Solid-state structural transformation doubly triggered by reaction temperature and time in 3D metal-organic frameworks: great enhancement of stability and gas adsorption†

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In this work, we have demonstrated an unprecedented single-crystal-to-single-crystal (SCSC) transformation between two 3D metal–organic frameworks (MOFs). The centrosymmetric IFMC-68 [(Zn4O)2(L)3·10H2O·46DMA) transforms into a chiral IFMC-69 [(Zn4O)2(L)3·10H2O·46DMA) doubly triggered by reaction temperature and time simultaneously in the presence or absence of solvent. To our knowledge, this is the first representative that the non-interpenetrated structure transforms into self-penetrated structure in MOFs. For the first time, we have studied the influence of reaction temperature and time on SCSC transformation, simultaneously, and get the transformation relationship among IFMC-68, IFMC-69 and the intermediate coming from the direct synthesis method and stepwise synthesis method at different temperatures and for different times. Meanwhile, we have achieved the conversion from an air-unstable to air-stable structure. Air-stable IFMC-69 exhibits the selective CO2 uptake over N2 and more excellent gas adsorption ability than IFMC-68. In addition, IFMC-69 shows an efficient capability in reversible adsorption of iodine. The electrical conductivity value (σ) of I2@IFMC-69 is much higher than the pristine MOF and thus is promising for potential semiconductor materials in the future.

Introduction

Single-crystal-to-single-crystal (SCSC) structural transformations, which involve cooperative movements of atoms in the solid state, are very fascinating and one of the hot topics in solid-state chemistry.1 The first report of SCSC transformations was a photoreaction in organic complexes,2 and then the SCSC transformations were extended to other complexes.3 In the past decades, the studies of SCSC structural transformation in metal-organic frameworks (MOFs) have been met with great interest and have developed rapidly, because it allows direct visualization of how the crystal structure is changing during the transformation process.4 Most of these reports are the transformations caused by sliding of layers or the breathing of 3D porous MOFs through guest removal or solvent exchange.5 The SCSC transformations caused by photochemical [2 + 2] cycloadditions generating new organic molecules have been well studied in coordination polymers (or MOFs).6 However, the SCSC transformations including the cleavage and regeneration of coordination bonds remain less common.7 In particular, the SCSC transformations between 3D structures are still quite rare, because it is difficult for 3D MOFs to retain their crystallinity after breaking and forming coordination bonds in the solid phase.8 Hitherto, only limited examples of 3D → 3D SCSC transformations have been observed by the groups of Kim, zur Loye and Chen.9 Therefore, studying the SCSC transformation resulting from the cleavage and regeneration of coordination bonds between 3D structures is one of the most challenging issues in synthetic chemistry and solid-state chemistry.

Almost all MOF materials that have been published thus far are synthesized in a solvothermal black box using the concepts of zeolite chemistry. The reaction process is so mysterious that it prompts us to investigate what on earth happened in it, especially for the crystals synthesis process of SCSC transformation in the solid state. SCSC transformation can be triggered by external stimuli, such as light, heat, guest removal, uptake or exchange, expansion of coordination numbers, oxidation of metal centers, or reactions between the ligands.10 In previous reports on SCSC transformation reactions caused by
heat, chemists have taken into consideration the temperature influences on the reaction. However, SCSC transformation studies involving both the reaction temperature and time are rarely reported, and may help us understand whether the formation process of crystals via SCSC transformation is kinetically or thermodynamically controlled. It is a challenge to find a suitable system to investigate the influence of both reaction temperature and time on the SCSC transformation simultaneously.

Herein, we report an unprecedented SCSC transformation system between two 3D MOFs. The centrosymmetric IFMC-68 \[{\left[ \left[ \text{Zn}_4\text{O}\left(\text{H}_2\text{O}\right)_{10}\right]\right]}_{\text{-46DMA}}\] (IFMC corresponds to Institute of Functional Material Chemistry) transforms into chiral IFMC-69 \[{\left[ \left[ \text{Zn}_4\text{O}\left(\text{H}_2\text{O}\right)_{12}\right]\right]}_{\text{-4DMA}}\] doubly triggered by reaction temperature and time simultaneously in solvent and solid state, where \(\text{H}_4\text{L}\) is methanetetra(tetrakis[4-(carboxyphenyl)oxamethyl]methane acid). To our knowledge, there are no examples of SCSC transformations between 3D structures via the dimerization of Zn10O(CO2)26 clusters by one \(\text{H}_2\text{O}\) molecule. More importantly, we have achieved the conversion from an air-unstable structure to an air-stable one. Meanwhile, it is the first representative that the non-interpenetrated structure transforms into self-penetrated structure in MOFs. Air-stable IFMC-69 exhibits the more excellent gas adsorption ability than IFMC-68. In addition, IFMC-69 shows an efficient capability in reversible adsorption of iodine, and the electrical conductivity value \((\sigma)\) for \(\text{I}_2@\text{IFMC-69}\) is \(2.80 \times 10^{-6} \text{ S cm}^{-1}\), which is obviously higher than that of IFMC-69 \((1.25 \times 10^{-13} \text{ S cm}^{-1})\).

**Results and discussion**

A single-crystal X-ray diffraction study reveals that IFMC-68 crystallizes in the trigonal space group \(R\bar{3}c\). The asymmetric unit (Fig. 1a) contains one \(\text{Zn}_4\text{O}\) cluster consisting of four \(\text{Zn}\) cations, one \(\mu_4\)-\(\text{O}\) atom, and one \(\text{L}^4\) ligand. The tetrahedral \(\text{Zn}_4\text{O}\) cluster is encapsulated by six carboxylate groups from different \(\text{L}^4\) to form a classic \(\text{Zn}_4\text{O}(\text{CO}_2)_{12}\) secondary building unit (SBU). The overall structure of IFMC-68 is a 3D (4,6)-connected network (Fig. S1†) with ideal corundum structure, in which the \(\text{L}^4\) is regarded as a four-connected node and the \(\text{Zn}_4\text{O}(\text{CO}_2)_{12}\) SBU is regarded as a six-connected node. The resultant non-interpenetrated IFMC-68 features a quadrangular opening, and two types of microporous and mesoporous cages (Fig. 1c). With such an assembly, each microporous cage is surrounded by eight mesoporous cages, which results in very high free porosities of 80% in IFMC-68 (Fig. 1e). The structure of IFMC-68 is isomorphic to the mesoporous MOFs in Lan and Xu’s paper, and the cage-based MOF has been reported by the Cao group.

IFMC-69 crystallizes in the chiral space group \(P2\bar{3}\). The asymmetric unit (Fig. 1b) contains four kinds of \(\text{Zn}\) ions, two kinds of \(\mu_4\)-\(\text{O}\) atoms, one \(\text{L}^4\) ligand and one coordination water molecule. \(\text{Zn}1\) and \(\text{Zn}2\) are five-coordinated trigonal bipyramidal geometries, which are surrounded by three carboxylic oxygen atoms from different ligands, one \(\mu_4\)-\(\text{O}\) atom and one water molecule. \(\text{Zn}3\) and \(\text{Zn}4\) show tetrahedral coordinated geometries which are formed by three carboxylic oxygen atoms from different ligands and one \(\mu_4\)-\(\text{O}\) atom. Different from the structure of IFMC-68, there are two \(\text{Zn}_{10}\text{O}(\text{CO}_2)_{26}\) clusters in IFMC-69. These two \(\text{Zn}_{10}\text{O}(\text{CO}_2)_{26}\) clusters are connected by one water molecule to generate a new \([\text{Zn}_{10}\text{O}(\text{CO}_2)_{12}]_{\text{2H}_2\text{O}}\) SBU. To the best of our knowledge, it represents the first example that the classic \(\text{Zn}_{10}\text{O}(\text{CO}_2)_{26}\) SBU connected by water to form a new \([\text{Zn}_{10}\text{O}(\text{CO}_2)_{12}]_{\text{2H}_2\text{O}}\) SBU. One \(\text{Zn}_4\text{O}\) cluster is coordinated by six ligands and one water molecule, which can be regarded as a 7-connected node, and each \(\text{L}^4\) ligand is bonded to four \(\text{Zn}_4\text{O}\) clusters (two kinds of clusters), acting as a 4-connected node. Therefore, the overall 3D framework can be regarded as a (4,7)-connected net (Fig. S2†), which has not been reported yet. In the (4,7)-connected topology, two kinds of rings (in red and green) interpenetrate with each other, and a linker (in purple) connects the two kinds of rings to form a self-penetrated structure of IFMC-69 (Fig. S3†). If regarding the \([\text{Zn}_{10}\text{O}(\text{CO}_2)_{12}]_{\text{2H}_2\text{O}}\) SBU, which is connected by twelve ligands, as a 12-connected node and each \(\text{L}^4\) ligand as a 4-connected node, the 3D framework is going to be a (4,12)-connected topology (Fig. S4†). A more interesting feature in this resultant MOF is that there are interweaved channels along the three directions (Fig. 1f), the diameter of which is 6.46 Å (Fig. 1d and S8†). The calculated free volume in fully desolvated IFMC-69 is 37.9% by PLATON.

Then we perform the further study into the nature of these intricate architectures. When taking no account of the
coordination water molecule in the \([\text{Zn}_4\text{O} (\text{CO}_2)_6]_2\text{H}_2\text{O}\) SBU (Fig. S5c†), one \(\text{Zn}_4\text{O}\) cluster is coordinated by six ligands to be a 6-connected node and each tetratopic ligand is bonded to four \(\text{Zn}_4\text{O}\) clusters (two kinds of clusters) to be a 4-connected node, and this results in a (4,6)-connected 3D MOF (Fig. S5d and S7b†). The whole structure is composed of three parts. Two of them are separated 2-fold units which can coincide with each other by a rotation of 45° in the plane. Additionally, these two units connect with each other by sharing the third part consisting of ligands (shown in black in Fig. S5g†) to form a complicated 3D structure with self-penetrated character (Fig. S5c, S5e and S5f†).

**IFMC-68** was synthesized via solvothermal reactions of semi-rigid carboxylate linker \(\text{H}_4\text{L}\), \(\text{Zn(NO}_3)_2\cdot 6\text{H}_2\text{O}\) and 5 mL DMA or DMF at 85 °C for 72 h. For **IFMC-69**, the other synthetic condition is similar to that for **IFMC-68** only by increasing the temperature to 140 °C. Owing to the similarity and the continuity of the synthesis process of these two crystals, we discuss the products obtained at 140 °C for different time. Powder X-ray diffraction (PXRD) data (Fig. 2) shows the products are pure **IFMC-68** heated at 140 °C for 24 h. After 48 h, PXRD of the products shows that they are the intermediates including **IFMC-68** and **IFMC-69**, and the small single crystals in the intermediate are determined as **IFMC-68** by X-ray single-crystal diffraction. More importantly, we obtain the photos of the intermediates, which provide more direct evidence for the existence of intermediates (Fig. 2). The single crystal in red circle is determined as **IFMC-69** by X-ray single-crystal diffraction, and the remaining part is **IFMC-68**. After 72 h, **IFMC-69** has been completely obtained based on the original reactant \(\text{H}_4\text{L}\) and \(\text{Zn(NO}_3)_2\cdot 6\text{H}_2\text{O}\). These investigation results demonstrate **IFMC-68** is a precursor in the formation process of **IFMC-69** in direct synthesis method. There may be a SCSC transformation from **IFMC-68** to **IFMC-69** during the process.

Hence, we assume that **IFMC-69** may be obtained by using the step-wise method. The as-synthesized **IFMC-68** (50 mg) was put into a Teflon liner with 5 mL DMA and heated at 140 °C for 72 h. As expected, **IFMC-69** is successfully obtained from the precursor of **IFMC-68**, and it may be a SCSC transformation. Experiments were performed following the reported method to explore whether the transformation from **IFMC-68** to **IFMC-69** belongs to a solid to solid mechanism or a dissolution and recrystallization mechanism.† One crystal of **IFMC-68** was selected and inserted into a 0.8 mm diameter melting point tube 0.3 mL DMA (Fig. 3a), and then was heated at 140 °C for 72 h. The outline of the gathered crystals remained the same as **IFMC-68**. When pressed lightly, we got the dispersive little single crystals of **IFMC-69** which can be confirmed by X-ray single-crystal analysis (Fig. 3b). The photographs taken under the optical microscope prove that there is no dissolving or recrystallizing of any crystals, so it is a real SCSC transformation (Fig. 3). The PXRD results show that the SCSC transformation from **IFMC-68** to **IFMC-69** can be successfully achieved in DMF or DMA, but failed in ethanol or methanol (Fig. S9†).

We try to achieve this SCSC transformation in solid-state without any solvent. The single crystal of **IFMC-68** was selected and sealed in a 0.8 mm diameter melting point tube without solvent (Fig. 3c), and then it was heated at 140 °C for 72 h. The result of this solid transformation was similar to the solvent transformation described above, except the crystallization of **IFMC-69** changed a little, meanwhile the cubic **IFMC-68** transformed to smaller irregular shape microcrystalline of **IFMC-69** (Fig. 3d). PXRD results indicate that the as-synthesized samples match the simulated pattern of **IFMC-69** very well (Fig. S10†). The aforementioned transformation process can be also achieved in a sealed Teflon liner, and it proves that the solid-state SCSC transformation from **IFMC-68** to **IFMC-69** can be realized by thermal method without any solvent.

Furthermore, we discussed the reaction conditions of the SCSC transformation from **IFMC-68** to **IFMC-69**. Firstly, **IFMC-68** was heated at different temperatures ranging from 85 °C to 160 °C for 72 h in Teflon reactor without solvent, and the PXRD

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**Fig. 2** Powder X-ray diffraction patterns of simulated **IFMC-68** (dark red), the products from direct synthesis method at 140 °C for 24 h (green), 48 h (pink), 72 h (red) and simulated **IFMC-69** (blue). Photos of crystals (left) after heating to 140 °C for 24 h, 48 h and 72 h, respectively.

**Fig. 3** Photographs of the SCSC transformation from **IFMC-68** to **IFMC-69**. Photos of single crystal of **IFMC-68** sealed in a melting point tube before (left) and after (right) heating at 140 °C for 72 h in 0.3 mL DMA (a), and without solvent (c), respectively. Enlarged photos of crystals sealed in a melting point tube and dispersive crystals heating at 140 °C for 72 h in DMA (b), and without solvent (d), respectively.
patterns reveal that the SCSC transformation can take place from 140 °C to 160 °C (Fig. S10†). Then 140 °C was selected as a representative temperature to investigate the SCSC transformation in solid state. We also try to monitor the SCSC transformation by variable-temperature (VT)-PXRD of IFMC-68 under air, but the results show IFMC-68 can not transform into IFMC-69 (Fig. S11†). This may be because the testing time is so short that the transformation does not have enough time to complete. Keeping this in mind, we supposed that the reaction time may be another important factor during the SCSC transformation. Then the influence of the reaction time has been studied. When IFMC-68 is heated at 140 °C without solvent for 6 h, it is still IFMC-68; the product is intermediate for 12–21 h; after 24 h until up to 72 h, IFMC-68 is attained. The area between IFMC-68 and IFMC-69 represents the synthesis condition for the intermediate. Similarly, for the step-wise synthesis method [IFMC-68] in DMA or DMF (Fig. S12†) and without solvent (Fig. S14†), the areas between IFMC-68 and IFMC-69 represent the synthesis condition for the intermediate, respectively. To sum up, the SCSC transformations between IFMC-68 and IFMC-69 are triggered by reaction temperature and time simultaneously in either solvent or solid state. When 50 mg IFMC-68 was sealed in a Teflon liner with 5 mL DMA and heated at 85, 100, 120 or 140 °C for 72 h, IFMC-69 still remained. IFMC-69 cannot turn to IFMC-68 in solvent under lower temperature. Therefore, the SCSC transformation is irreversible.

According to the phenomenon occurring in the SCSC transformation, we suppose the solvent molecules move faster in channels with heating, which results in the partial coordination bonds of unstable IFMC-68 breaking. Then different Zn4O(CO2)6 SBU moves closer to each other and coordinate with the water molecules to form new [Zn4O(CO2)6]2H2O SBUs which recombine to generate the new compound (IFMC-69) in certain time. IFMC-68 is a kinetic product, formed easily from the components at relatively low temperature. With the increasing the time and temperature, this unstable product progressively converts into the thermodynamic product of IFMC-69. During the SCSC transformation process, the transformation from the Zn4O(CO2)6 SBU to the [Zn4O(CO2)6]2H2O SBU is very crucial. In order to confirm this prediction, quantum chemical calculations have been performed to simulate the reaction on the basis of density functional theory method (DFT) by selecting Zn4O(CO2)6 SBU and [Zn4O(CO2)6]2H2O SBU as simple models, with the benzenes substituted by H atoms (Fig. S15†). All calculations are performed at PCM/B3LYP/[LANL2DZ(Zn)/6-31 + g**(O, H, C)] level with Gaussian 09 software package. According to the experimental conditions reported above, the formation of IFMC-69 is carried out at 140 °C. Thus the calculation condition

![Fig. 4 Powder X-ray diffraction patterns of simulated IFMC-68 (dark red), IFMC-68 in a sealed Teflon reactor heated at 140 °C for 6 h (gray), 12 h (blue), 18 h (green), 21 h (purple), 24 h (pink), 48 h (dark green) and 72 h (orange), and simulated IFMC-69 (red).](image)

Scheme 1 The scheme of SCSC transformation between IFMC-68 and IFMC-69.
has been set at 438.15 K and the standard atmosphere pressure. The calculated results demonstrate the generation process of the [Zn₄O(CO₂)₆]H₂O SBU is strongly exothermic, with enthalpy of −180.60 kcal mol⁻¹. As a result, this enthalpic contribution may drive the formation of the complex IFMC-69. Moreover, ΔrG is an important parameter in thermodynamic analysis, and the Gibbs free energy for this reaction shows that the formation of the [Zn₄O(CO₂)₆]H₂O SBU is spontaneous with value of −51.94 kcal mol⁻¹. Therefore, it is clear from the theoretical simulations that the formation of IFMC-69 is thermodynamically favorable.

Stability is one of the most crucial properties in the practical application for MOF materials. Therefore the measurements of the stability based on IFMC-68 and IFMC-69 in air have also been conducted. When IFMC-68 is exposed in air for 6 h, the framework is collapsed (Fig. S16†). Nevertheless IFMC-69 can retain the integrity of the framework well after exposure in air for 2 months (Fig. S17†), presenting remarkable stability. Through the SCSC transformation we have achieved the conversion from an air-unstable MOF to an air-stable MOF.

The structure features of these two compounds encourage us to study the gas sorption properties of the evacuated frameworks. The samples were fully activated by the procedure described in ESI†. The PXRD results indicate that the integrity of IFMC-69 was well maintained (Fig. S19†), but the framework of IFMC-68 collapsed to some extent since some peaks of activated IFMC-68 weakened obviously (Fig. S18†). N₂ adsorption of IFMC-68 and IFMC-69 were carried out at 77 K (Fig. 5a). On the contrary to the porosity of these two compounds calculated by PLATON,¹² the high porosity crystal IFMC-68 only has a N₂ adsorption amount of 4.50 cm³ g⁻¹. This may be attributed to the collapse of the framework of IFMC-68 after the removal of the solvent molecules, which is consistent with the PXRD results (Fig. S18†). All of these results (the stability of these two compounds) well agree with those from the theoretical calculations. IFMC-69 displays typical Type-I sorption isotherm for microporous materials. The BET and Langmuir surface areas are 581.00 and 664.33 m² g⁻¹, respectively, and the pore volume of IFMC-69 is 0.25 cm³ g⁻¹. The adsorption amount of N₂ at saturation is approximately 165.9 cm³ g⁻¹, which is equivalent to 71.4 N₂ per unit cell. Using the Horváth–Kawazoe (HK) method on the N₂ adsorption isotherms, the pore size distribution of IFMC-69 shows its pore size is about 5.9 Å (Fig. S20†).

The H₂ adsorption amount of IFMC-69 is 119.33 cm³ g⁻¹ (1.07 wt%) and 85.46 cm³ g⁻¹ (0.74 wt%) at 77 K and 87 K (Fig. S21†), which corresponds to 51.3 and 36.8 H₂ per unit cell, respectively. The H₂ adsorption enthalpy of IFMC-69 is 6.63 kJ mol⁻¹ at zero coverage, which is calculated from a variant of the Clausius–Clapeyron equation,¹⁷ shown in Fig. S22b†.

We also study the possible application for IFMC-69 on selective gas separation. As shown in Fig. 5b, the N₂ and CO₂ sorption isotherms were measured at 273 K and 298 K, respectively, and the adsorption data was listed in Table S2.† To our delight, the CO₂ uptake capacity is much higher than that of N₂. The calculated CO₂/N₂ adsorption selectivity is 32.7 : 1 at 298 K, and it is higher than those of zeolitic imidazolate frameworks (ZIFs) with colloidal cages, ZIF-100 (25.0 ± 2.4 : 1) and ZIF-95 (18.0 ± 1.7 : 1),¹⁸ which is regarded as excellent selective carbon dioxide reservoir. The CO₂/N₂ adsorption selectivity for IFMC-69 is also better than that of our reported zeolite-like MOF (IFMC-1, 26.9 : 1 at 298 K).¹⁹ In addition, the distinct difference of adsorption capacities between CO₂ and N₂ prompts us to survey the enthalpy of CO₂ adsorption. The CO₂ adsorption enthalpy of IFMC-69 is 17.45 kJ mol⁻¹ at zero coverage (Fig. S22a†). All the data reveals that IFMC-69 shows the ability to absorb CO₂ selectively and may be used for potential materials to separate the CO₂/N₂ mixture.

The existing microporous pores of IFMC-69 make it suitable as a host for absorbing small molecules. When IFMC-69 (100 mg) was immersed in a hexane solution of I₂ (3 mL, 0.01 mol L⁻¹) at room temperature, colorless IFMC-69 gradually intensified to dark brown, and the dark purple solution faded in 2 h (Fig. S23a†). The entry of I₂ into the IFMC-69 host framework leads to a distinct decrease of the emission intensity with the guest inclusion amount increasing (Fig. S26b†), which is ascribed to the host–guest photoinduced electron transfer (PET) effect.¹⁸ TGA analyses (Fig. S29†) show that the encapsulated amount of I₂ is 29.48% and each unit cell in IFMC-69 can accommodate about 13.86 I₂ molecules according to the molar ratios of I₂/Zn. IFMC-68 can also adsorb I₂, however, the framework of IFMC-68 partially collapsed as adsorbing I₂, just as shown in the picture (Fig. S30†). So we mainly study the

Fig. 5  (a) The N₂ gas–sorption isotherms for IFMC-68 and IFMC-69 at 77 K, 1 atm. (b) CO₂ and N₂ sorption isotherms of IFMC-69 at different temperatures (blue: CO₂, 273 K; pink: CO₂, 298 K; red: N₂, 273 K; black: N₂, 298 K). The filled and open squares represent adsorption and desorption branches, respectively.
property of adsorbing I$_2$ for IFMC-69. When the crystals of L$_2$@IFMC-69 were soaked in dry ethanol, the color of the crystals changed gradually from dark brown to light yellow in about 2.5 h and the colorless solution deepened into dark brown (Fig. S23b†). The release of I$_2$ resulted in the emission spectra intensity recovering by degrees (Fig. S26c†), the concentration of I$_2$ in ethanol increased with time. So the photographs and luminescent spectrum for IFMC-69 releasing I$_2$ demonstrated that the I$_2$ sorption progress of IFMC-69 is reversible. The tests of the electrical conductivity values ($\sigma$) of L$_2$@IFMC-69 and IFMC-69 were carried out. Notably, we get the electrical conductivity values ($\sigma$) of 2.80 \times 10^{-8} \text{ S cm}^{-1} for L$_2$@IFMC-69 which is 2.24 \times 10^{7} times higher than IFMC-69 (1.25 \times 10^{-13} \text{ S cm}^{-1}). When IFMC-69 is adsorbing I$_2$, the potential intermolecular interactions between I$_2$ and \textpi-electron walls are important, as they allow a single path for I$_2$ molecules to access and be restricted within well-regulated narrow limits within the channels, inducing $n \rightarrow \sigma^*$ charge transfer (CT). Such an arrangement can result in cooperative electrical conductivity for L$_2$@IFMC-69. Therefore, L$_2$@IFMC-69 could be used for potential semiconductor materials in the future.

**Experimental**

**Synthesis of IFMC-68** ([Zn$_2$(CO$_2$)$_6$]-H$_2$O-4DMA)

A solution of Zn(NO$_3$)$_2$-6H$_2$O (0.150 g, 0.504 mmol) and H$_2$L (0.050 g, 0.081 mmol) in DMA (5 mL) was heated at 85 °C for 72 h in a Teflon-lined steel container. The resulting colorless crystals were collected, washed with Et$_2$O, and dried at room temperature (yield: 79% based on H$_4$L). Elemental microanalysis for [Zn$_2$(CO$_2$)$_6$]-H$_2$O-4DMA = C$_{283}$H$_{506}$O$_{94}$N$_{46}$Zn$_8$, calculated (%): C, 51.68; H, 7.69; N, 9.80; Zn, 7.96. Found (%): C, 51.36; H, 7.97; O, 23.15; N, 9.83; Zn, 7.69. IR (cm$^{-1}$): 3438.95 (m), 2937.81 (w), 1667.23 (s), 1604.47 (s), 1559.61 (s), 1409.51 (s), 1304.52 (m), 1243.34 (s), 1170.22 (m), 1077.46 (w), 1030.91 (m), 925.29 (w), 856.92 (w), 782.54 (m), 712.24 (m), 653.26 (s), 544.47 (s), 406.85 (s).

**Synthesis of IFMC-69** ([Zn$_2$(CO$_2$)$_6$]H$_2$O-4DMA)

A solution of Zn(NO$_3$)$_2$-6H$_2$O (0.150 g, 0.504 mmol) and H$_4$L (0.050 g, 0.081 mmol) in DMA (5 mL) was heated at 140 °C for 72 h in a Teflon-lined steel container. The resulting colorless crystals were collected, washed with Et$_2$O, and dried at room temperature (yield; 63% based on H$_4$L). Elemental microanalysis for [Zn$_2$(CO$_2$)$_6$]H$_2$O-4DMA = C$_{283}$H$_{506}$O$_{94}$N$_{46}$Zn$_8$, calculated (%): C, 49.75; H, 4.03; O, 25.36; N, 2.02; Zn, 18.84. Found (%): C, 51.36; H, 7.97; O, 23.15; N, 9.83; Zn, 7.69. IR (cm$^{-1}$): 3438.95 (m), 2937.81 (w), 1667.23 (s), 1604.47 (s), 1559.61 (s), 1409.51 (s), 1304.52 (m), 1243.34 (s), 1170.22 (m), 1077.46 (w), 1030.91 (m), 925.29 (w), 856.92 (w), 782.54 (m), 712.24 (m), 653.26 (s), 544.47 (s), 406.85 (s).

**The process of SCSC transformation**

Method 1: 50 mg IFMC-68 was sealed in a Teflon liner with 5 mL DMA and heated at 140 °C for 72 h, the colorless block single crystals of IFMC-68 were collected.

Method 2: 50 mg IFMC-68 was sealed in a Teflon liner without solvent and heated at 140 °C for 24 h, the colorless block single crystals of IFMC-69 were collected.

**Conclusions**

In summary, we have reported here an interesting example of a solid-state SCSC transformation from an achiral MOF into a chiral MOF. To our knowledge, it is the first representative that the non-interpenetrated structure transforms into a self-penetrated structure in MOFs. There are the dimerization of Zn$_2$O clusters [Zn$_2$O(CO$_2$)$_6$]$_2$H$_2$O in IFMC-69, and it represents the first example that the classic Zn$_2$O(CO$_2$)$_6$ SBU connected by water. More importantly, we have achieved the conversion from an air-unstable structure to an air-stable one, and the air-stable IFMC-69 exhibits the selective CO$_2$ uptake over N$_2$ and more excellent gas adsorption ability than IFMC-68. We unprecedentedly studied the influence of reaction temperature and time on SCSC transformation simultaneously, and then get the transformation relationship diagrams of IFMC-68, IFMC-69 and the intermediate coming from the direct synthesis method and stepwise synthesis method based on different temperatures and time. Unusually, it is doubly triggered by reaction temperature and time simultaneously in either solvent or solid-state. I$_2$ adsorption experiments of IFMC-69 exhibit a reversible process, and the electrical conductivity value ($\sigma$) of L$_2$@IFMC-69 is much higher than that of IFMC-69. Therefore, L$_2$@IFMC-69 can be used for potential semiconductor materials. Taking advantage of the above-mentioned study, the progress and mechanism of the SCSC transformation have been well understood, which can help us to learn more about the conversion nature of SCSC transformation and synthesize more SCSC materials in the future.

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**Notes and references**

† Crystal data for IFMC-68: C$_{6576.33}$H$_{506}$O$_{94}$N$_{46}$Zn$_8$, M = 6576.33, trinodal, space group R3c, a = 26.660(9) Å, c = 86.622(4) Å, V = 53 355(9) Å$^3$, Z = 12, $\mu = 0.554$ mm$^{-1}$, $\omega_r = 14.47$ Mg m$^{-3}$, $F(000) = 86379$, 10 440 unique ($R_{int} = 0.1222$), $R_1 = 0.1675$, $wR_2 = 0.0780$ [I $> 2\sigma (I)$], GOF = 0.700. Max/min residual electron density 0.234 and $-0.177$ e Å$^{-3}$. A total of 10 440 data were measured in the range 1.29 < $\theta$ < 24.98°.

Crystal data for IFMC-69: C$_{1129.84}$H$_{123.4}$O$_{46}$N$_{46}$Zn$_8$, M = 2776.23, cubic, space group P2$_1$2$_1$2$_1$, a = 23.9647(14) Å, V = 13 763.1(14) Å$^3$, Z = 12, $\mu = 1.434$ mm$^{-1}$, $\omega_r = 1.161$ Mg m$^{-3}$, $F(000) = 70389$, 8180 unique ($R_{int} = 0.1134$), $R_1 = 0.1697$, $wR_2 = 0.0780$ [I $> 2\sigma (I)$], GOF = 0.700. Max/min residual electron density 0.234 and $-0.177$ e Å$^{-3}$. A total of 10 440 data were measured in the range 1.29 < $\theta$ < 24.98°.

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