

A Highly Porous Metal–Organic Framework: Structural Transformations of a Guest-Free MOF Depending on Activation Method and Temperature

Hye Jeong Park, Dae-Woon Lim, Woo Seung Yang, Tae-Rog Oh, and Myunghyun Paik Suh*^[a]

Abstract: A doubly interpenetrating porous metal–organic framework (SNU-77) has been synthesized from the solvothermal reaction of the extended carboxylic acid tris(4'-carboxy-biphenyl)amine (H₃TCBPA) and Zn(NO₃)₂·6H₂O in *N,N*-dimethylacetamide (DMA). SNU-77 undergoes single-crystal-to-single-crystal transformations during various activation processes, such as room-temperature evacuation, supercritical CO₂ drying, and high temperature evacuation, to afford

SNU-77R, SNU-77S, and SNU-77H, respectively. These guest-free MOFs exhibited different fine structures with different window shapes and different effective window sizes at room temperature. Variable-temperature synchrotron single-crystal X-ray analyses reveal that the guest-free structure is

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also affected by changes in temperature. Despite the different fine structures, SNU-77R, SNU-77S, and SNU-77H show similar gas sorption properties due to the nonbreathing nature of the framework and an additional structural change upon cooling to cryogenic gas sorption temperature. SNU-77H exhibits a large surface area (BET, 3670 m² g^{−1}), a large pore volume (1.52 cm³ g^{−1}), and exceptionally high uptake capacities for N₂, H₂, O₂, CO₂, and CH₄ gases.

Introduction

Porous metal–organic frameworks (MOFs) have received considerable attention because of their diverse chemical compositions and architectures as well as their potential applications in gas storage and separation,^[1–5] catalysis,^[6,7] and in the fabrication of metal nanoparticles.^[8–11] The potential applications of MOFs are attributed to their permanent microporosity and large internal surface areas. It has been reported that the gas sorption capacities of desolvated MOFs are significantly affected by the method of preparation and the handling of the as-synthesized samples, such as reaction temperature and heating time during the solvothermal synthesis as well as the exposure of the products to air.^[12,13] Furthermore, it has recently been reported that MOFs activated by treatment with supercritical CO₂ and freeze-drying adsorb much greater amounts of gases than those activated by thermal or room-temperature evacuation.^[14,15] These observations have been explained by the inhibition of the collapse of interparticle mesopores and the breathing effect of the framework, respectively. However, there has been no clear experimental evidence showing how the structure of the framework changes depending on the activation method, although this must be an important factor deter-

mining the gas sorption properties. In particular, the compounds used in those experiments contained solvent molecules coordinated to the metal centers. Therefore, whether the coordinated solvent molecules are removed or not during the activation must affect the gas sorption properties, but this was not considered by the authors.^[14,15] The single-crystal structures have not revealed how the structure of a guest-free MOF is changed by a change in temperature, although there have been some reports of temperature-dependent structural transformations of guest-free MOFs as evidenced from the powder X-ray diffraction patterns.^[16,17]

To investigate how the guest-free structures of a MOF vary depending on the activation method and temperature, the crystal should retain its single-crystal nature throughout the process, but this rarely happens. Even though a considerable number of studies have been conducted on single-crystal-to-single-crystal (SCSC) transformations of MOFs,^[8,18–22] to the best of our knowledge there has been no report of a single-crystal analysis revealing how the framework structure changes depending on the activation method.

In this study we have synthesized a new Zn₄O-type MOF that cannot coordinate solvent molecules to eliminate the possible ambiguities arising from the removal of coordinated solvent molecules during the activation process. We expected that the Zn₄O-type MOF may maintain its single-crystal nature during the various activation processes because of the rather rigid nature of the (6,3)-connected net. In the synthesis of the MOF, we have used an elongated organic building block, tris(4'-carboxybiphenyl)amine (H₃TCBPA), because a higher surface area can be achieved for an MOF constructed of an elongated organic building block.^[23–25]

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Herein we report a porous MOF, $[\text{Zn}_4\text{O}(\text{TCBPA})_2] \cdot 19\text{DMA} \cdot 4\text{H}_2\text{O}$ (**SNU-77**, DMA = *N,N*-dimethylacetamide), which undergoes SCSC transformations during various activation processes, such as room-temperature evacuation, supercritical CO_2 drying, and high-temperature evacuation, to afford **SNU-77R**, **SNU-77S**, and **SNU-77H**, respectively. The X-ray crystal data collected at room temperature for the three different activated samples indicate that the molecular components of the framework undergo rotational rearrangements and that the extent of the rearrangements depend significantly on the activation method to afford different effective window sizes and shapes. Synchrotron single-crystal X-ray studies on **SNU-77R** with sequential temperature changes ($293 \rightarrow 373 \rightarrow 293 \rightarrow 100$ K) indicate that the structure of the guest-free framework also depends on the temperature. Despite the different fine structures at room temperature, the guest-free samples of **SNU-77** exhibit similar gas sorption properties due to the nonbreathing nature of the framework and additional structural transformation at the cryogenic gas adsorption temperature. **SNU-77H** shows an exceptionally large surface area (Langmuir, $4180 \text{ m}^2 \text{ g}^{-1}$; BET, $3670 \text{ m}^2 \text{ g}^{-1}$), large pore volume ($1.52 \text{ cm}^3 \text{ g}^{-1}$), and high uptake capacities for N_2 , H_2 , O_2 , CO_2 , and CH_4 gases.

Results and Discussion

Synthesis and X-ray crystal structure of $[\text{Zn}_4\text{O}(\text{TCBPA})_2] \cdot 19\text{DMA} \cdot 4\text{H}_2\text{O}$ (SNU-77**):** Brown crystals of **SNU-77** were obtained by heating a mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_3TCBPA in DMA at 115°C for 2 days. Thermogravimetric analysis (TGA) reveals 53.6% weight loss between 25 and 400°C , which corresponds to the loss of all the guest solvent molecules (calcd 53.8%), and no chemical decomposition occurs below 430°C (Figure S1). The X-ray crystal structure (Figure 1) indicates that a $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster is formed as an octahedral secondary building unit (SBU), each of which is linked to six trigonal units of TCBPA^{3-} , giving rise to a (6,3)-connected net that mimics a PdF_2 net topology.^[22,26] The network is doubly interpenetrating. In **SNU-77**, two crystallographically different TCBPA^{3-} units, TCBPA1 and TCBPA2, are located in *trans* positions around a Zn_4O cluster and show a dihedral angle of $79.2(2)^\circ$ between the outer phenyl rings of the ligand. The TCBPA^{3-} unit resembles a propeller because the inner phenyl rings are tilted relative to each other, and the central nitrogen is sp^2 -hybridized instead of sp^3 -hybridized with C–N–C angles of approximately 120° . Edge-to-face π – π interactions exist between two interpenetrating nets [the shortest C–C distance, $3.675(9) \text{ \AA}$; dihedral angle, $53.3(3)^\circ$; Figure S2]. Three-dimensional channels with an effective window size of $4.0 \times 4.9 \text{ \AA}$ are generated along the three orthogonal directions. Because the guest molecules of **SNU-77** could not be located due to thermal disorder, the formula of **SNU-77** was determined on the basis of the IR, elemental analysis, and TGA data.

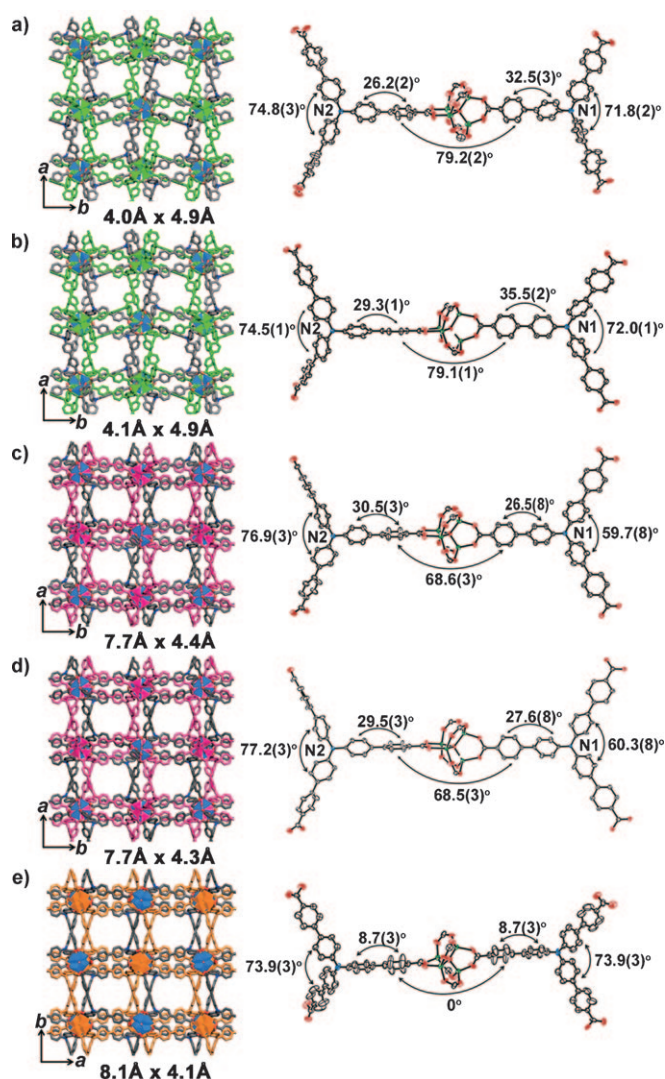


Figure 1. X-ray crystal structures of a) **SNU-77**, b) **SNU-77'**, c) **SNU-77R**, d) **SNU-77S**, and e) **SNU-77H**. Doubly interpenetrating networks are represented in two different colors. The numbers below each structure represent the effective aperture size.

Single-crystal-to-single-crystal transformations of **SNU-77 through various activation processes:** To remove the guest solvent molecules of **SNU-77**, we employed three different activation methods: 1) Guest–solvent exchange with toluene followed by evacuation at room temperature, 2) the direct activation of **SNU-77** by treatment with supercritical CO_2 , and 3) evacuation of the guest-exchanged sample at high temperature. These processes yielded **SNU-77R**, **SNU-77S**, and **SNU-77H**, respectively. The chemical formulae of **SNU-77R**, **SNU-77S**, and **SNU-77H** are $[\text{Zn}_4\text{O}(\text{TCBPA})_2]$, as characterized by IR spectroscopy, elemental analysis, and TGA. During these activation processes, the MOFs retained their single-crystal nature and the X-ray crystal structures of three different guest-free samples were elucidated (Figure 1). The X-ray crystal data for **SNU-77R**, **SNU-77S**, and **SNU-77H** are summarized in Table 1.

Table 1. Crystallographic data for **SNU-77**, **SNU-77'**, **SNU-77R**, **SNU-77S**, and **SNU-77H**.

	SNU-77 ^[a]	SNU-77' ^[a]	SNU-77R	SNU-77S	SNU-77H ^[a]
formula	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃
crystal system	cubic	cubic	cubic	cubic	cubic
space group	<i>Pa</i> -3	<i>Pa</i> -3	<i>Pa</i> -3	<i>Pa</i> -3	<i>Ia</i> -3
<i>M_r</i>	1482.76	1482.76	1482.76	1482.76	1482.76
<i>a</i> [Å]	32.6570(9)	32.5926(6)	32.407(5)	32.4053(7)	32.2713(18)
<i>V</i> [Å ³]	34 828.0(17)	34 622.4(11)	34 034(9)	34 028.9(13)	33 609(3)
<i>Z</i>	8	8	8	8	8
ρ_{calcd} [g cm ⁻³]	0.566	0.569	0.579	0.579	0.586
<i>T</i> [K]	293	293	293	293	293
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
μ [mm ⁻¹]	0.570	0.574	0.584	0.584	0.591
GOF (<i>F</i> ²)	0.703	0.796	1.072	1.053	0.868
<i>R</i> ₁ ^[b] <i>wR</i> ₂ ^[c] [<i>I</i> > 2σ(<i>I</i>)]	0.0890, 0.2052	0.0522, 0.1337	0.0925, 0.2503	0.0883, 0.2459	0.0957, 0.2470
<i>R</i> ₁ ^[b] <i>wR</i> ₂ ^[c] (all data)	0.2182, 0.2327	0.1222, 0.1465	0.2025, 0.3318	0.2219, 0.3348	0.2028, 0.2852

[a] The residual electron densities were flattened by using the SQUEEZE option of PLATON. [b] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [c] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ in which $w = 1/[\sigma^2(F_o^2) + (0.1160P)^2 + (0.000)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **SNU-77**, $w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + (0.000)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **SNU-77'**, $w = 1/[\sigma^2(F_o^2) + (0.1696P)^2 + (26.59)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **SNU-77R**, $w = 1/[\sigma^2(F_o^2) + (0.1776P)^2 + (4.96)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **SNU-77S**, and $w = 1/[\sigma^2(F_o^2) + (0.1569P)^2 + (0.000)P]$, $P = (F_o^2 + 2F_c^2)/3$ for **SNU-77H**.

When crystals of **SNU-77** were immersed in toluene for 24 h, the DMA guest molecules were exchanged with toluene to yield [Zn₄O(TCBPA)₂]₂·14PhCH₃·3H₂O (**SNU-77'**), as characterized by IR spectroscopy, elemental analysis, and TGA. The X-ray crystal structure of **SNU-77'** is very similar to that of **SNU-77** (Figure 1).

When **SNU-77'** was activated at room temperature under a pressure of 10⁻⁵ torr for 24 h, [Zn₄O(TCBPA)₂]₂ (**SNU-77R**) resulted. The X-ray diffraction data of **SNU-77R** collected at room temperature indicates that many of its key dihedral angles are different to those of **SNU-77** and **SNU-77'**. In particular, the dihedral angle between the two outer phenyl rings of the ligands located in the *trans* positions around the Zn₄O cluster is 68.6(3)° compared with 79.1(1)° in **SNU-77'**, and the dihedral angles between the inner phenyl rings of TCBPA1 and TCBPA2 are 76.9(3) and 59.7(8)°, respectively, compared with 74.5(1) and 72.0(1)° in **SNU-77'** (Figure 1). These angles indicate that the phenyl rings in TCBPA³⁻ in the framework rotate upon removal of the guests even at room temperature. **SNU-77R** exhibits edge-to-face π - π interactions between two interpenetrating nets [the shortest C-C distance, 3.806(30) Å], but the dihedral angle [24.6(7)°] is remarkably different to that in **SNU-77'** [48.3(1)°; Figure S2]. Due to these rotational rearrangements, the shape of the channel is different to that of **SNU-77'** and the effective window size is enlarged to 7.7 × 4.4 Å compared with 4.1 × 4.9 Å for **SNU-77'**. A few examples of enlarged pore windows on desolvation have been reported in the literature.^[27,28] The void volume of **SNU-77R** estimated by PLATON^[29] is 69.9% (1.21 cm³ g⁻¹), similar to the value of 70.3% (1.24 cm³ g⁻¹) for **SNU-77**.

Supercritical drying is a common washing method in polymer synthesis and aerogel production. Recently, supercritical CO₂ drying has been applied to MOFs as an efficient activation method that leads to increased surface areas of the MOFs.^[14] In this study, when single crystals of **SNU-77** were

activated by treatment with supercritical CO₂ (see the Experimental Section), a single crystal of [Zn₄O(TCBPA)₂]₂ (**SNU-77S**) resulted. The X-ray crystal structure of **SNU-77S** is similar to that of **SNU-77R**, as shown in Figure 1, which indicates that treatment with supercritical CO₂ is as mild as room-temperature evacuation and induces rather small structural rearrangements.

Interestingly, however, [Zn₄O(TCBPA)₂]₂ (**SNU-77H**), which was obtained by heating **SNU-77'** at 110 °C under a pressure of 10⁻⁵ torr for 2 h, exhibits a significantly different structure to those of **SNU-77**, **SNU-77'**, **SNU-77R**, and **SNU-77S**.

The crystal space group is *Ia*-3, compared with *Pa*-3 for the others, and only one kind of TCBPA³⁻ unit exists. Most importantly, the TCBPA³⁻ unit within the structure exhibits large rotational rearrangements: The dihedral angle between the outer phenyl rings of the biphenyl groups located in the *trans* positions around the Zn₄O cluster is 0.0°, compared with 79.1(1)° in **SNU-77'** and 68.6(3)° in **SNU-77R**, and the dihedral angles between the two phenyl rings of the biphenyl groups in TCBPA³⁻ are 8.7(3)°, compared with an average of 30.5(1)° in **SNU-77'** and an average of 30.3(3)° in **SNU-77R** (Figure 1). Face-to-face π - π interactions exist between two interpenetrating nets in **SNU-77H** [the shortest C-C distance, 3.693(2) Å; dihedral angle, 8.8(4)°], in contrast to edge-to-face π - π interactions in the others (Figure S2). The effective window size (8.1 × 4.1 Å) is larger than those of **SNU-77'**, **SNU-77R**, and **SNU-77S**. The void volume of **SNU-77H** estimated by PLATON^[29] is 69.1% (1.18 cm³ g⁻¹).

The major structural differences between **SNU-77'** (= **SNU-77**), **SNU-77R** (= **SNU-77S**), and **SNU-77H** are the effective window sizes and shapes, which are determined by the dihedral angles between the phenyl rings around a Zn₄O cluster (Table 2), although they have similar cell parameters and only 2.3–3.0% differences in cell volumes. **SNU-77R** and **SNU-77S** have intermediate structures between **SNU-77'** and **SNU-77H**. Despite the different fine structures revealed by the single-crystal X-ray data, the simulated powder X-ray diffraction (PXRD) patterns of **SNU-77R**, **SNU-77S**, and **SNU-77H** are very similar: Only the small peaks at 2 θ = 9.4, 10.1, and 11.2° for **SNU-77** and **SNU-77'** are significantly weaker in the patterns of **SNU-77R** and **SNU-77S**, and they disappear in **SNU-77H** (Figure S3). This indicates that the rearrangements of the molecular components can barely be recognized by the PXRD patterns unless extremely careful attention is paid to the very small peaks.

Table 2. Comparison of crystal structures.

MOF	Dihedral angles between the phenyl rings [°]			π - π interaction	
	Biphenyls of TCBPA ³⁻	Inner rings of TCBPA ³⁻	Outer rings of TCBPA ^{3-[a]}	Shortest C-C distance [Å]	Dihedral angle [°]
SNU-77	26.2(2), 32.5(3)	71.8(2), 74.8(3)	79.2(2)	3.675(9)	53.3(3)
SNU-77'	29.3(1), 35.5(2)	72.0(1), 74.5(1)	79.1(1)	3.559(4)	48.3(1)
SNU-77R	26.5(5), 30.5(3)	59.7(8), 76.9(3)	68.6(3)	3.806(30)	24.6(7)
SNU-77S	27.6(8), 29.5(3)	60.3(8), 77.2(3)	68.5(3)	3.787(32)	24.1(7)
SNU-77H	8.7(3)	73.9(3)	0.0(0)	3.693(2)	8.8(4)
SNU-77R					
293 K	29.8(2), 30.5(4)	64.1(4), 76.7(2)	79.2(2)	3.504(7)	34.7(2)
373 K	6.4(3)	74.8(2)	0.0(4)	3.990(12)	10.4(3)
293 K (2 nd)	4.8(3)	74.8(2)	0.0(4)	3.926(12)	7.7(4)
100 K	34.3(1), 41.7(1)	65.6(1), 78.0(1)	76.6(1)	3.482(4)	37.5(1)

[a] Outer rings of two TCBPA³⁻ located in *trans* positions around the Zn₄O cluster.

Structural transformations of a guest-free MOF upon temperature change:

Previously we reported that the phenyl rings of NTB³⁻ in [Zn₄O(NTB)₂], where NTB is 4,4',4''-nitrotrisbenzoate, underwent rotational motion when the as-synthesized MOF was activated at 400 °C and a pressure of 10⁻⁵ torr.^[22] However, we could not verify whether the rotational motion occurred as a result of the applied heat or simply by removal of the guest molecules because we failed to exchange all the guest molecules with a lower-boiling-point solvent to obtain the crystal that could be activated at room temperature. The results presented herein indicate that the degree of rotational movement of the molecular components in the crystal actually depends on the activation temperature. On the basis that all X-ray diffraction data were collected at room temperature, including those of **SNU-77H**, it is evident that once the molecular components have rearranged during the removal of guests at high temperature, their positions do not easily change to those of **SNU-77R**, even after cooling to room temperature. This prompted us to investigate whether the structure of a guest-free MOF depends on the temperature or not.

We performed synchrotron single-crystal X-ray diffraction studies on **SNU-77R** by changing the temperature sequentially from 293 to 373 K, and then to 293 and 100 K (Table 3). As shown in Figure 2, on heating **SNU-77R** at 373 K for 2 h, the structure becomes similar to that of **SNU-77H**. This implies that the previously mentioned structural transformation of **SNU-77'** to **SNU-77R** is triggered mainly by guest removal and that of **SNU-77R** to **SNU-77H** is induced by thermal energy. Interestingly, cooling from 373 to 293 K for 2 h did not reverse the structure of **SNU-77H** to that of **SNU-77R**. However, on further cooling to 100 K, the structure was reversed and changed further. Figures 1 and 2 suggest that as the guests are removed and the temperature is elevated, decreases are observed in the dihedral angles between the outer phenyl rings of the biphenyl moieties located in the *trans* positions around the Zn₄O(CO₂)₆ unit as well as between the two phenyl rings of the biphenyl groups in TCBPA³⁻. To the best of our knowledge, this is the first report of single-crystal structures revealing the temperature-induced structural transformation of a guest-free MOF rather than powder diffraction analyses.^[16,17] The results sug-

gest that at the cryogenic temperature of gas sorption measurements, the structures of **SNU-77R**, **SNU-77S**, and **SNU-77H** would become similar to each other as a result of temperature-induced structural transformations.

Luminescence properties: The solid samples of **SNU-77** and **SNU-77'** exhibit photoluminescence at λ_{max} = 477 and 488 nm,

Table 3. Crystallographic data for **SNU-77R** upon temperature change.

	293 K	373 K	293 K (2nd)	100 K
formula	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃	Zn ₄ C ₇₈ H ₄₈ N ₂ O ₁₃
crystal system	cubic	cubic	cubic	cubic
space group	<i>Pa</i> -3	<i>Ia</i> -3	<i>Ia</i> -3	<i>Pa</i> -3
<i>M_r</i>	1482.76	1482.76	1482.76	1482.76
<i>a</i> [Å]	32.387(5)	32.374(5)	32.359(5)	32.443(4)
<i>V</i> [Å ³]	33 971(9)	33 930(9)	33 883(9)	34 148(7)
<i>Z</i>	8	8	8	8
ρ_{calcd} [g cm ⁻³]	0.580	0.580	0.581	0.577
<i>T</i> [K]	293	373	293	100
λ [Å]	0.77000	0.77000	0.77000	0.77000
μ [mm ⁻¹]	0.585	0.585	0.586	0.582
GOF (<i>F</i> ²)	1.103	1.106	1.072	1.104
<i>R</i> ₁ ^[a]	0.0725,	0.0956,	0.1071,	0.0740,
<i>wR</i> ₂ ^[b]	0.2330	0.2993	0.3486	0.2153
[<i>I</i> > 2 σ (<i>I</i>)]				
<i>R</i> ₁ ^[a]	0.0993,	0.1519,	0.1426,	0.0831,
<i>wR</i> ₂ ^[b] (all data)	0.2568	0.3414	0.3826	0.2218

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $wR(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ in which $w = 1/[\sigma^2(F_o^2) + (0.1521P)^2 + (10.47)P]$, $P = (F_o^2 + 2F_c^2)/3$ for the data at 293 K, $w = 1/[\sigma^2(F_o^2) + (0.1879P)^2 + (9.08)P]$, $P = (F_o^2 + 2F_c^2)/3$ for the data at 373 K, $w = 1/[\sigma^2(F_o^2) + (0.2000P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$ for the data at 293 K (2nd), and $w = 1/[\sigma^2(F_o^2) + (0.1577P)^2 + (0.00)P]$, $P = (F_o^2 + 2F_c^2)/3$ for the data at 100 K.

respectively, whereas **SNU-77R**, **SNU-77S**, and **SNU-77H** show photoluminescence at λ_{max} = 512, 510, and 506 nm, respectively, upon photoexcitation at 410 nm (Figure 3). This indicates that the photoluminescence of the host framework is strongly dependent upon the presence and absence of the guest solvent molecules as well as the type of guests, but scarcely on the rearrangement of the host framework caused by different activation methods. The luminescence seems to originate from the ligand because the luminescent spectra are comparable to that of Na₃TCBPA, which emits at 478 nm.

Gas sorption properties of SNU-77R, SNU-77S, and SNU-77H: The gas sorption isotherms were measured for N₂, H₂, O₂, CO₂, and CH₄ gases (Table 4). Because zinc MOFs con-

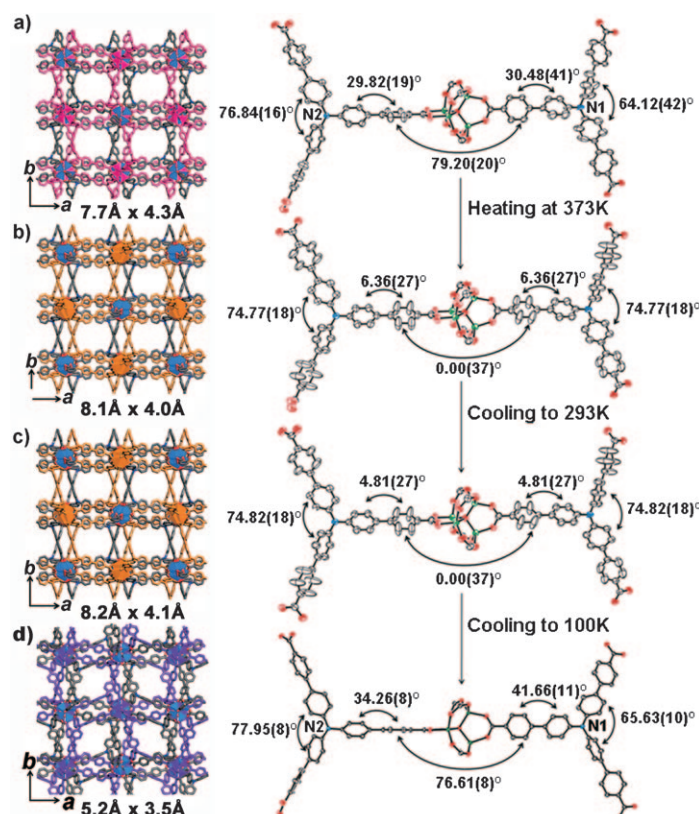


Figure 2. Structural transformations of **SNU-77R** upon sequential changes in temperature: a) 293, b) 373, c) 293 (2nd), and d) 100 K. The ORTEP views are drawn with the thermal ellipsoids at the 30% probability level. Zn, green; O, red; N, blue; C, black.

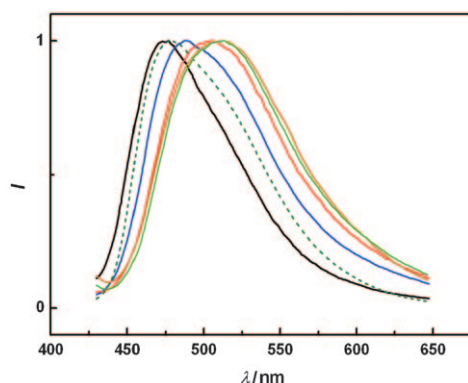


Figure 3. Luminescence spectra with normalized intensity: **SNU-77** (black), **SNU-77'** (blue), **SNU-77R** (orange), **SNU-77S** (green), **SNU-77H** (red), and solid **Na₃TCBPA** (olive) upon photoexcitation at 410 nm.

structed of carboxylates are frequently air- or moisture-sensitive and the gas sorption capacities decrease on exposure to air,^[12,13] we took special care in handling the samples (see the Experimental Section).

In contrast to previous reports that treatment with supercritical CO₂ and freeze-drying significantly enhanced the gas adsorption capacities of MOFs compared with thermal or room-temperature evacuation methods,^[14,15] all the desolvat-

Table 4. Gas uptake capacity data for **SNU-77H**.

Gas	<i>T</i> [K]	<i>P</i> [bar]	STP [cm ³ g ^{−1}]	wt % gas	Gas adsorbed ^[a] [g L ^{−1}]	<i>v</i> (STP)/ <i>v</i> ^[a]
N ₂	77	0.91	1050	131	768	615
	298	1.0	3.19	0.40	2.3	1.9
H ₂	77	1.0	200	1.79	10.5	117
	87	1.0	112	1.01	5.90	65.6
	77	90	907 (1230)	8.10 (11.0)	47.4 (64.5)	532 (722)
	298	90	56.3 (133)	0.50 (1.19)	2.93 (6.97)	33.0 (77.9)
O ₂	77	0.2	1201	172	1006	704
	298	1.0	3.56	0.51	3.0	2.1
CO ₂	195	1.0	860	169	990	504
	231	1.0	660	130	760	387
	273	1.0	41.8	8.21	48.1	24.6
	298	1.0	20.1	3.94	23.1	11.8
CH ₄	298	40	475 (523)	93.3 (103)	547 (601)	278 (306)
	195	1.0	122	8.70	50.9	71.5
	231	1.0	57.6	4.12	24.2	33.8
	273	1.0	17.0	1.20	7.00	10.0
	298	1.0	8.68	0.62	3.6	5.1
	298	35	199 (242)	14.2 (17.3)	83.2 (101)	117 (142)
	298	60	248 (308)	17.7 (22.0)	104 (129)	145 (180)

[a] Gas adsorbed per volume of sample: The values were calculated as mass of adsorbed gas × density of sample (586 g L^{−1} for **SNU-77H**). The values in parentheses indicate the total amount of adsorbed gas.

ed solids of the present MOF show similar gas sorption properties (Figure 4). This can be attributed to the fact that the present doubly interpenetrating Zn₄O-type MOF exhibits no breathing effect and only its organic components perform rotational motion. Furthermore, all of them should have similar structures at the gas sorption temperature (77 or 87 K) due to temperature-induced structural transformation. If a MOF is much more flexible and exhibits a strong breathing effect, the guest-free MOF prepared by heat evacuation should be significantly different to that prepared by treatment with supercritical CO₂. In that case, their structures would hardly be similar, even at the gas adsorption temperature, leading to different gas sorption capacities.

SNU-77R, **SNU-77S**, and **SNU-77H** adsorb N₂ gas at 77 K, showing type I isotherms characteristic of microporous materials (Figure 4a). The BET surface areas of **SNU-77R**, **SNU-77S**, and **SNU-77H** estimated from the N₂ gas sorption data are similar: 3560, 3660, and 3670 m² g^{−1} (Langmuir surface areas: 4020, 4120, and 4180 m² g^{−1}), respectively, which are comparable to those of MOF-5 (3800 m² g^{−1})^[12] and MOF-177 (4630 m² g^{−1}).^[30] Their pore volumes, determined by the Dubinin–Radushkevich (DR) equation, are 1.45, 1.48, and 1.52 cm³ g^{−1}, respectively. The plots of pore-size distribution based on the Horváth–Kawazoe (HK) method^[31] indicate that all have pore sizes of 8.1 Å. The surface areas calculated from the X-ray crystal structures by using the Materials Studio program^[32] with a probe radius of 1.82 Å and a grid interval of 0.25 Å are 4450 m² g^{−1} for **SNU-77R** and **SNU-77S**, and 4390 m² g^{−1} for **SNU-77H**.

SNU-77R, **SNU-77S**, and **SNU-77H** adsorb almost same amount of H₂ gas, up to 1.8 wt % at 77 K and 1 atm, and up to 1.0 wt % at 87 K and 1 atm (Figure 4b). The H₂ uptake capacities at 77 K are higher than that of MOF-177 (1.24 wt %) with larger pores (11.8 Å) in the noninterpen-

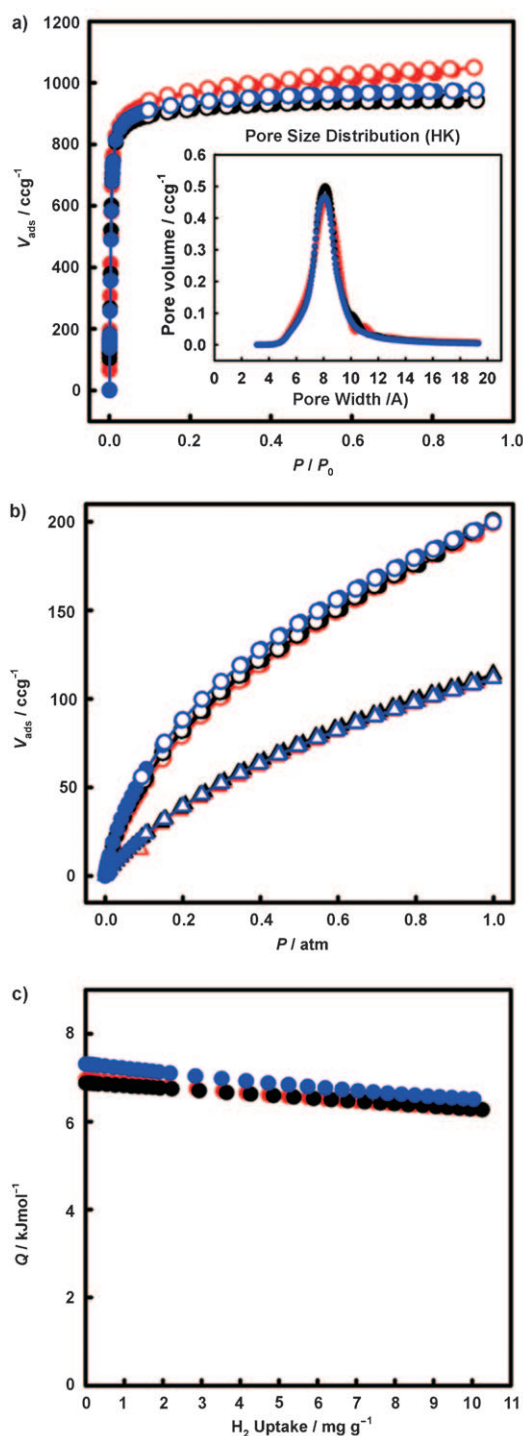


Figure 4. Gas sorption isotherms of **SNU-77R** (black), **SNU-77S** (blue), and **SNU-77H** (red). Filled shapes: adsorption; open shapes: desorption. a) N₂ at 77 K. Inset: pore-size distributions estimated by the Horváth–Kawazoe method. b) H₂ at 77 K (circles) and 87 K (triangles). c) Isosteric heats of H₂ adsorption.

trating (6,3)-connected net,^[30] but lower than that of [Zn₄O-(NTB)₂] (1.9 wt %) with much smaller pores (5.0 Å) in the doubly interpenetrating nets.^[22] The isosteric heats (Q_{st}) of H₂ adsorption estimated from the isotherms at 77 and 87 K

by using the virial equation^[33] are rather insensitive to the amount of H₂ loading (Figure 4c), which can be attributed to the interpenetration leading to a smaller pore size and an overlap of energy potentials between the opposing walls. The average zero coverage isosteric heats for the three desolvated samples is 7.05 kJ mol⁻¹, which is higher than those of noninterpenetrating Zn₄O-based MOFs such as MOF-5 (4.7 kJ mol⁻¹)^[34] and MOF-177 (4.4 kJ mol⁻¹).^[30] When **SNU-77H** was exposed to air for 6 days, the H₂ uptake capacity was significantly reduced to 1.51 wt % at 77 K and 1 atm, similarly to previous reports,^[12,13] even though the PXRD patterns indicate an intact framework structure (Figure S4).

Because the gas sorption properties of **SNU-77R**, **SNU-77S**, and **SNU-77H** are similar, the high-pressure H₂, CO₂, and CH₄ gas adsorption isotherms and the low-pressure O₂, CO₂, and CH₄ adsorption isotherms were measured only for **SNU-77H** (Figure 5). **SNU-77H** adsorbs large amounts of these gases (Table 4). In particular, the high-pressure H₂ gas uptake capacity at 77 K and 90 bar is exceptionally high (Figure 5a), with an excess of 8.1 wt % (47.4 g L⁻¹) and a total of 11.0 wt % (64.5 g L⁻¹). The best H₂ uptake at 77 K reported so far for MOFs is 9.95 wt % (total 16.4 wt %) at 56 bar for NU-100^[35] and 8.6 wt % (total 16.7 wt %) at 70 bar for MOF-210.^[36]

The O₂ adsorption capacity at 77 K and 0.2 atm (172 wt %, 1201 cm³ g⁻¹ at STP) is the best reported for MOFs because of the large void volume of the MOF (Figure 5b). It is close to the value (1280 cm³ g⁻¹) calculated from the void volume of **SNU-77H** (1.52 cm³ g⁻¹) and the density of liquid O₂ (1.205 g cm⁻³) at 77 K over 0.2 atm. At room temperature, however, it falls to 3.56 cm³ g⁻¹ at 1 atm.

The CO₂ and CH₄ uptake capacities are also high, reaching 93.5 wt % at 298 K and 42 bar and 14.2 wt % [117 v-(STP)/v] at 298 K and 35 bar, respectively (Figure 5c and d). The isosteric heats of the CO₂ and CH₄ adsorption at low coverage are 19.9–19.4 and 14.3–14.2 kJ mol⁻¹, respectively, as estimated from the isotherms recorded at 195, 231, 273, and 298 K by using the Clausius–Clapeyron equation (Figure S6).

Conclusion

We have revealed for the first time through complete single-crystal X-ray analyses that the guest-free structures of a MOF are determined not only by the activation method but also by the temperature. For the doubly interpenetrating Zn₄O-type MOF studied herein, the different activation methods, such as room-temperature evacuation, treatment with supercritical CO₂, and high-temperature evacuation, provide different fine structures at room temperature with pore shapes and window sizes that differ by several Å. However, they show similar gas sorption properties because the framework does not breathe and the fine structures are similar to each other at the cryogenic gas sorption temperature due to further temperature-induced structural transformations. The results presented herein together with the pre-

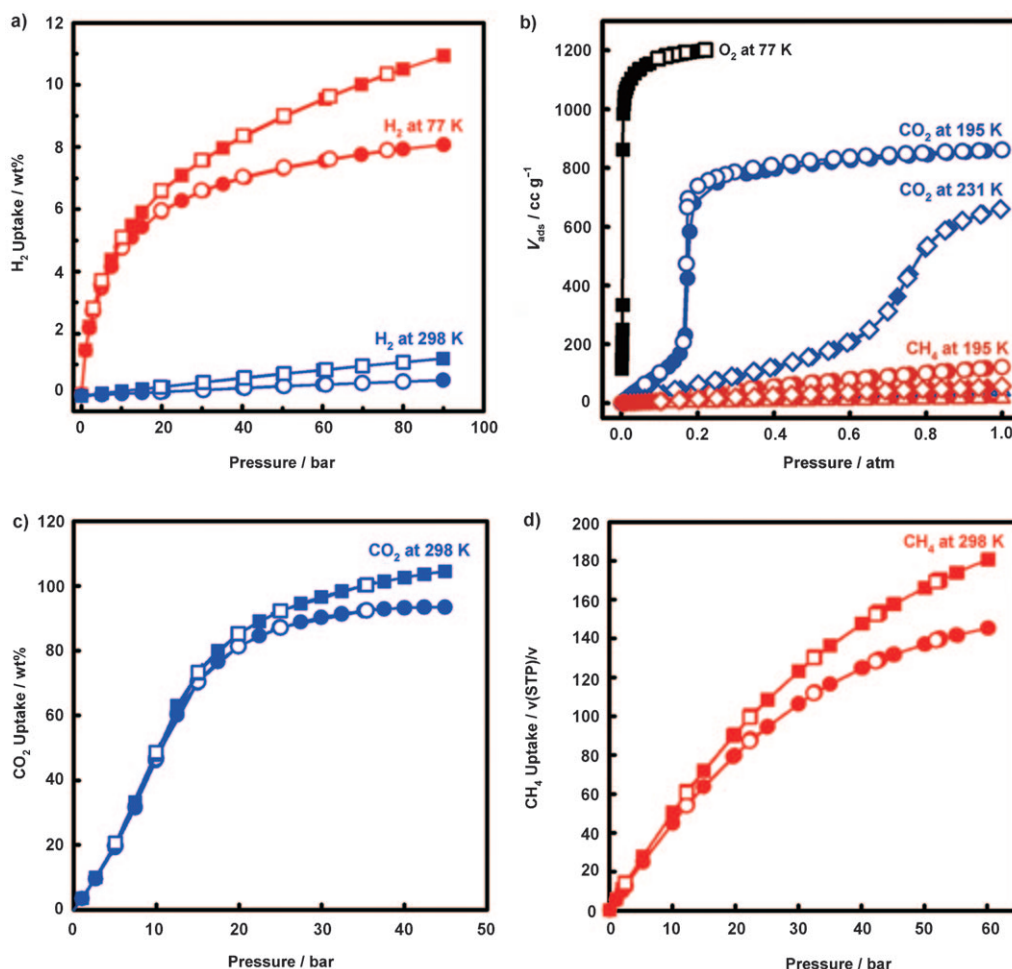


Figure 5. Gas sorption isotherms of **SNU-77H**. a) H_2 sorption at 77 (red) and 298 K (blue) at high pressures. b) O_2 (black) sorption at 77 K and CO_2 (blue) and CH_4 (red) sorption at 195 (●), 231 (◆), and 273 K (▲). c) CO_2 and d) CH_4 sorption at 298 K and high pressures. In a), c), and d), circles and squares represent the excess and the total adsorptions, respectively. Filled shapes: adsorption; open shapes: desorption.

vious reports by Hupp^[14] and Lin^[15] and their co-workers suggest that MOFs that collapse on thermal evacuation or highly flexible MOFs exhibiting a breathing effect would show increased gas sorption capacity when activated by treatment with supercritical CO_2 or freeze-drying than by thermal evacuation methods. The MOF described herein can be applied to the storage of gases as well as to the development of crystalline devices because of its exceptionally high porosity and ability to retain its single-crystal nature.

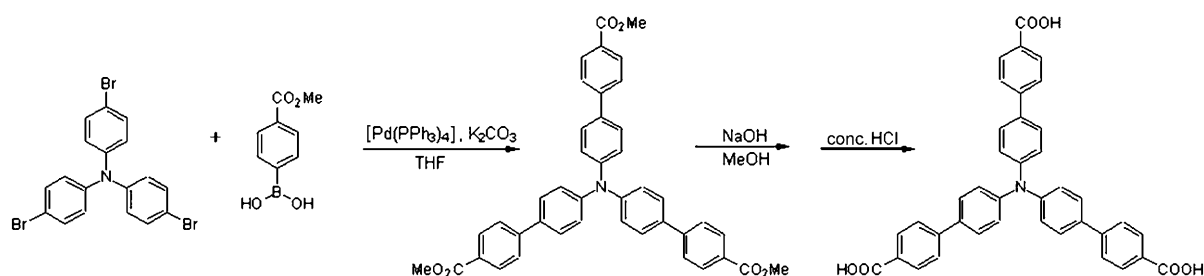
Experimental Section

General methods: All chemicals and solvents used in the syntheses were of reagent grade and used without further purification. Infrared spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer. NMR spectra were measured on a Bruker Spectrospin 300 spectrometer. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 35 UV/Vis spectrophotometer. Emission spectra were recorded with a Perkin–Elmer LS-55 luminescence spectrophotometer. Elemental analyses were performed with a Perkin–Elmer 2400 Series II CHN analyzer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed at a scan rate of 5°Cmin^{-1} by using TGA Q50 and DSC Q10 of TA instruments. Powder X-ray diffraction (PXRD) data were recorded on a Bruker D5005 diffractometer at 40 kV and 40 mA with $\text{Cu}_{\text{K}\alpha}$ radiation ($\lambda = 1.54050 \text{ \AA}$) at a scan rate of 5°min^{-1} and a step size of 0.02° in 2θ .

Synthesis of the novel ligand, tris(4'-carboxybiphenyl)amine (H_3TCBPA): H_3TCBPA was synthesized by the Suzuki–Miyaura coupling reaction,^[37] purified by column chromatography, and characterized by IR and NMR spectra. FTIR (KBr pellet): $\tilde{\nu} = 1687 \text{ cm}^{-1}$ (C=O); ^1H NMR (300 MHz, DMSO): $\delta = 7.23$ (s, 6H), 7.77 (s, 6H), 7.82 (s, 6H), 8.03 ppm (s, 6H).

Synthesis of $[\text{Zn}_4\text{O}(\text{TCBPA})_2] \cdot 19\text{DMA} \cdot 4\text{H}_2\text{O}$ (SNU-77**):** $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (180 mg, 0.61 mmol) and tris(4-carboxybiphenyl)amine (40 mg, 0.070 mmol) were dissolved in anhydrous DMA (7 mL) and the mixture was then placed in a Teflon vessel within the autoclave and heated at 115°C for 2 days. On cooling to room temperature, brown crystals were formed, which were filtered off, washed with anhydrous DMA, and dried briefly in air. Yield: 0.12 g, 54%. FTIR (KBr pellet): $\tilde{\nu} = 2929$ (C–H (DMA)), 1633 (C=O (DMA)), 1600 (O–C=O), 1521 cm^{-1} (C=C); UV/Vis (diffuse reflectance): $\lambda_{\text{max}} = 410 \text{ nm}$; luminescence (solid): $\lambda_{\text{max}} = 477 \text{ nm}$ (excitation at $\lambda_{\text{max}} = 410 \text{ nm}$); elemental analysis calcd (%) for $\text{Zn}_4\text{C}_{154}\text{H}_{227}\text{N}_{21}\text{O}_{36}$: C 57.62, H 7.13, N 9.16; found: C 57.61, H 6.95, N 9.15.



Preparation of $[\text{Zn}_4\text{O}(\text{TCBPA})_2] \cdot 14\text{PhCH}_3 \cdot 3\text{H}_2\text{O}$ (SNU-77): Crystals of as-synthesized SNU-77, which were still in the mother liquor, were transferred into a 20 mL vial. The mother liquor was decanted and the crystals were washed with anhydrous DMA (2×20 mL). The product was immersed in anhydrous toluene (20 mL) for 2 days. During the guest-exchange process, toluene was replenished four times. FTIR (KBr pellet): $\tilde{\nu} = 3026$ (C–H(toluene)), 1599 (O–C=O), 1521 cm^{-1} (C=C); UV/Vis (diffuse reflectance): $\lambda_{\text{max}} = 410$ nm; luminescence (solid): $\lambda_{\text{max}} = 488$ nm (excitation at $\lambda_{\text{max}} = 410$ nm); elemental analysis calcd (%) for $\text{Zn}_4\text{C}_{176}\text{H}_{166}\text{O}_{16}\text{N}_2$: C 74.73, H 5.99, N 0.99; found: C 74.61, H 5.93, N 0.99.

Preparation of $[\text{Zn}_4\text{O}(\text{TCBPA})_2]$ (SNU-77R): Crystals of SNU-77 were introduced into a 9 mm cell of the gas sorption apparatus and evacuated at room temperature under a pressure of 10^{-5} torr for 24 h. FTIR (KBr pellet): $\tilde{\nu} = 1596$ (O–C=O), 1522 cm^{-1} (C=C); UV/Vis (diffuse reflectance): $\lambda_{\text{max}} = 410$ nm; luminescence (solid): $\lambda_{\text{max}} = 512$ nm (excitation at $\lambda_{\text{max}} = 410$ nm); elemental analysis calcd (%) for $\text{Zn}_4\text{C}_{78}\text{H}_{48}\text{O}_{13}\text{N}_2$: C 63.18, H 3.26, N 1.89; found: C 62.73, H 3.18, N 2.03.

Preparation of $[\text{Zn}_4\text{O}(\text{TCBPA})_2]$ (SNU-77S) by the supercritical drying method: Prior to drying, crystals of 1 as-synthesized, which were still in the mother liquor, were transferred into a vial (20 mL). The mother liquor was decanted and the crystals were washed briefly with anhydrous DMA (2×15 mL). The crystals were placed inside the supercritical dryer together with the solvent and the drying chamber was sealed. The temperature and pressure of the chamber were raised to 40°C and 200 bar with CO_2 , above the critical point (31°C, 73 atm) of CO_2 . The chamber was vented at a rate of 15 mL min^{-1} and then filled with CO_2 again. The cycles of refilling with CO_2 , pressurizing, and venting were repeated for 4 h. After drying, the closed container with the dried crystals (SNU-77S) was transferred to a glove bag to prevent exposure of the crystals to air. The gas sorption isotherms were measured without further activation. FTIR (KBr pellet): $\tilde{\nu} = 1603$ (O–C=O), 1521 cm^{-1} (C=C); UV/Vis (diffuse reflectance): $\lambda_{\text{max}} = 410$ nm; luminescence (solid): $\lambda_{\text{max}} = 510$ nm (excitation at $\lambda_{\text{max}} = 410$ nm); elemental analysis calcd (%) for $\text{Zn}_4\text{C}_{78}\text{H}_{48}\text{O}_{13}\text{N}_2$: C 63.18, H 3.26, N 1.89; found: C 62.96, H 3.20, N 2.01.

Preparation of $[\text{Zn}_4\text{O}(\text{TCBPA})_2]$ (SNU-77H): Crystals of SNU-77 were evacuated in a Schlenk tube at a pressure of 10^{-5} torr at room temperature for 1 h and then heated at 110°C for 12 h. FTIR (KBr pellet): $\tilde{\nu} = 1596$ (O–C=O), 1521 cm^{-1} (C=C); UV/Vis (diffuse reflectance): $\lambda_{\text{max}} = 410$ nm; luminescence (solid): $\lambda_{\text{max}} = 506$ nm (excitation at $\lambda_{\text{max}} = 410$ nm); elemental analysis calcd (%) for $\text{Zn}_4\text{C}_{78}\text{H}_{48}\text{O}_{13}\text{N}_2$: C 63.18, H 3.26, N 1.89; found: C 62.82, H 3.01, N 1.97.

X-ray crystallography: The diffraction data of SNU-77, SNU-77', SNU-77R, SNU-77S, and SNU-77H were collected at room temperature with an Enraf–Nonius Kappa CCD diffractometer ($\text{Mo K}\alpha$, $\lambda = 0.71073$ Å, graphite monochromator). For the collection of X-ray diffraction data of SNU-77, the crystal was introduced into a glass capillary together with the mother liquor. To observe the SCSC transformation from SNU-77 to SNU-77', a crystal of SNU-77 was removed from the capillary after its X-ray diffraction data were collected and then it was dropped into toluene in a 1.5 mL vial. After immersion in toluene for 1 day, the crystal (SNU-77') was sealed in a glass capillary together with toluene and the X-ray diffraction data were collected. To observe the SCSC transformation from SNU-77' to SNU-77R, single crystals of SNU-77' were introduced into a 9 mm cell of the gas sorption apparatus and evacuated at room

temperature and a pressure of 10^{-5} torr for 24 h. One of the crystals was coated with epoxy resin immediately and sealed in a glass capillary to prevent exposure of the crystal to air. To observe the SCSC transformation from SNU-77 to SNU-77S, single crystals of SNU-77 were desolvated by the supercritical drying method and then introduced into a glove bag in which one of the crystals was coated with epoxy resin and sealed in the glass capillary. For single-crystal X-ray crystallography of SNU-77H, a single crystal of SNU-77' was introduced into the empty space created at the bottom of the 0.5 mm glass capillary with an open end in which toluene was already filled and then the toluene was removed. The glass capillary with SNU-77' was placed in a Schlenk tube, heated at 110°C under vacuum for 2 h, and then cooled to room temperature. The capillary was taken out from the Schlenk tube and immediately sealed for X-ray crystal data collection. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first 10 frames and then refined by using the whole data set. Frames were integrated and corrected for Lorentzian and polarization effects using DENZO.^[38] The scaling and global refinement of crystal parameters were performed by using SCALEPACK.^[38] No correction for absorption was made. The crystal structures were solved by direct methods^[39] and refined by full-matrix least-squares refinement using the SHELXS-97 computer program.^[40] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically and refined by using a riding model. In SNU-77H, all zinc and carboxylate oxygen atoms were statistically disordered over two sites. The site occupancy factors were given as 0.1667 for the Zn(1) atom, which sits on a three-fold crystallographic axis, and 0.5 for the Zn(2) atom, which sits in a general position. The site occupancy factors were given as 0.5 for all carboxylate oxygen atoms. For SNU-77 and SNU-77', the electron densities of the disordered guest molecules were flattened by using the SQUEEZE option of PLATON.^[29] Therefore, the formula of SNU-77 and SNU-77' were determined on the basis of IR spectroscopy, elemental analyses, and TGA. Although electron densities associated with guest molecules were not observed, two residual electron densities found around the phenyl rings of TCBPA³⁻ in SNU-77H were flattened by using the SQUEEZE option of PLATON,^[29] which provided a slightly lower *R* value than that determined without SQUEEZE. However, geometrical differences with and without the SQUEEZE procedure were not observed and the X-ray crystal structure of SNU-77H after SQUEEZE was the same as that before SQUEEZE.

CCDC-726040 (SNU-77), 726041 (SNU-77'), 771231 (SNU-77R), 771232 (SNU-77S), and 726042 (SNU-77H) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

In situ synchrotron single-crystal X-ray diffraction studies of SNU-77R: Variable-temperature single-crystal X-ray diffraction data were measured with $\lambda = 0.77000$ Å synchrotron radiation on a 6B MX-I ADSC Quantum-210 detector with a silicon (111) double-crystal monochromator at the Pohang Accelerator Laboratory (PAL), Korea. A crystal of SNU-77R was coated with epoxy resin immediately to prevent exposure to air, sealed in a glass capillary, and the X-ray diffraction data were collected at room temperature (293 K). To observe the structural transformation induced by the temperature change, the X-ray diffraction data were collected sequentially at 293, 373, 293, and then 100 K. The temperature was controlled by the cryostream and the sample was maintained at the re-

quired temperature for 2–2.5 h to attain an equilibrium before collecting the X-ray data. The ADSC Quantum-210 ADX program (Ver. 1.96)^[41] was used for data collection and HKL2000 (Ver. 0.98.699)^[38] was used for cell refinement, reduction, and absorption correction. The structures were solved by direct methods^[39] and refined by full-matrix least-squares refinement using the SHELXS-97 computer program.^[40] The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. The hydrogen atoms were positioned geometrically by using a riding model. For the X-ray data measured at 373 and 293 K (2nd), all the zinc and oxygen atoms of TCPBA were statistically disordered over two sites. The site occupancy factors were given as 0.1667 for the Zn(1) atom, which sits on a three-fold crystallographic axis and as 0.5 for the Zn(2) atom, which sits in a general position.

CCDC-783398, -783399, -783400, and -783401 contain the corresponding supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Low-pressure gas sorption measurements: The gas adsorption/desorption experiments were performed on **SNU-77R**, **SNU-77S**, and **SNU-77H** using an automated micropore gas analyzer Autosorb-3B (Quantachrome Instruments). All the gases used were of 99.999 % purity. The N₂ and O₂ sorption isotherms were measured at 77 K. The H₂ sorption isotherms were measured at 77 and 87 K and the CO₂ and CH₄ gas sorption isotherms were measured at 195, 231, 273, and 298 K at each equilibrium pressure by the static volumetric method. During the preparation and handling of the samples we took great care to prevent them from being exposed to air. The samples for the gas sorption experiments were prepared as follows. For **SNU-77R** and **SNU-77H**, crystals of **SNU-77'** in a suspension of toluene were transferred into a 9 mm cell of the gas sorption apparatus by using a glass pipette to prevent exposure of the sample to air. The crystals were evacuated at 10^{−5} torr and room temperature for 24 h to afford **SNU-77R**. For **SNU-77H**, crystals were evacuated at 10^{−5} torr, first at room temperature for 1 h and then at 110 °C for 12 h. The outgassing procedure was repeated between every experiment. After the gas sorption measurement was finished, the weight of the sample was measured precisely. The surface area was determined from the N₂ adsorption isotherm at 77 K by using the Brunauer–Emmett–Teller (BET) and Langmuir models, taking the data in the range $P/P_0 = 0.01–0.1$. The pore volume was determined from the Dubinin–Radushkevich (DR) equation.

Estimation of the isosteric heats of the H₂ adsorption: The isosteric heats of H₂ adsorption were estimated for **SNU-77R**, **SNU-77S**, and **SNU-77H** from the H₂ sorption data measured at 77 and 87 K. A virial-type expression was used [Eq. (1)], which is composed of parameters a_i and b_i that are independent of temperature.^[33,24] In Equation (1), P is the pressure in atm, N is the amount adsorbed H₂ gas in mg g^{−1}, T is the temperature in K, and m and n represent the number of coefficients required to adequately describe the isotherms. The equation was fitted by using the R statistical software package.^[42]

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

To estimate the values of the Q_{st} of H₂ adsorption, Equation (2) was applied in which R is the universal gas constant.

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

Calculation of isosteric heats of the CO₂ and CH₄ adsorption: The isosteric heats of the CO₂ and CH₄ adsorptions by **SNU-77H** were calculated from the adsorption isotherms measured at 195, 231, 273, and 298 K by using the Clausius–Clapeyron equation [Eq. (3)].^[33] As a result of the significantly reduced uptake with increasing temperature, the isosteric heats were estimated only at very low gas coverage range.

$$\frac{\partial(\ln P)}{\partial(1/T)} = -\frac{Q_{st}}{R} \quad (3)$$

High-pressure gas sorption measurements: High-pressure gas sorption isotherms of **SNU-77H** were measured by the gravimetric method using a Rubotherm MSB (magnetic suspension balance) apparatus. The H₂ sorption isotherms were measured at 77 and 298 K, and the CO₂ and CH₄ sorption isotherms were measured at 298 K. All the gases used were of 99.999 % purity and the traces of moisture were removed by using a drying trap filled with 5 Å molecular sieves, which was purchased from the Chromatography Research Supplies (model 500). Desolvated solid **SNU-77H** (more than 200 mg) was quickly introduced into the apparatus and then activated by evacuation at 110 °C under vacuum. Prior to gas sorption measurement, the He isotherm (up to 90 bar) was measured at 298 K to obtain the volume of the framework skeleton. The excess sorption isotherms were measured and corrected for the buoyancy of the system and sample. The buoyancy correction of the sample was made by multiplying the volume of the framework skeleton by the density of the corresponding gas at each pressure and temperature.^[43] In the unit conversion from gravimetric (wt %) to volumetric (g L^{−1}), the crystallographic density of the sample was applied.

Estimation of the total amount of adsorbed gas at high pressures: The total amount of adsorbed gas and the pore volume are expressed in Equations (4) and (5) in which N_{tot} is the total adsorption in wt %, N_{ex} is the excess adsorption in wt %, which is the quantity being measured, d_{gas} is the density of the compressed gas at given temperature and pressure in g cm^{−3}, V_{pore} is the pore volume in cm³ g^{−1}, d_{bulk} is the crystallographic density of the sample, and $d_{skeletal}$ is the skeletal density of the material. The skeletal density can be calculated from Equation (6) in which m is the sample mass expressed in g and $V_{skeletal}$ is the sample volume in cm³, which is determined by using He expansion measured at 298 K up to 100 bar. The d_{bulk} and $d_{skeletal}$ values used to calculate the V_{pore} of **SNU-77H** are 0.586 and 1.491 g cm^{−3}, respectively.

$$N_{tot} = N_{ex} + 100 d_{gas} V_{pore} \quad (4)$$

$$V_{pore} = 1/d_{bulk} - 1/d_{skeletal} \quad (5)$$

$$d_{skeletal} = m/V_{skeletal} \quad (6)$$

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