Control of Interpenetration and Gas-Sorption Properties of Metal–Organic Frameworks by a Simple Change in Ligand Design

Thazhe Kootteri Prasad and Myunghyun Paik Suh*\[a\]

Abstract: In metal–organic framework (MOF) chemistry, interpenetration greatly affects the gas-sorption properties. However, there is a lack of a systematic study on how to control the interpenetration and whether the interpenetration enhances gas uptake capacities or not. Herein, we report an example of interpenetration that is simply controlled by the presence of a carbon–carbon double or single bond in identical organic building blocks, and provide a comparison of gas-sorption properties for these similar frameworks, which differ only in their degree of interpenetration. Noninterpenetrated (SNU-70) and doubly interpenetrated (SNU-71) cubic nets were prepared by a solvothermal reaction of [Zn(NO₃)₂]·6H₂O in N,N-diethylformamide (DEF) with 4-(2-carboxyvinyl)benzoic acid and 4-(2-carboxylethyl)benzoic acid, respectively. They have almost-identical structures, but the noninterpenetrated framework has a much bigger pore size (ca. 9.0×9.0 Å) than the interpenetrated framework (ca. 2.5×2.5 Å). Activation of the MOFs by using supercritical CO₂ gave SNU-70 and SNU-71'. The simulation of the PXRD pattern of SNU-71' indicates the rearrangement of the interpenetrated networks on guest removal, which increases pore size. SNU-70 has a Brunauer–Emmett–Teller (BET) surface area of 5290 m² g⁻¹, which is the highest value reported to date for a MOF with a cubic-net structure, whereas SNU-71' has a BET surface area of 1770 m² g⁻¹. In general, noninterpenetrated SNU-70' exhibits much higher gas-adsorption capacities than interpenetrated SNU-71' at high pressures, regardless of the temperature. However, at P<1 atm, the gas-adsorption capacities for N₂ at 77 K and CO₂ at 195 K are higher for noninterpenetrated SNU-70' than for interpenetrated SNU-71', but the capacities for H₂ and CH₄ are the opposite; SNU-71' has higher uptake capacities than SNU-70' due to the higher isosteric heat of gas adsorption that results from the smaller pores. In particular, SNU-70' has exceptionally high H₂ and CO₂ uptake capacities. By using a post-synthetic method, the C=C double bond in SNU-70 was quantitatively brominated at room temperature, and the MOF still showed very high porosity (BET surface area of 2285 m² g⁻¹).

Keywords: carbon dioxide • adsorption • hydrogen • interpenetration • metal–organic frameworks

Introduction

Porous metal–organic frameworks (MOFs) have received considerable attention due to their high surface areas and excellent gas-sorption properties.\[1–3\] In MOF chemistry, control of the interpenetration is of high importance because the degree of interpenetration significantly affects the gas-sorption properties of the material.\[2\] There have been a few reports of methods to control the interpenetration of MOFs. Some reported methods include the addition of a template during the synthesis\[4,5\] rational design of ligands\[6,7\] and adjustment of the reaction conditions, such as the concentration of building blocks and temperature.\[8\] In particular, if the length of the ligand is elongated then the MOF has a better tendency to form an interpenetrated structure.

However, when using ligands with similar length it is difficult to predict which framework will be interpenetrated and which will be noninterpenetrated. Previously, it was reported that interpenetrated structures showed higher gas-sorption capacities for N₂ and H₂ gases at 77 K under both low and high pressures, and at 298 K under high pressure.\[6,7,4\] In contrast, theoretical calculations have predicted that noninterpenetrated structures should have better gas-sorption capacities than interpenetrated structures.\[9\] Despite these contradictory arguments, it is difficult to prove which is the more general case because gas-sorption properties should be compared between frameworks with similar structures that only differ in their degree of interpenetration. However, such cases are difficult to find.\[4,7\]

Herein, we report an example of interpenetration and consequent gas-sorption properties of MOFs, which is simply controlled by the presence of a carbon–carbon double or single bond in identical organic building blocks (Scheme 1). This is significant in several respects: 1) reports of the systematic comparison of gas sorption properties for similar frameworks that differ only in the degree of interpenetration are very rare; 2) highly porous SNU-70' is presented, which has an extraordinary high surface area and ex-
exceptionally high H₂, CO₂, and CH₄ gas-sorption capacities;
3) the rearrangement of the interpenetrated networks upon
guest removal, which leads to expansion of pore size, is re-
vealed; 4) the post-synthetic bromination of the C=C double
bonds in the MOF is reported, in particular quantitatively
and at room temperature.

Results and Discussion

Syntheses and X-ray crystal structures of SNU-70 and SNU-
71: Pale-yellow cubic crystals of [Zn₄O(CVB)₃]·13DEF·2H₂O (SNU-70) and [Zn₄O(CEB)₃]·6DEF·H₂O (SNU-71) were obtained by heating
[Zn(NO₃)₂]·6H₂O with 4-(2-carboxyvinyl)benzoic acid (H₂CVB) or 4-(2-carboxyethyl)benzoic acid (H₂CEB), re-
spectively, at 105 °C for 12 h in N,N-diethylformamide
(DEF). X-ray crystal structures (Figure 1) of SNU-70 and
SNU-71 indicate that they have similar cubic-net structures
that are constructed from [Zn₄O]⁶⁺ octahedral secondary
building units (SBUs) and linear dicarboxylate linkers, simi-
larly to MOF-5.⁷⁶ In both frameworks, the distances be-
tween the nearest [Zn₄O] clusters in a cubic net is 15 Å.
However, SNU-70 has a noninterpenetrated structure whereas SNU-71 has a doubly interpenetrated structure. Noninterpenetrated SNU-70 generates square channels with dimensions of approximately 9.0 × 9.0 Å in three orthogonal
directions, which is much larger than those of interpenetrat-
ed SNU-71 (ca. 2.5 × 2.5 Å). The guest solvent molecules in
SNU-70 and SNU-71 could not be located from the difference map due to significant thermal disorder, and were de-
termined by elemental analyses and thermogravimetric analysis (TGA) data. As expected, the amount of guest solvent
molecules per formula unit in doubly interpenetrated SNU-
71 is nearly half that in SNU-70.

Activation of the MOFs by using supercritical CO₂ gives
completely desolvated materials, [Zn₄O(CVB)₃] (SNU-70') and [Zn₄O(CEB)₃] (SNU-71'). The powder X-ray diffraction
(PXRD) patterns indicate that SNU-70 retains its structure
but SNU-71 undergoes a structural rearrangement upon re-
moval of the guest solvent molecules (Figure 2).¹⁰ The pos-


Schem 1. Ligands used in SNU-70 and SNU-71.

Figure 1. X-ray crystal structures of: a) noninterpenetrated SNU-70, and
b) doubly interpenetrated SNU-71. The interpenetrated two independent
frameworks are represented in red and blue.

Figure 2. PXRD patterns: a) as-synthesized SNU-70, b) pattern of SNU-
70 simulated based on X-ray crystallographic data, c) SNU-70' resulting
from supercritical CO₂ treatment of SNU-70, d) as-synthesized SNU-71, e) pattern of SNU-71 simulated based on X-ray crystallographic data,
f) SNU-71' resulting from supercritical CO₂ treatment of SNU-71, and
g) simulated pattern of the modeled structure of SNU-71', which is de-
scribed in Figure 3.

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Gas sorption properties: Gas-sorption isotherms of SNU-70' and SNU-71' were measured for N₂, H₂, CO₂, and CH₄, and the data are summarized in Table 1 together with the data for other MOFs for comparison. Noninterpenetrated SNU-70' has a pore volume of 2.17 cm³ g⁻¹ and a BET surface area of 5290 m² g⁻¹ (Langmuir 6100 m² g⁻¹), which is the highest of all MOFs with cubic-net structures and is comparable to the highest values reported so far for MOFs such as MOF-210 [1] (BET 6240 m² g⁻¹) and NU-100 (BET 6143 m² g⁻¹) [2]. Although the pore size of as-synthesized SNU-71 is much smaller than the kinetic diameter of N₂ (3.64 Å), the desolvated SNU-71' sample adsors a large amount of N₂ due to the increase in pore size on desolvation, as discussed earlier. The SNU-71' sample has a pore volume of 0.709 cm³ g⁻¹ and a BET surface area of 1770 m² g⁻¹ (Langmuir 1923 m² g⁻¹).

The H₂ adsorption isotherms of SNU-70' and SNU-71' were measured at 77 and 87 K (Figure 5b), and the isosteric heats (Qₛₒₜ) of the H₂ adsorption were estimated from the data by using the virial equation [13]. In contrast to the N₂ adsorption, SNU-71' adsorbs a higher amount of H₂ gas than SNU-70' at 77 and 87 K below P < 1 atm. This might be related to the isosteric heat of H₂ adsorption in SNU-71', which is approximately 2 kJ mol⁻¹ higher than that of SNU-70'. The smaller pore size of SNU-71' increases the overlap potential between the framework and hydrogen [14]. However, at 77 K and high pressure, the H₂ uptake capacity of SNU-70' becomes greater than that of SNU-71' (Figure 6). The excess H₂ uptake capacity of SNU-70' is greater than SNU-71' by a factor of 1.85 at 77 K and 1.54 at 298 K. The total H₂ uptake capacity of SNU-70' is 2.1 times greater than that of SNU-71' at 77 K and 2.4 times greater at 298 K. In particular, the H₂ uptake capacity of SNU-70' at 77 K and high pressure is extraordinarily high, with an excess of 73.8 mg g⁻¹ (total 117.4 mg g⁻¹) at 77 K and 70 bar. This is comparable to the highest reported H₂ uptake capacities, such as 99.5 mg g⁻¹ excess at 56 bar (total 164 mg g⁻¹ at 70 bar) for NU-100 [12], 86 mg g⁻¹ excess (total 176 mg g⁻¹ at 80 bar) for MOF-210 [1], 74.0 mg g⁻¹ excess (total 163 mg g⁻¹ at 80 bar) for MOF-200 [1], and 81.0 mg g⁻¹ excess (total 110.6 mg g⁻¹ at 90 bar) for SNU-77H' [13].

Table 1. Gas adsorption properties of SNU-70' and SNU-71', with comparisons to other MOFs.

<table>
<thead>
<tr>
<th>MOF</th>
<th>SNU-70'</th>
<th>SNU-71'</th>
<th>SNU-77H¹</th>
<th>MOF-5¹ [a]</th>
<th>MOF-177¹</th>
<th>MOF-210¹</th>
<th>NU-100³ [b]</th>
<th>PCN-68² [b]</th>
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<tr>
<td>BET S.A. [m² g⁻¹]</td>
<td>5290</td>
<td>1770</td>
<td>3670</td>
<td>4400</td>
<td>4500</td>
<td>6240</td>
<td>6143</td>
<td>5109</td>
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<tr>
<td>V₂ₐₛ [cm³ g⁻¹]</td>
<td>2.17</td>
<td>0.709</td>
<td>1.52</td>
<td>1.55</td>
<td>1.89</td>
<td>3.60</td>
<td>2.82</td>
<td>2.13</td>
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<tr>
<td>H₂, 77 K [mg g⁻¹][¹]</td>
<td>12.4</td>
<td>14.4</td>
<td>17.9</td>
<td>1.32</td>
<td>1.25[²]</td>
<td>–</td>
<td>18.2</td>
<td>18.7</td>
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<tr>
<td>H₂, 77 K [mg g⁻¹][¹]</td>
<td>73.8/117.4/70</td>
<td>39.9/54.6/70</td>
<td>81.0/110/90</td>
<td>53/82/80</td>
<td>73/116/80</td>
<td>86/176/80</td>
<td>99.5/164/70</td>
<td>73.2/135/50</td>
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<td>H₂, 298 K [mg g⁻¹][¹]</td>
<td>4.0/14.5/70</td>
<td>2.66/1.70</td>
<td>5.0/11.9/90</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>10.1/29/90</td>
</tr>
<tr>
<td>Qₛₒₜ (H₂) [kJ mol⁻¹][¹]</td>
<td>5.12</td>
<td>7.22</td>
<td>7.05</td>
<td>4.8</td>
<td>–</td>
<td>–</td>
<td>6.1</td>
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<td>CO₂, 195 K [mg g⁻¹][¹]</td>
<td>2210</td>
<td>580</td>
<td>1690</td>
<td>1500[³]</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<tr>
<td>CO₂, 298 K [mg g⁻¹][¹]</td>
<td>35</td>
<td>46</td>
<td>39</td>
<td>46[³]</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td>CO₂, 1420/1640/45 [mg g⁻¹][¹]</td>
<td>1420/1640/45</td>
<td>493/564/45</td>
<td>933/1030/40</td>
<td>864/1030/50</td>
<td>1356/1550/80</td>
<td>2396/2870/50</td>
<td>2043/2315/40</td>
<td>1338/1804/100</td>
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<tr>
<td>Qₛₒₜ (CO₂) [kJ mol⁻¹][¹]</td>
<td>17.2</td>
<td>17.8</td>
<td>19.9</td>
<td>16.5[³]</td>
<td>14[³]</td>
<td>–</td>
<td>–</td>
<td>21.2</td>
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<tr>
<td>CH₄, 195 K [mg g⁻¹][¹]</td>
<td>39</td>
<td>49</td>
<td>87</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<tr>
<td>CH₄, 298 K [mg g⁻¹][¹]</td>
<td>4.9</td>
<td>5.2</td>
<td>6.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Qₛₒₜ (CH₄) [kJ mol⁻¹][¹]</td>
<td>9.4</td>
<td>14.6</td>
<td>14.3</td>
<td>12.2[³]</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
</tbody>
</table>

[a] At 1 atm. [b] At high pressure. Excess/total capacity/pressure in bar. [c] Isosteric heat of adsorption at zero coverage.

Figure 3. Simulated structural transformation of SNU-71 on removal of guest molecules. a) X-ray crystal structure of SNU-71, and b) simulated structure of desolvated SNU-71 based on its PXRD pattern.

Figure 4. Simulated structure of SNU-71'. a) View along the ac or bc plane, and b) view along the ab plane.
similar conditions. However, at 298 K and 1 atm, the CO$_2$ uptake capacity of SNU-71 becomes 1.3 times greater than that of SNU-70 (35 mg g$^{-1}$ in SNU-70 and 46 mg g$^{-1}$ in SNU-71). There have been some MOFs that adsorb CO$_2$ with high uptake capacity and high selectivity, such as SNU-M10 (9.2 wt%), SNU-21S (11.1 wt%), and Mg$_2$(dobdc) (35.2 wt%). At 298 K and 45 bar, SNU-70 adsors CO$_2$ with an excess 1420 mg g$^{-1}$ (total 1640 mg g$^{-1}$; Figure S3 in the Supporting Information), which is comparable to that of MOF-177 (excess 1493 mg g$^{-1}$, total 1656 mg g$^{-1}$ at 298 K and 42 bar). The reported highest excess CO$_2$ uptake capacities at 298 K and high pressures are 2400 mg g$^{-1}$ at 50 bar for MOF-200 and MOF-210, and 14.6 kJ mol$^{-1}$ for NU-100. The isosteric heats of CO$_2$ adsorption in SNU-70 and SNU-71 are 17.2 and 17.8 kJ mol$^{-1}$, respectively, as calculated from the isotherms measured at 195, 273, and 298 K up to 1 atm by using the Clausius–Clapeyron equation.

The CH$_4$ adsorption isotherms show relatively high adsorption capacities. At 298 K and up to 1 atm, SNU-71 shows slightly higher CH$_4$ uptake than SNU-70 (Figure 8), similar to the results for H$_2$ adsorption at 77 K and P < 1 atm. The zero coverage isosteric heats of CH$_4$ adsorption in SNU-70 and SNU-71 are 9.4 and 14.6 kJ mol$^{-1}$.
respectively. However, at 298 K and 45 bar, the CH$_4$ uptake capacity of SNU-70 (excess 168 mg g$^{-1}$, total 224 mg g$^{-1}$) are much higher than those of SNU-71 (excess 101 mg g$^{-1}$, total 121 mg g$^{-1}$; Figure S4 in the Supporting Information).

Post-synthetic bromination of SNU-70: The C=C double bond in the ligand of SNU-70 was brominated at room temperature, then dried by using supercritical CO$_2$ to give SNU-70Br. The elemental analysis data and the NMR spectra measured in [D$_6$]DMSO for the crystals that were digested in DCl indicated that all C=C bonds in SNU-70 were brominated (see Figure S5 in the Supporting Information). Previously, it was reported that the C=C bonds in a MOF were partially brominated at room temperature in 24 h, and quantitative bromination was possible only at 100°C.[22] In the present case, the diffusion of Br$_2$ into the pores must be much easier due to the very large pore size of SNU-70, which leads to more efficient bromination even at room temperature. For SNU-70Br, the BET surface area is 2285 m$^2$ g$^{-1}$ (Langmuir 2550 m$^2$ g$^{-1}$) and the pore volume is 0.908 cm$^3$ g$^{-1}$, which indicates that it still retains high porosity, although its porosity is reduced compared with that of SNU-70. SNU-70Br has H$_2$ uptake capacities of 7.3 mg g$^{-1}$ at 77 K and 1 atm and 4.2 mg g$^{-1}$ at 87 K and 1 atm (Figure 9). The isosteric heat of the H$_2$ adsorption is 6.14 to 4.41 kJ mol$^{-1}$, which is slightly higher than that of SNU-70.

![Graph](image1)

**Figure 7.** The gas-adsorption isotherms of SNU-70$^\bullet$ (●, ○) and SNU-71$^\bullet$ (●, ●) for CO$_2$ at: a) 195, and b) 273 and 298 K. Filled shapes: adsorption; open shapes: desorption.

![Graph](image2)

**Figure 8.** The gas-adsorption isotherms of SNU-70$^\bullet$ (●, ○) and SNU-71$^\bullet$ (●, ●) for CH$_4$ at: a) 195, and b) 273 and 298 K. Filled shapes: adsorption; open shapes: desorption.
In particular, the SNU-70 sample shows an extraordinarily high surface area and exceptionally high H₂ and CO₂ gas-sorption capacities. However, it should be noted here that gas-sorption properties cannot be easily predicted from the interpenetration. As seen in Figures 5 and 8, at P < 1 atm, the gas-adsorption capacities for N₂ at 77 K and CO₂ at 195 K are higher for noninterpenetrated SNU-70 than interpenetrated SNU-71', but H₂ and CH₄ adsorptions are the reverse, that is, SNU-71' has higher uptake capacities than SNU-70. By a post-synthetic method, the C=C bonds in SNU-70 were quantitatively brominated at room temperature and a noninterpenetrated MOF with a C=C bond in the ligand, which still shows a high porosity (BET 2285 m² g⁻¹; pore volume 0.908 cm³ g⁻¹), was also successfully constructed. The present results might be useful for future construction of highly porous MOFs with interpenetration that may be controlled by a small change in the ligand to fine-tune the gas-sorption properties.

Experimental Section

Synthesis of ligands: 4-(2-Carboxyvinyl)benzoic acid (H₂CVB) and 4-(2-carboxethyl)benzoic acid (H₂CEB) were synthesized by using previously reported procedures (see the Supporting Information). [23] [Zn₂O(CVB)₃]·13DEF·2H₂O (SNU-70): [Zn(NO₃)₂]·6H₂O (0.030 g, 0.101 mmol) and H₂CVB (0.015 g, 0.075 mmol) were dissolved in DEF (5 mL) in a glass bottle, which was sealed and heated at 105 °C for 12 h in a programmable furnace. Pale-yellow cubic crystals were formed, which were filtered and washed with DEF (yield: 0.030 g, 55%). FTIR (KBr pellet): ν = 1667 (DEF), 1607 cm⁻¹ (carboxylate); elemental analysis calcd (%) for C₆₀H₹₂N₆O₂₀Zn₄: C 51.89, H 7.56, N 8.28; found: C 52.26, H 8.10, N 8.87.

[Zn₂O(CEB)₃]·6DEF·H₂O (SNU-71): [Zn(NO₃)₂]·6H₂O (0.030 g, 0.101 mmol) and H₂CEB (0.015 g, 0.075 mmol) were dissolved in DEF (5 mL) in a glass bottle, which was sealed and heated at 105 °C for 12 h in a programmable furnace. Pale-yellow cubic crystals were formed, which were filtered and washed with DEF (yield: 0.020 g, 55%). FTIR (KBr pellet): ν = 1670 (DEF), 1609 cm⁻¹ (carboxylate); elemental analysis calcd (%) for C₉₅H₁₆₅N₁₃O₂₈Zn₄: pale-yellow cubic crystal (0.2/C1480.2/C1480.2 mm); M.P. 27637(6)/C1383; Z = 8; F = 27637(6) Å²; V = 27637(6) Å³; Z = 8; F = 27637(6) Å³; Z = 8;

Conclusion

The present study demonstrates that the interpenetration of MOFs with almost-identical network structures can be controlled by a simple change in the ligand, that is, the presence of a C=C or a C=C bond. Comparison of the gas-sorption properties indicate that the noninterpenetrated structure (SNU-70) exhibits generally much higher gas adsorption capacities than the interpenetrated structure (SNU-71) at high pressures regardless of the temperature, whereas the opposite is observed at low pressures due to the higher isosteric heats of the gas adsorption resulting from the smaller pores.

Figure 9. The adsorption isotherms of SNU-70Br⁺ for: a) N₂ at 77 K, and b) H₂ at 77 and 87 K. Filled shapes: adsorption; open shapes: desorption.
were exchanged for CH₂Cl₂. The guest-exchanged crystals (100 mg) were moved by passing the gases through a drying trap (model 500) filled with therm magnetic suspension balance. The trace water impurity was determined from the N₂ gas isotherm at 77 K. The high-pressure sorption was measured for H₂ (77 K, 298 K), CO₂ (298 K), and CH₄ (298 K). Post-synthetic bromination of SNU-70 module was compared with the experimental pattern.

 Activation of MOFs with supercritical CO₂: Crystals of as-synthesized MOFs (≈ 0.3 g) were placed inside a supercritical dryer together with DEF and the drying chamber was sealed. The temperature and pressure of the chamber were increased to 40°C and 200 bar with CO₂. The chamber was vented at a rate of 10 mL min⁻¹ and then filled with CO₂ again. The cycles of refilling with CO₂ pressurizing, and venting were repeated for at least 3 h. After drying, the closed container was transferred to a glovebox filled with argon and transferred to a gas-sorption cell. The gas sorption isotherms were measured without further activation. Elemental analysis calcd (%) for C₈₃H₇₄N₆O₅Zn₄ (SNU-70): C 42.49, H 2.14; found: C 42.62, H 2.17.

Gas sorption measurements: Low-pressure gas adsorption-desorption measurements were performed by using Autosorb-1 or Autosorb-3B (Quantachrome Instruments). All gases used in the studies were of 99.999% purity. Before and after gas-sorption measurement, the sample was weighed precisely. The surface area and total pore volume were determined from the N₂ gas isotherm at 77 K. The high-pressure sorption was measured for H₂ (77 K, 298 K), CO₂ (298 K), and CH₄ (298 K) in the range of 0–70 bar by the gravimetric method using a Robu therm magnetic suspension balance. The trace water impurity was removed by passing the gases through a drying trap (model 500) filled with molecular sieve (5 Å), which was purchased from the Chromatography Research Supplies. The dried crystals (~0.8 g) prepared by using supercritical CO₂ were transferred to the instrument and kept under vacuum for at least 3 h. All data were corrected for the buoyancy of the system and sample. The sample density used in the buoyancy correction was determined from the He displacement isotherms (up to 60 bar) measured at 298 K.

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