

# Topology Conversions of Non-Interpenetrated Metal–Organic Frameworks to Doubly Interpenetrated Metal–Organic Frameworks

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**(5)** Supporting Information

**ABSTRACT:** Non-interpenetrated three-dimensional (3D) metalorganic frameworks (MOFs) with both an interpenetration-favorable (3,5)-c **hms** topology and an interpenetration-unfavorable (3,5)-c **gra** topology are converted to doubly interpenetrated analogues with **hms**c topology by thermal treatment, even in the absence of solvent. Depending on the conversion temperature and the properties of the pillaring ligand in the non-interpenetrated 3D MOF, which is based on two-dimensional sheets with 3-c **hcb** topology pillared by neutral ditopic linkers, the pillaring ligands in the interpenetrated MOFs produced are partially removed during the thermal conversions, leading to interpenetrated MOFs that simultaneously contain both micro- and mesopores.

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Metal-organic frameworks (MOFs) are interesting microporous materials that are composed of metal ions and/or metal clusters that act as multitopic inorganic nodes with organic ligands acting as linkers.<sup>1–4</sup> It is important to control the degree of interpenetration in MOFs because this affects not only their porosity but also their stability. MOFs thermodynamically prefer a densely packed interpenetrated structure when the net topology and dimensions of the building blocks allow for it. $5^{-8}$ It is well-known that MOFs of interpenetration-favorable selfdual topologies such as dia and pcu show strong tendencies for interpenetration.<sup>9-11</sup> When the net topology of a MOF does not allow interpenetration because of collision between the networks,<sup>12</sup> a non-interpenetrated MOF can be prepared that can have an extremely large porosity.<sup>13–18</sup> Interpenetration can be controlled, even for the MOFs with interpenetrationfavorable topologies, either through ligand design<sup>19,20</sup> or by controlling synthetic conditions such as the reactant concentration, temperature, counterions, and use of different solvents or templating agents.<sup>21-24</sup>

The degree of interpenetration of MOFs could also be controlled by postsynthetic modification. Non-interpenetrated MOFs with an interpenetration-favorable topology can be transformed into their more densely packed interpenetrated analogues. For instance, the non-interpenetrated MOF-123, which has **pcu** topology, was transformed into the doubly interpenetrated MOF-246, which possesses **pcu-c** topology, via removal of its coordinated solvent molecules.<sup>25</sup> Similar transformations from non-interpenetrated to 2-fold interpenetrated MOFs have been reported for two other systems:



[Cd(tp)(bipy)] (H<sub>2</sub>tp = terephthalic acid; bipy = 4,4'bipyridine) and [Cd(atp)(bipy)] (H<sub>2</sub>atp = 2-aminoterephthalic acid).<sup>26</sup> Heating the doubly interpenetrated MOF  $[Zn_2(ndc)_2-$ (bipy)] (H<sub>2</sub>ndc = naphthalene dicarboxylic acid) with **pcu**topology resulted in a triply interpenetrated analogue with **pcu**c3 topology in a single-crystal-to-single-crystal (SCSC) fashion.<sup>27</sup> A conversion from the 5-fold interpenetrated MOF  $[Ag_6Cl(atz)_4](OH)$  (atz = 3-amino-1,2,4-triazolate) to a 6-fold interpenetrated analogue has even been observed.<sup>28</sup>

A network with a hms topology, which is a (3,5)-c threedimensional (3D) network with ditopic pillars between twodimensional (2D) sheets with 3-c hcb topologies stacked in an eclipsed fashion via alternating 3-c nodes, is favorable for interpenetration because hms is self-dual.<sup>9</sup> However, a network with gra topology, which is another (3,5)-c 3D network with ditopic pillars between 2D sheets stacked in staggered fashion via alternating 3-c nodes, is less favorable for self-interpenetration than the isomeric network with hms topology because gra is not self-dual.<sup>29</sup> Self-interpenetrated networks with gra-c (catenated gra) topologies will face the more steric repulsions between the interpenetrated networks than isomeric networks with hms-c topology. When the organic linkers of a MOF with gra topology are long enough, the steric repulsion between the interpenetrated networks can be released, allowing a triply interpenetrated MOF with gra-c3 topology to form.<sup>3</sup>

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Here, we report the preparation of non-interpenetrated 3D MOFs with not only (3,5)-c hms topologies but also with (3,5)-c gra topologies, where the non-interpenetrated MOFs are based on 2D sheets with 3-c hcb topologies pillared by two different neutral ditopic linkers. The less densely packed non-interpenetrated MOFs with both the interpenetration-favorable hms topology and the self-interpenetration-unfavorable gra topology can be thermally converted to generate more densely packed 2-fold interpenetrated MOFs with hms-c topologies even in the absence of solvent (Scheme 1). However,

Scheme 1. Conversion of Non-Interpenetrated Networks with Interpenetration-Favorable hms Topology and with Self-Interpenetration-Unfavorable gra Topology to Doubly Interpenetrated Networks with hms-c Topologies



conversion to a 2-fold interpenetrated MOF with gra-c topology was not observed regardless of the net topologies of the non-interpenetrated MOFs because of severe repulsion or collision between interpenetrated networks.

### EXPERIMENTAL SECTION

Preparation of Non-Interpenetrated MOFs. [Ni(HBTC)(bipy)]hms (1) and [Ni(HBTC)(bipy)]-gra (2). [Ni(HBTC)(bipy)]-hms (1) (HBTC<sup>2-</sup> = singly protonated 1,3,5-benzene tricarboxylate), which has hms topology, and [Ni(HBTC)(bipy)]-gra (2), which exhibits gra topology, were prepared according to previously reported procedures.<sup>31–33</sup> Activated 1a and 2a were obtained by vacuuming ( $\sim 10^{-2}$ Torr) the corresponding as-synthesized crystals presoaked in methylene chloride (MC) at ambient temperature for 1 day.

[Ni(HBTC)(azpy)]-hms (3). A mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.029 g, 0.100 mmol), 1,3,5-benzene tricarboxylic acid (H\_3BTC, 0.021 g, 0.10  $\,$ mmol), and 4,4'-azopyridine (azpy, 0.037 g, 0.20 mmol) was dissolved in an N,N-dimethylformamide (DMF)/MeOH mixture (10 mL, 1:1 ratio). The solution was heated at 85 °C for 1 day in a tightly sealed 20 mL vial to form red crystals of [Ni(HBTC)(azpy)]-hms (3) with hms topology. The crystals were harvested and washed with fresh DMF and then air-dried under ambient conditions for 1 h. The yield was 0.029 g (61%). Activated 3a was prepared by vacuuming ( $\sim 10^{-2}$  Torr) assynthesized 3 presoaked in MC at ambient temperature for 1 day: IR (KBr) 3195 (w, b), 3099 (w, b), 1694 (w), 1660 (m), 1605 (s), 1538 (s), 1494 (w), 1434 (s), 1417 (m), 1360 (s), 1225 (m), 1100 (m), 1050 (m), 1020 (m), 932 (w), 838 (s), 757 (w), 742 (w), 714 (m), 680 (w) cm<sup>-1</sup>. EA was performed using activated 3a that had been exposed to ambient conditions for 1 day prior to analysis. EA for  $Ni(HBTC)(azpy)(H_2O)_{1.5}$  ( $C_{19}H_{15}N_4O_{7.5}Ni$ , fw = 478.04 g/mol). Found (calcd): C, 47.82% (47.74%); H, 3.18% (3.16%); N, 12.18% (11.72%)

[*Ni(HBTC)(azpy)*]-*gra (4).* A mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.029 g, 0.10 mmol), H<sub>3</sub>BTC (0.021 g, 0.10 mmol), and azpy (0.037 g, 0.20 mmol) was dissolved in 10 mL of DMF. The solution was heated at 85



Figure 1. Ball-and-stick diagrams of the single-crystal structure of 3 with (3,5)-c hms topology: (a) top and (b) side views. Ball-and-stick diagrams of the single-crystal structure of 4 with (3,5)-c gra topology: (c) top and (d) side views. The red and green spheres and sticks in panels c and d represent the two alternating 2D sheets in the framework with gra topology.

°C for 1 day in a tightly sealed 10 mL vial to form red crystals of [Ni(HBTC)(azpy)]-gra (4) with gra topology. The crystals were harvested and washed using fresh DMF and then air-dried under ambient conditions for 1 h. The yield was 0.028 g (57%). Activated 4a was prepared by vacuuming (~10<sup>-2</sup> Torr) as-synthesized 4 presoaked in MC at ambient temperature for 1 day: IR (KBr) 3355 (s, b), 1700 (w), 1663 (m), 1608 (s), 1558 (s), 1490 (w), 1433 (s), 1419 (s), 1366 (s), 1261 (m), 1228 (m), 1189 (w), 1102 (m), 1051 (m), 1021 (m), 933 (w), 844 (m), 761 (m), 742 (w), 717 (m) cm<sup>-1</sup>. EA was performed using activated 4a exposed to ambient conditions for 1 day prior to analysis. EA for Ni(HBTC)(azpy)(H<sub>2</sub>O)<sub>0.9</sub> (C<sub>19</sub>H<sub>166</sub>N<sub>4</sub>O<sub>8.3</sub>Ni, fw = 492.5 g/mol). Found (calcd): C, 46.46% (46.34%); H, 3.87% (3.40%); N, 11.20% (11.38%).

Preparation of Doubly Interpenetrated [Ni(HBTC)(bipy)]-hms-c (5). Approximately 10 mg of single crystals of as-synthesized 1 was prewashed with fresh DMF and air-dried under ambient conditions for 3 h. The sample was then heated to 300 °C under a flow of nitrogen gas at a heating rate of 5 °C min<sup>-1</sup>, aged for 30 min at 300 °C, and then slowly cooled to room temperature. 5 was also obtained from single crystals of as-synthesized 2 instead of as-synthesized 1 by the same procedure described above. EA for Ni(HBTC)-(bipy)<sub>0.89</sub>(H<sub>2</sub>O)<sub>0.72</sub> (C<sub>17.9</sub>H<sub>12.56</sub>N<sub>1.78</sub>O<sub>6.72</sub>Ni, fw = 418.79 g/mol). Found (calcd): C, 51.35% (51.34%); H, 3.19% (3.02%); N, 5.93% (5.95%). Activated 5a was prepared by vacuuming (~10<sup>-2</sup> Torr) as-synthesized 5 at 100 °C for 3 h.

Preparation of Doubly Interpenetrated [Ni(HBTC)(azpy)]-hms-c (6). Approximately 10 mg of single crystals of as-synthesized 3 was prewashed with fresh DMF and air-dried under ambient conditions for 3 h. The sample was heated to 250 °C under flowing nitrogen gas at a heating rate of 5 °C min<sup>-1</sup>, aged for 30 min at 250 °C, and then slowly cooled to room temperature. 6 was also obtained from single crystals of as-synthesized 4 instead of as-synthesized 3 by the same procedure described above. EA for Ni(HBTC)(azpy)<sub>0.95</sub>(H<sub>2</sub>O)<sub>0.56</sub>(C<sub>18.5</sub>H<sub>12.72</sub>N<sub>3.8</sub>O<sub>6.56</sub>Ni, fw = 451.89 g/mol). Found (calcd): C, 49.16% (49.17%); H, 2.84% (2.84%); N, 11.78% (11.78%). Activated 6a was prepared by vacuuming (~10<sup>-2</sup> Torr) as-synthesized 6 at 100 °C for 3 h.

#### RESULTS AND DISCUSSION

Preparation of Non-Interpenetrated MOFs. De novo solvothermal reaction of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and H<sub>3</sub>BTC in the presence of the pillaring ditopic linker bipy in DMF solvent led to the formation of [Ni(HBTC)(bipy)]-hms (1) with hms topology.<sup>31,32</sup> [Ni(HBTC)(bipy)]-gra (2) with gra topology can be obtained postsynthetically by exchanging the pillaring ligand of [Ni(HBTC)(pz)]-gra, which possesses gra topology.<sup>33</sup> [Ni(HBTC)(azpy)]-hms (3) with hms topology was prepared via a procedure similar to that used for the preparation of 1 with hms topology, but using azpy, which is slightly longer than bipy, as a pillaring ligand in a mixed solvent (DMF/MeOH). As shown in panels a and b of Figure 1, singlecrystal structure analysis shows that 3 is a 3D MOF based on 2D sheets pillared via the metal ions by ditopic linkers. 3 is isoreticular to 1, with (3,5)-c hms topology. The 2D sheets with 3-c hcb topology in 3 consist of two different 3-c nodes, one based on metal ions and the other based on the organic ligand HBTC, as was the case for the 2D sheet in 1. While the sheets in 1 are pillared by bipy linkers, the sheets in 3 are pillared by azpy linkers. The bulk identity of the sample was confirmed by comparing the observed powder X-ray diffraction (PXRD) pattern of as-synthesized 3 with the simulated PXRD pattern of the single-crystal structure model of 3 (Figure 2).

[Ni(HBTC)(azpy)]-gra (4) with gra topology was prepared in a manner similar to that used for the preparation of 3 with hms topology, but using DMF as the only solvent. As shown in panels c and d of Figure 1, single-crystal structure analysis shows that 4 is also a 3D MOF based on 2D sheets pillared via



**Figure 2.** Comparison of the PXRD patterns of as-synthesized **3** with **hms** topology and as-synthesized **4** with **gra** topology. The peaks marked with an asterisk in the PXRD pattern of as-synthesized **4** are ( $h \ k \ l$ ) reflections with odd l indices.

the metal ions by ditopic linkers. However, while the pillared 2D sheets in 3 are stacked in an eclipsed fashion (Figure 1a), the pillared 2D sheets in 4 are stacked in a staggered fashion (Figure 1c). 4 is isoreticular to 2, with (3,5)-c gra topology.

The PXRD pattern of 4 with gra topology at ambient temperature is similar to but not the same as that of 3 with hms topology (Figure 2), with the former showing additional diffraction peaks at  $2\theta = 11.2^{\circ}$  and  $14.6^{\circ}$ . The peaks marked with an asterisk in the PXRD pattern of as-synthesized 4 are (h k l) reflections with odd l indices. The reflections with odd l indices are observed only in the structural model with gra topology and a *c*-axis distance of 26.148(5) Å, which is twice the *c*-axis distance of 3 with hms topology, 13.079(3) Å.

Gas Sorption Behavior of the Non-Interpenetrated MOFs, 3a and 4a. The N<sub>2</sub> sorption behaviors of activated 3a and activated 4a were similar to the reported behaviors of activated 1a and activated 2a,<sup>31-33</sup> where the activated MOFs were prepared by presoaking the as-synthesized MOFs in MC and then vacuuming them at ambient temperature for 1 day. The N<sub>2</sub> adsorption isotherms of both 3a and 4a at 77 K are typical type I plots (Figure S1), which confirms the microporosity of both frameworks. The specific pore volume of 3a as estimated from the uptake amount (495  $\text{cm}^3/\text{g}$  at 0.97  $P/P_0$ ) was 0.765 cm<sup>3</sup>/g, which is slightly smaller than the calculated specific pore volume of 3 from the single-crystal structure, 0.865 cm<sup>3</sup>/g. The BET surface area<sup>34,35</sup> of 3a as calculated using a  $P/P_0$  between 0.0004 and 0.0322 was 1953  $m^2/g$  (Figure S2). The specific pore volume of 4a as estimated from the uptake amount (486 cm<sup>3</sup>/g at 0.98  $P/P_0$ ) was 0.751  $cm^3/g$  (Figure S2), which is similar to that of 3a. The BET surface area calculated using the adsorption isotherm data of P/ $P_0$  between 0.00004 and 0.0428 was 1861 m<sup>2</sup>/g (Figure S3). The pore size analyses of 3a and 4a using nonlocalized density



Figure 3. Temperature-dependent PXRD patterns of (a) as-synthesized 1 and (b) as-synthesized 2. The peaks marked with asterisks in the PXRD pattern of as-synthesized 2 are  $(h \ k \ l)$  reflections with odd l indices.



**Figure 4.** Temperature-dependent PXRD patterns of as-synthesized **3** and as-synthesized **4**. The peaks marked with asterisks in the PXRD pattern of as-synthesized **4** are  $(h \ k \ l)$  reflections with odd *l* indices, which do not appear in the simulated pattern of **3** with **hms** topology but appear in the simulated pattern of **4** with **gra** topology.

functional theory<sup>36</sup> indicate that they have similar average pore dimensions but different distributions (Figure S4).

Thermal Properties of the Non-Interpenetrated

MOFs. We measured the PXRD patterns of the non-

interpenetrated MOFs, 1–4, at several points while increasing the temperature of the MOFs under flowing  $N_2$  to observe their thermal stabilities and structural conversions. The temperature-dependent PXRD patterns of as-synthesized 1 indicate that it

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Figure 5. Single-crystal structure of 5 with hms-c topology. (a) Top and (b) side views of a single network with hms topology. (c) Top and (d) side views of a 2-fold interpenetrated network with hms-c topology. In panels c and d, the two interpenetrated networks are colored red and blue, respectively. The yellow and pink dummy spheres in panels c and d represent the locations of two different types of cagelike pores in the structure.

was stable up to 350 °C and lost its crystallinity at 400 °C (Figure 3a). Careful examination of the PXRD patterns shows that most diffraction peaks were slightly broadened as the temperature increased to ~200 °C. However, some peaks, such as those at ~15.8° and ~18.5°, were sharpened again around 300-350 °C, while the other peaks like the peaks at ~8° and ~23.8° disappeared around the same temperature. This indicates that 1 converted to a new crystalline phase around 300 °C. The thermal behavior of 2 with gra topology was similar to that of 1 with hms topology (Figure 3b). The temperature-dependent PXRD patterns of as-synthesized 2 also show that 2 converted to the same new crystalline phase around 300 °C via similar broadening. The PXRD pattern of the new phase is similar to but distinctively different from those of both 1 and 2.

The thermal behaviors of as-synthesized **3** and as-synthesized **4** were similar to those of as-synthesized **1** and as-synthesized **2**. The temperature-dependent PXRD patterns of as-synthesized **3** and as-synthesized **4** show that the both crystals also maintained their crystallinity up to 350 °C (Figure 4). The diffraction peaks broadened at ~100 °C, much lower than the broadening temperatures of as-synthesized **1** and as-synthesized **2**, but some of them either sharpened or disappeared as the temperature-dependent PXRD patterns of as-synthesized **1** and as-synthesized **2**, the PXRD patterns of as-synthesized **3** and as-synthesized **4** also converted to the same new crystalline phase around 250 °C, which is distinctively different from the PXRD patterns of either as-synthesized **3** or as-synthesized **4**.

Conversion of Non-Interpenetrated MOFs to Corresponding Interpenetrated MOFs. Regardless of their net topologies and pillars, non-interpenetrated MOFs 1–4 can be transformed to the corresponding interpenetrated MOFs with hms-c topology, 5 and 6, by thermal treatment. 1 and 2 were transformed to the same new crystalline phase, [Ni(HBTC)-(bipy)]-hms-c (5). Single crystals of 5 can be obtained by heating either as-synthesized 1 with hms topology or assynthesized 2 with gra topology at 300  $^{\circ}$ C under flowing N<sub>2</sub>. Single-crystal structure analysis revealed that 5 consisted of 2fold interpenetrated [Ni(HBTC)(bipy)] with hms-c topology (Figure 5). The structure of a single network is indistinguishable from the framework structure of 1, the non-interpenetrated [Ni(HBTC)(bipy)] with hms topology. 2D layers with hcb topology are stacked in an eclipsed fashion with an interlayer distance of 11.2 Å and are pillared by bipy linkers (Figure 5a,b). The 2-fold interpenetration generates two different disc-shaped pores, an A-type cage (6.5 Å in diameter, 2.2 Å in height) and a B5-type cage (7.3 Å in diameter, 2.2 Å in height), in a 2:1 ratio (Figure S4). B-Type cages have no meaningful portals and are surrounded by six A-type cages in the crystallographic a-bplane, while the A-type cages are interconnected via small portals (3.0 Å  $\times$  2.2 Å) in the same plane to form 2D porous channels. The void volume of the structure (585 Å<sup>3</sup>, 21.2% of the total unit cell volume) is significantly reduced compared to those of the corresponding non-interpenetrated analogues.

The other new crystalline phase, [Ni(HBTC)(azpy)]-hms-c (6), was obtained via similar thermal treatment of either assynthesized 3 with hms topology or as-synthesized 4 with gra topology, using a temperature slightly lower than that used for the preparation of 5 (250 °C vs 300 °C). 6 is isoreticular to 5 (Figure S6), with the 2D layers in 6 being stacked in the same eclipsed fashion as those in 5 and pillared by azpy linkers with an interlayer distance of 13.2 Å (Figure S7a,b). Even though the azpy pillars are statistically disordered, the 2-fold interpenetration again generates two different types of disc-shaped pores, albeit with slightly larger heights in their cavity dimensions compared to those in 5 because of the slightly longer pillars in 6: A-type cages (6.7 Å in diameter, 3.1 Å in height) and B-type cages (6.4 Å in diameter, 3.1 Å in height) (Figure S7). B-Type cages have no meaningful portals and are surrounded by six A-type cages in the crystallographic a-bplane, while the A-type cages are interconnected to form 2D Scheme 2. Proposed Conversion Mechanisms from Non-Interpenetrated Networks with hms Topology and with gra Topology to a Doubly Interpenetrated Network with hms-c Topology



porous channels via more flexible portals with dimensions (1.7 Å  $\times$  3.1 Å) similar to those in 5. The potential pore volume of the structure (717 Å<sup>3</sup>, 22.7% of the total unit cell volume) is again significantly reduced compared to those of the corresponding non-interpenetrated analogues.

Structural Conversion with No Solvent Assistance. Solvent-assisted linker exchange (SALE) [which is also known as postsynthetic ligand exchange (PLE)] requires participation of the solvent in the formation and stabilization of either intermediates or transition states during the structural conversion.<sup>37-40</sup> Conversion of non-interpenetrated MOFs to corresponding interpenetrated MOFs requires bond dissociation and reassociation; however, this structural conversion can occur without solvent assistance. Thermal treatment of the non-interpenetrated MOFs led to the corresponding 2-fold interpenetrated MOFs both before and after the complete removal of the solvent from the pores (Figure S8). The complete removal of the solvents from the non-interpenetrated MOFs was confirmed from using the <sup>1</sup>H NMR spectra of 1' and 3', which were prepared by drying as-synthesized 1 and assynthesized 3, respectively, that had been presoaked in MC at 150 °C for 30 min under flowing N<sub>2</sub> and then digested in  $d_{6^-}$ DMSO/DCl or D<sub>2</sub>O/DCl solvent (Figure S9). No proton peaks from DMF or MC molecules were observed in the <sup>1</sup>H NMR spectra. The thermal energy at 250-300 °C is high enough for the activation of the metal centers of the frameworks, allowing successful structural conversions via

either unstable intermediates or transition states without solvent assistance.

Conversion Mechanisms. The conversion of a noninterpenetrated network based on pillared 2D layers into a corresponding 2-fold interpenetrated network must be accomplished via sequential pillar dissociation, structural reorganization, and pillar reassociation (Scheme 2). The pillars in 2 (or 4) with gra topology must be either fully or partially dissembled from the 2D layers for network conversion. Then, the 2D layers need to be reorganized to staggered stacked layers via layer translation, followed by layer contraction. Finally, the stacked 2D layers must be reassembled with pillars into doubly interpenetrated 5 (or 6) with hmc-c topology. The conversion to a doubly interpenetrated MOF with gra-c topology is not observed because such a conversion would require layer rotation, which is energetically more demanding than layer translation. Even successful layer rotation will lead to either collision or at least severe steric repulsion between interpenetrated networks with gra-c topology. While the conversion of a MOF with gra topology to a doubly interpenetrated MOF with hmc-c topology can proceed via the less energetically demanding layer translation, the conversion from non-interpenetrated 1 (or 3) with hms topology to doubly interpenetrated 5 (or 6) with hms-c topology cannot proceed via the same layer translation. Such a layer translation would lead to doubly interpenetrated networks with gra-c topology, which is again frustrated by the steric repulsion between the interpenetrated networks as described above. Although conversion by layer rotation can lead to doubly interpenetrated networks with hmc-c topology, it is not a likely process because such a conversion demands an extremely large amount of energy for the structural reorganization. The network conversion can proceed via localized structural reorganization within a 2D layer. Instead of rotation of a whole 2D layer, localized rotations of the HBTC ligands within a 2D layer could lead to a conversion of non-interpenetrated 1 (or 3) with hms topology into doubly interpenetrated 5 (or 6) with hms-c topology. For complete conversion, every HBTC ligand of the monodentate binding mode must rotate  $\sim 30^{\circ}$  in a direction opposite to that of the adjacent HBTC ligands of the same monodentate binding mode within a 2D layer. The HBTC ligand of the chelating bidentate binding mode must rotate  $\sim 60^{\circ}$  in any direction within a 2D layer. The localized rotations of the two different types of HBTC ligands allow network conversion without extensive structural reorganization that does not lead to collision between the interpenetrated networks.

Gas Sorption Behavior of the Interpenetrated MOFs, 5a and 6a. The  $N_2$  sorption of activated 6a also follows a type I adsorption with some hysteric desorption (Figure 6), where



Figure 6.  $N_2$  sorption isotherms of 5a and 6a at 77 K. Adsorption and desorption isotherms are represented by filled and empty squares, respectively.

activated 6a was prepared by vacuuming as-synthesized 6 at 100 °C for 3 h. The BET surface area calculated using  $P/P_0$  values between 0.00001 and 0.0585 was 392 m<sup>2</sup>/g (Figure S10), and the N<sub>2</sub> uptake amount at 77 K and 0.98 bar was 132 cm<sup>3</sup>/g. The specific pore volume as estimated from the uptake amount was 0.204  $\text{cm}^3/\text{g}$ , slightly larger than the calculated specific void volume of the single-crystal structure model,  $0.160 \text{ cm}^3/\text{g}$ . Even though the single-crystal structure of 5 was similar to that of 6, the N<sub>2</sub> sorption behavior of activated 5a, prepared by vacuuming as-synthesized 5 at 100 °C for 3 h, was significantly different from that of activated 6a. The N<sub>2</sub> adsorption isotherm of 5a shows features of both type I and type IV isotherms simultaneously. The type I feature, a steep rise in the N<sub>2</sub> uptake at very low  $P/P_0$  values, indicates the presence of micropores. The subsequent slow increase in the rate of N<sub>2</sub> uptake up to a  $P/P_0$  of ~0.86 and the hysteresis loop between  $P/P_0$  values of 0.86 and 0.97 are type IV features of mesoporous materials. The BET surface area of 5a as calculated using  $P/P_0$  values

between 0.00002 and 0.0802 was 259 m<sup>2</sup>/g (Figure S11). The specific pore volume estimated from the uptake amount (495 cm<sup>3</sup>/g at 77 K and 0.97 bar) was 0.767 cm<sup>3</sup>/g, significantly larger than the calculated specific void volume of the single-crystal structure model, 0.139 cm<sup>3</sup>/g. The pore size analyses of **Sa** and **6a** as performed using nonlocalized density functional theory<sup>36</sup> indicate that the both have two different types of pores, micro- and mesopores (Figure 7). **6a** had micropores



Figure 7. (a) Pore size distributions and (b) cumulative pore volumes of 5a and 6a.

with an average dimension of ~5.8 Å and mesopores with an average dimension of ~3.7 nm, in an ~3:1 volume ratio. The formation of the mesopores was probably due to the partial removal of the neutral azpy pillars during the thermal treatment at 250 °C during the structural conversion of non-interpenetrated 3 to 2-fold interpenetrated 6. The HBTC:azpy ratio in the <sup>1</sup>H NMR spectrum of **6a** digested in D<sub>2</sub>O/DCl solvent supports the partial removal (~8%) of the neutral azpy pillars from the structure during the thermal treatment (Figure S12). The EA result also supports the partial removal ( $\sim$ 5%) of the neutral azpy pillars from the structure. 5a also had micropores with an average dimension of ~5.2 Å and mesopores with an average dimension of ~31 nm, in a volume ratio of approximately 1:6. Both the size and the cumulative volume of the micropores in 5a were slightly smaller than the corresponding values for 6a. In contrast, the dimension and the cumulative volume of the mesopores of 5a were much larger than the corresponding values for 6a. Some neutral bipy pillars were also removed from the structure during the thermal

treatment at 300 °C for the structural conversion from noninterpenetrated 1 to doubly interpenetrated 5. Both the <sup>1</sup>H NMR spectrum (Figure S13) and the EA of 5a support the partial removal (~8 and ~11%, respectively) of the neutral bipy pillars from the framework during the thermal treatment.

# CONCLUSIONS

Microporous MOFs with not only interpenetration-favorable (3,5)-c hms topology but also with interpenetration-unfavorable (3,5)-c gra topology were prepared by either de novo solvothermal syntheses or postsynthetic ligand exchange. Thermal treatment of the less densely packed non-interpenetrated MOFs led to the more densely packed doubly interpenetrated MOFs in SCSC fashion in the solid state, and even in the absence of solvent molecules in the pores. The conversion occurred regardless of the net topologies of the non-interpenetrated MOFs and the pillaring linkers. The conversions of non-interpenetrated MOFs with gra topology to the corresponding doubly interpenetrated MOFs with hms-c topology occurred via 2D layer translation. In contrast, the conversion from non-interpenetrated MOFs with hms topology to the corresponding doubly interpenetrated MOFs with hms-c topology occurred via localized rotations of HBTC ligands within the 2D layer. Thermal treatment of non-interpenetrated microporous MOFs thermodynamically generated the more stable interpenetrated microporous MOFs. Depending on thermal treatment conditions and the properties of the neutral pillaring linkers, MOFs that contain both micro- and mesopores were generated by partial removal of the neutral pillaring linkers. Nonstoichiometric removal of neutral pillaring linkers from MOFs by thermal treatment could lead to new interpenetrated MOFs that simultaneously contain micro- and mesopores. The pore dimension distributions could be controlled depending on the properties of the pillars and the thermal treatment conditions.

# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b05277.

Crystal structure analyses of the MOFs; PXRD data, crystal structure drawings of the MOFs;  $N_2$  sorption isotherms, BET surface area calculations and pore size distributions of **3a**, **4a**, **5a** and **6a**; <sup>1</sup>H NMR spectra of **5a** and **6a** (PDF)

Crystallographic data of **3** (CIF) Crystallographic data of **4** (CIF) Crystallographic data of **5** (CIF) Crystallographic data of **6** (CIF)

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#### Notes

The authors declare no competing financial interest.

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