (Figure 1). The SCSC transformation from 1 to 3 was also checked by soaking one single crystal of 1 in a 0.05 M dabco DMF solution. The PXRD patterns of the crystals of 1 soaked in the dabco solution also showed gradual intensity decreases of the $(h,k,l)$ reflections with a non-zero $l$ index while the intensities of the $(h,k,0)$ reflections were retained as the soaking proceeded, and the change to the post-synthetically modified crystals 3 was completed within 48 h (Figure 4a). New broad peaks appeared at $\theta \approx 4.9^\circ$, $9.8^\circ$, $14.7^\circ$, and $24.5^\circ$ that could be assigned as the peaks of $(0,0,1)$,
(0, 0, 2), (0, 0, 3), and (0, 0, 5) reflections, respectively; the c-axis dimension of the crystal increased from ∼11 to ∼18 Å (Figure 4b). The elongated c-axis dimension of the crystal suggests that the alternating pillaring bipy layers have been selectively exchanged for the dabco linkers.

Although the random substitution of the pillaring ligand from bipy to dabco linker is an entropically more favorable process, the exchange in a lower-concentration dabco DMF solution occurs via the entropically less favorable selective substitution of the alternating pillaring layers. While the exchange of the pillaring ligand in a 1.0 M dabco DMF solution occurs via the random substitution of the pillaring ligand, the exchange in a 0.05 M dabco DMF solution occurs via the selective and systematic substitution of the alternating bipy/dabco pillaring layers. The single-crystal X-ray diffraction analysis showed that 3 has a [Ni₂(HBTC)₂(bipy)₀.₆(dabco)₁.₄] structure, where the ligand exchange from bipy to dabco had occurred only in the alternating layers (Figure 5). Even though the intersheet distance pillared by bipy linkers is ∼11 Å, the occupancy factor for the bipy site in the single-crystal structure indicated that more than 60% of the bipy sites were replaced by either dabco or solvent DMF/water molecules, which agrees with the EA result.

When single crystals of 3 were soaked in a 0.1 M bipy DMF solution at ambient temperature for 7 days, there was no apparent change in the PXRD pattern of the sample. The X-ray diffraction analysis of a single crystal of the soaked sample, 4, also showed no apparent changes in its lattice parameters or the space group. However, the structural refinement of 4 of with a formula unit of [Ni₂(HBTC)₂(bipy)₀.₆(dabco)₁.₄] could be performed with the fully occupied bipy site in the alternating pillaring layer. The EA result also supports the formula unit of 4.

When the crystals of 1 were soaked in a 0.3 M dabco DMF solution for 8 h at 100 °C, the PXRD pattern of the crystals showed the simultaneous appearance of the peaks related to the structures of 1–3 [the peaks at 2θ ≈ 7.9°, 15.8°, and 23.8° for (0, 0, 1), (0, 0, 2), and (0, 0, 3) reflections of 1, respectively; the peaks at 2θ ≈ 12.6° and 24.6° for (0, 0, 1) and (0, 0, 2) reflections of 2, respectively; the peaks at 2θ ≈ 4.9°, 9.8°, 14.7°, and 25.2° for (0, 0, 1), (0, 0, 2), (0, 0, 3), and (0, 0, 5)
reflections of 3, respectively] (Figure 6). In the substitution of the pillaring linker of 1 soaked in the intermediate concentration of a dabco DMF solution, the reaction proceeds via both random substitution and systematically alternating substitution of the bipy pillaring linkers. The extended soaking of 1 in the 0.3 M dabco DMF solution for more than a month completely exchanged all bipy pillaring linkers in 1 with dabco pillaring linkers to form 2, as in the soaking of 1 in the 1.0 M dabco DMF solution.

**Reverse PSLE of the MOFs.** 2 and 3 could be reversibly transformed back to 1 by simply soaking the crystals in a bipy DMF solution (Figure S3 of the Supporting Information). While the soaking of the crystals of 3 in a 0.05 M bipy DMF solution at 100 °C led to complete replacement of the pillaring dabco linker back with the bipy linker within 6 h (Figure S3b of the Supporting Information), a similar soaking of the crystals of 2 in a 0.1 M bipy DMF solution at 100 °C led to incomplete replacement of the pillaring dabco linker and generated a crystalline mixture of 1–3 (Figure S3a of the Supporting Information). The PXRD pattern of the mixture showed the simultaneous presence of three sets of (0, 0, l) reflections related to the crystals of 1–3. The soaking of the crystals of 2 in a higher-concentration bipy DMF solution (1.0 M) for 1 day at 100 °C finally led to complete exchange of the pillaring linker.

**Entropically and Enthalpically Favorable Pillaring Ligand Exchanges.** To understand the formation of the entropically unfavorable, selectively exchanged structure 3 rather than the entropically favorable, randomly exchanged structural model 3a (Scheme 1), we constructed three different types of 2D sheet structural models of an hcb net topology consisting of [bipy-Ni^{II}-bipy], [bipy-Ni^{II}-dabco], and [dabco-Ni^{II}-dabco] coordination sites (Figure 7).

While the selectively exchanged structure, 3, contains only the [bipy-Ni^{II}-dabco] coordination site, the [bipy-Ni^{II}-bipy], [bipy-Ni^{II}-dabco], and [dabco-Ni^{II}-dabco] coordination sites can be observed in the randomly exchanged structural model, 3a. Using the total energies of the three aforementioned structural models and isolated bipy and dabco,11 we evaluated the formation enthalpy of the coordination sites. Compared with the [bipy-Ni^{II}-bipy] coordination site, the [bipy-Ni^{II}-dabco] and [dabco-Ni^{II}-dabco] coordination sites are unfavorable by ∼11.12 and ∼34.30 kJ/mol, respectively (Figure S4 of the Supporting Information). The energy difference obviously originates from the difference in the coordination strength of Ni^{II}-bipy and Ni^{II}-dabco sites. Even though dabco is a stronger base than bipy, the calculation shows that the Ni-N_{dabco} bond at the [bipy-Ni^{II}-dabco] coordination site is ∼0.15 Å more longer than the Ni-N_{bipy} bond at the [bipy-Ni^{II}-bipy] coordination site (Table 1). More interestingly, there is ∼0.05 Å more elongation of the Ni-N_{dabco} bond at the [dabco-Ni^{II}-dabco] coordination site than at the [bipy-Ni^{II}-dabco] coordination site. Similar elongations of the Ni-N_{dabco} bond were also observed in the single-crystal structures of 2–4. The elongation is caused by the repulsion of the sterically more demanding ligated dabco linker with the BTC ligands. While the BTC plane in the [bipy-Ni^{II}-bipy] coordination site is almost planar, that in the [bipy-Ni^{II}-dabco] coordination site is distorted to release the strain incurred by the steric repulsion. The puckering of the BTC plane in the [dabco-Ni^{II}-dabco] coordination site is unavailable because of the symmetry, and thus, the strain originated from the steric repulsion is instead
The bond distances around the Ni(II) ion are from the reported single-crystal structure of \[\text{Ni(bipy) \_2} \]. Optimized 2D sheet structural models of an hcb net topology consisting of \([\text{bipy-Ni}^\text{II}-\text{bipy}], [\text{bipy-Ni}^\text{II}-\text{dabco}], \) and \([\text{dabco-Ni}^\text{II}-\text{dabco}] \) coordination sites. \(\text{Ni(bipy)}_2 = \) the \([\text{bipy-Ni}^\text{II}-\text{bipy}] \) coordination site. \(\text{Ni(dabco)}_2 = \) the \([\text{dabco-Ni}^\text{II}-\text{dabco}] \) coordination site.

The N\(_2\) uptake amount and the BET specific area of 2a are 251 cm\(^3\)/g and 930 m\(^2\)/g, respectively, which are significantly smaller than those of 1a (391 cm\(^3\)/g and 1540 m\(^2\)/g, respectively). The complete exchange of the longer pillaring ligand bipy by the shorter pillaring ligand dabco in 2a significantly reduced the pore volume and the specific surface area. The partial exchange of the pillaring ligand by the shorter pillaring ligand dabco in 3a also led to a reduced N\(_2\) uptake amount and BET surface area compared with those of 1a. The N\(_2\) uptake amount and the BET specific area of 3a were 305 cm\(^3\)/g and 1150 m\(^2\)/g, respectively. As expected from the intermediate dimension with the selectively and alternatively exchanged mixed pillars, these values are smaller than those of 1a with pure bipy pillar, but larger than those of 2a with pure dabco pillar. All the activated samples, 1a–3a, are stable in air at least for a couple of hours. The activated samples exposed in air for a couple of hours did not indicate any decrease in N\(_2\) uptake amounts. However, an extended exposure in air or a soaking in water led to the complete loss of the crystallinity and the porosity of the activated samples. The activated samples exposed to air for one month or soaked in water overnight did not show any powder diffraction peaks and did not adsorb any N\(_2\) at 77 K.

CO\(_2\) and CH\(_4\) Sorption Behaviors of the MOFs. The effects of the modified pore dimensions of 2a and 3a compared with that of 1a are reflected in the sorption behavior of CH\(_4\) and CO\(_2\) (Figures 9 and 10 and Figures S4 and S5 of the Supporting Information). At 195 K, decreased CH\(_4\) uptake amounts on 2a and 3a (106 and 118 mg/g, respectively) were observed compared with that of 1a (152 mg/g) (Figure 9 and Figure S5 of the Supporting Information). However, at 273 K, slightly increased uptake amounts on 2a and 3a were observed compared with that on 1a (Figure 9a). The larger CH\(_4\) sorption

![Figure 8](image_url)  
**Figure 8.** N\(_2\) sorption isotherms of 1a, 2a, and 3a at 77 K.

![Figure 9](image_url)  
**Figure 9.** (a) CH\(_4\) sorption isotherms of 1a (black), 2a (red), and 3a (blue) at 195 and 273 K and (b) their adsorption enthalpies.
uptake amounts at 273 K on 2a and 3a with the smaller pore volumes compared with that on 1a with the larger pore volume are due to the larger CH4 adsorption enthalpy on 2a and 3a (approximately −21 and −23 kJ/mol, respectively) than that on 1a (approximately −17 kJ/mol) (Figure 9b). On the other hand, at 273 K, the CH4 uptake amount on 2a (38 mg/g) is similar to that on 3a (34 mg/g) even though the pore volume of 2a is significantly larger than that of 3a.

The sorption behavior of CO2 on 1a–3a is different from that of CH4 (Figure 10 and Figure S6 of the Supporting Information). The qualitative uptake behavior of CO2 on 1a–3a looks similar to that of CH4 (Figure 10a). Although, at 195 K, the CO2 uptake amount on 3a (447 mg/g) is ~1.2 times that on 2a (379 mg/g), at 273 K the CO2 uptake amount on 3a (261 mg/g) is ~2 times that on 2a (119 mg/g), which is caused by the larger CO2 adsorption enthalpy on 3a (approximately −27 kJ/mol) than that on 2a (approximately −22 kJ/mol) (Figure 10b). Although the pore dimension of 3a based on the N2 uptake amount is larger than that of 2a, the adsorption enthalpy of 3a on CO2 is larger than that of 2a, which is due to the combined effects of the different properties of the pillaring ligands and of the unsaturated metal sites generated from the solvent or monodentate dabco-ligated Ni(II) centers in 3a. The less hydrophobic nature of aromatic bipy and aliphatic dabco as mixed pillaring ligands in 3a compared to that of pure aliphatic dabco in 2a is responsible for the larger adsorption enthalpy of CO2 with a larger polarizability and quadrupole moment on 3a than 2a. In addition, the presence of the unsaturated metal sites is also contributing to the larger adsorption enthalpy of 3a versus that of 2a.

At 1 bar and 273 K, the CO2 uptake amount of 1a is 316 mg/g, which is the second largest amount yet reported at this temperature, and almost comparable with the largest amount of SNU-S, 385 mg/g. More interestingly, although the uptake amount of 3a at 1 bar and 273 K is smaller than those of 1a and SNU-S, the uptake amount at ~0.15 bar (which is the partial pressure of CO2 in flue gas), 141 mg/g, is almost twice the uptake amounts of 1a and SNU-S at the same pressure, 72 and 73 mg/g, respectively.

**H2 Sorption Behaviors of the MOFs.** At 77 K, interestingly, although the specific surface areas and the pore dimensions of 2a and 3a were significantly reduced compared with those of 1a, the H2 uptake amounts of 2a and 3a (19.5 and 21.1 mg/g, respectively) were only slightly reduced compared with that of 1a (23.1 mg/g) (Figure 11a). At 87 K, more interestingly, the H2 uptake amounts of 2a and 3a (16.5 and 16.6 mg/g, respectively) are even slightly larger than that of 1a (16.0 mg/g). The increased adsorption enthalpies of 2a and 3a (Figure 11b), which come from the more extensive interaction of the adsorbate H2 with the pore surface of the reduced pore dimensions, are responsible for the H2 sorption behaviors.

Surprisingly, the H2 adsorption enthalpy of 2a with no unsaturated metal sites is slightly larger than that of 3a with the unsaturated metal sites. The interaction of H2 with the pore surface of 2a with the smaller pore dimension compared with that of 3a with the larger pore dimension is responsible for the slightly larger H2 adsorption enthalpy of 2a versus that of 3a.

**CONCLUSIONS**

The preparations of the two isoreticular MOFs, 2 and 3, which cannot be attained via the conventional synthetic approach, were demonstrated via the PSLE of 1. By soaking 1 in a high-concentration dabco DMF solution, we completely exchanged all of the aromatic bipy pillaring linkers in 1 with the shorter aliphatic dabco pillaring linkers to form the isoreticular 3D MOF, 2, with reduced pore dimensions and a reduced volume. The reaction proceeded via the entropically favorable random substitution of the pillaring linker. This reaction process is enthalpically unfavorable because of the formation of the sterically more demanding dabco coordination site. In contrast, the soaking of 1 in a low-concentration dabco DMF solution led to the enthalpically favorable isoreticular MOF, 3, with the partially and selectively exchanged additional component, dabco linker. Even though the reaction toward selectively exchanged 3 is entropically less favorable than that toward randomly exchanged 3, 3 with no [dabco−NiII−dabco] coordination site is responsible for the enthalpically favorable exchange process.

The series of MOFs (1 with all aromatic bipy linkers, 2 with all aliphatic dabco linkers, and 3 with both aromatic and aliphatic pillaring linkers) provided an opportunity to assess the relationship between the pore dimension and hydrophobicity of the pore surface and the adsorption enthalpies of adsorbates. The CH4 adsorption enthalpy increases as the pore dimension decreases because of the more extensive interaction of the adsorbate with the pore surface with reduced pore dimensions. As expected, 2, with the smallest pore dimensions, showed the largest CH4 adsorption enthalpy, and 1, with the largest pore dimensions, showed the smallest CH4 adsorption enthalpy. However, 3, with an intermediate pore dimension and mixed pore surface properties, showed the largest CO2 adsorption enthalpy. The adsorption enthalpy is affected not only by the pore dimension but also by the pore surface properties.

Postsynthetic exchanges of a ligand involved in the network connectivity can be used as a general strategy for the preparation of isoreticular MOFs that are difficult to obtain.
or even cannot be attained via the conventional solvothermal reaction.

## ASSOCIATED CONTENT

S Supporting Information

CIF files for 2–4: tables of the crystal data and structure refinement for 2–4; PXRD patterns of the products obtained via conventional one-pot reactions of H$_2$BTC, Ni$^{II}$, and dabco; PXRD patterns of the products obtained via reverse PSLE of 2 and 3; and CH$_4$ and CO$_2$ sorption isotherms of 1a–3a at 195 and 273 K, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

BET, Brunauer–Emmett–Teller; bipy, 4,4’-bipyridine; 2D, two-dimensional; 3D, three-dimensional; dabco, 1,4-diazabicyclo[2.2.2]octane; DMF, N,N'-dimethylformamide; EA, elemental analysis; H$_2$BTC, 1,3,5-benzenetricarboxylic acid; MOFs, metal–organic frameworks; PSLE, postsynthetic ligand exchange; PSM, postsynthetic modification; PXRD, powder X-ray diffraction; SCSC, single-crystal-to-single-crystal

## REFERENCES


(5) Gao, C.; Liu, S.; Xie, L.; Ren, Y.; Cao, J.; Sun, C. CrystEngComm 2007, 9, 545–547. Here and in the reference, 1 is formulated as [Ni(HBTC)(bipy)]; however, the correct formulation for 1 is [Ni$_2$(BTC)$_2$(H$_2$BTC)$_2$(bipy)$_2$], because the H$_2$BTC ligands in the framework of 1 are in three different deprotonated states. One is in the form of a fully deprotonated BTC$^{3-}$ state, and the others are in the form of partially deprotonated H$_2$BTC$^-$/HBTC$^{2-}$ states. The ligands in the partially deprotonated H$_2$BTC$^-$/HBTC$^{2-}$ states are involved in interligand hydrogen bonding in the 2D sheet with an hcb net topology.

(6) Materials Studio, version 4.3; Accelrys: San Diego, 2008.

(6) Rapid Auto, R-Axis series, catalog no. 9220B101, Rigaku Corp.


(13) Even though the sample of 1 was activated according to the reported procedure at 150 °C under vacuum for 12 h, the N$_2$ uptake amount and the BET specific area of 1a are significantly larger than the reported values, 290 cm$^2$/g and 970 m$^2$/g, respectively. However, the pore volume calculated from the N$_2$ uptake amount of 1a, 0.605 cm$^3$/g, is still slightly smaller than that calculated from the solvent cavity volume of the reported single-crystal structure of 1, 0.700 cm$^3$/g.
