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Solvent-induced single-crystal to single-crystal transformation of a Zn₄O-containing doubly interpenetrated metal-organic framework with a *pcu* net

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Guest molecules in a metal-organic framework (MOF), [Zn₄O(CPMA)₃]·6DMF (DMF = *N,N*-dimethylformamide), with an interpenetrating *pcu* net were exchanged with benzene, *n*-hexane, and methanol in a single-crystal to single-crystal (SC-SC) manner, which involved the sliding motion of the interpenetrating network, as well as the dynamic movements of the molecular components, and were triggered by host-guest interactions.

Metal-organic frameworks (MOFs), which respond to external stimuli such as guest removal/reintroduction, guest exchange, oxidation, pressure, temperature, and light are potentially viable candidates for applications in sensing, separation, catalysis, and sorption.[1] The structural rearrangement of molecular components responding to a specific stimulus exerts an immediate effect on the chemical or physical properties of MOFs.[2] Thus, direct observations of structural changes in MOFs using single-crystal X-ray diffraction (SCD) facilitate the understanding of their behaviours, and aid in the design of MOFs with superior performance. Over the past decade after Fijita's and Suh's groups reported the first single-crystal to single-crystal to single-crystal (SC-SC) transformation phenomena for the coordination polymers,[3] numerous examples SC-SC transformations have been reported,[4-10] such as those on guest removal,[5] guest exchange,[6] temperature change,[7] ligand exchange,[8] and metal ion exchange,[9] and addition of metal ions and anions.[10]

The guest-induced dynamic structural changes of MOFs are the important phenomena that can be applied for sensor technologies. If the transformation occurs in a SC-SC manner on guest-exchange, it can provide meaningful and direct structural information for the property change such as a pore structure, luminescence, and magnetism. The SC-SC transformation occurs only when the framework is robust yet flexible in solvent exchange. In this context, interpenetrating MOFs can serve as appropriate systems, as several interesting observations regarding the same have been reported.[11-14] For example, Kitagawa *et al.* reported an α-polonium-type doubly interpenetrated 3-D MOF,[12] which retained single crystallinity during dehydration and rehydration with a concomitant colour change; moreover, the anion exchange between N(CN)₂⁻ and N₃⁻ induced slippage of the two independent networks and an increase in channel size. The same group developed the flexible doubly interpenetrated porous framework for a chemosensor by using its structural dynamics in response to the incorporation of chemically diverse analytes, which were proved by SCD studies.[13] Another interesting interpenetrating MOF showing SC-SC transformations was reported by Barbour's group.[14] As-
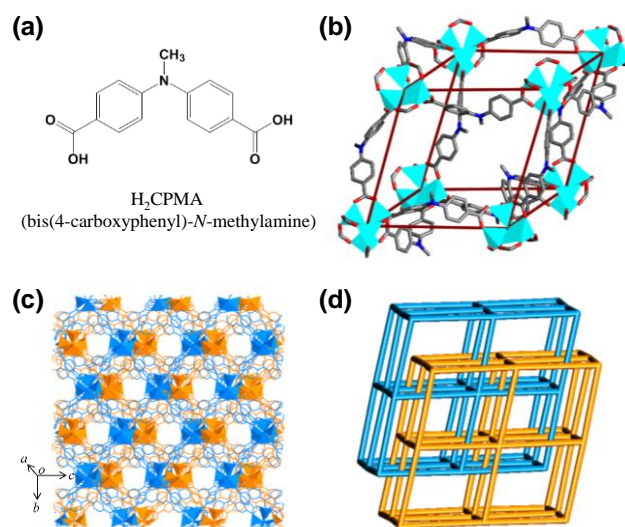

Fig. 1 (a) Organic ligand H₂CPMA. (b) A single network unit with **pcu** topology composed of Zn4O clusters and CPMA²⁻ ditopic ligands. (c) - (d) Doubly interpenetrated 3D framework and its simplified view.

synthesized doubly interpenetrated MOF converted to its triply interpenetrated analogue upon desolvation, as monitored by SCD, and its conversion mechanism was proposed by computational results.

Previously, we published a paper regarding SC-SC transformations of a Li-based MOF upon the immersion of explosive nitro compounds.[15] The results clearly revealed that the change of its fluorescence properties was originated by the newly formed host-guest interactions. This interesting behaviour was attributed to the flexible ligand, bis(4-carboxyphenyl)-*N*-methylamine (H$_2$CPMA), which contains electron-donating and withdrawing groups simultaneously, and also has the rotating sites on a tertiary amine and carboxylate groups (Fig. 1a). Thus, in this study, we chose the same flexible CPMA ligand to build a new 3-D doubly interpenetrated MOF, which was expected to exhibit dynamic structural changes upon guest-exchange with organic solvents. In order to explore the type and strength of the interactions with the phenyl rings in CPMA^{2-}, benzene, hexane, and methanol were selected as exchanging solvents. Due to the SC-SC transformation upon guest-exchange, the effects of host-guest interactions on the motions of the molecular components in the coordination framework were directly observed.

The solvothermal reaction of Zn(NO$_3$)$_2$·6H$_2$O and H$_2$CPMA in DMF (DMF = *N,N*-dimethylformamide) resulted in deep-orange coloured crystals of [Zn$_4$O(CPMA)$_3$]·6DMF (**1**), based on the elemental analysis result. SCD analysis revealed that **1** crystallized in trigonal space group *R*32 and had a **pcu** net topology comprised of Zn$_4$O clusters as an octahedral secondary building unit (SBU) and CPMA^{2-} ditopic ligands (Fig. 1b). The asymmetric unit of **1** contained two kinds of Zn$_4$O clusters with one third occupancy for each type of cluster, two CPMA^{2-} ligands, as well as disordered solvent molecules. Even though the electron densities of some guest solvent molecules were observed, they could not be suitably modelled owing to severe disorders. Thus, the SQUEEZE option of PLATON was used to remove the electron densities in the void.[16] The **pcu** net was distorted to a parallelepiped structure, due to the curved dicarboxylate ligand, CPMA^{2-} (Fig. 1b), and the framework was doubly interpenetrated to generate curved 3-D channels (Fig. 1c and d). There were π-π interactions between the phenyl rings of CPMA^{2-} belonging to two interpenetrated nets (shortest C···C distances, 3.519–3.703 Å; dihedral angles, 58.88–83.37°) (Fig. S1). PLATON calculations indicated that **1** contained 48.4% void space (103333.5 Å^3 per unit cell volume), which was occupied by the guest molecules. As seen in the thermogravimetric analysis (TGA) trace of as-synthesized **1** (Fig. S2, ESI†), the guest solvent molecules were completely removed upon heating from room temperature to ca. 150 °C with an experimentally determined weight loss of 28.7%, which was in good agreement with the calculated weight loss of 28.8%. However, the N$_2$-sorption isotherm of dried **1** revealed no porosity, because **1** showed flexible, as evidenced by the X-ray powder diffraction (XRPD) patterns shown in Fig. S3. Since dried MOF **1** lost transparency as well as single crystallinity, its SCD could not
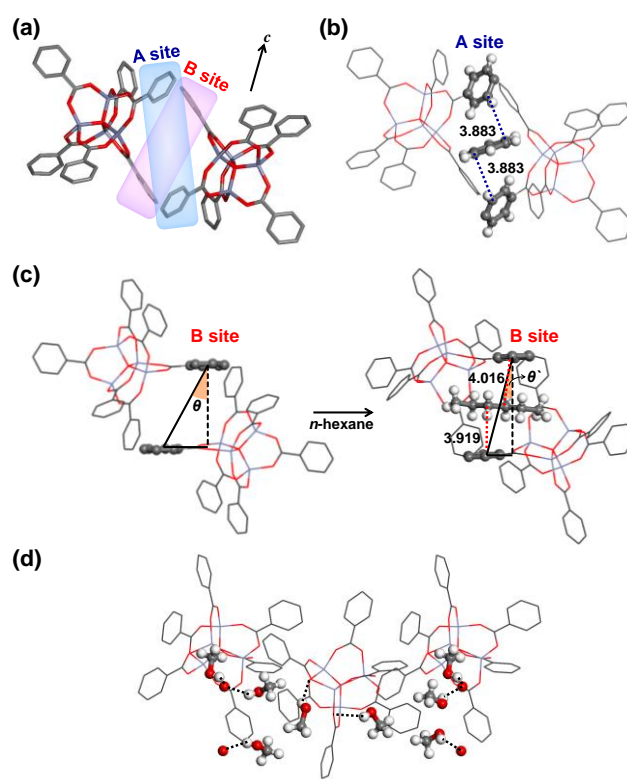

Fig. 2 Host-guest and guest-guest interactions in (a) **1**, (b) **1**$_{benzene}$, (c) **1**$_{hexane}$, and (d) **1**$_{MeOH}$. In (c), θ and θ' are the offset angles of the two phenyl rings. Colour scheme: C (grey), O (red), H (white), Zn (purple).

be obtained. However, the original structure of **1** was restored upon exposure to DMF vapour for 3 days at room temperature, indicating the reversibility of the structural movements.

As revealed by guest removal and re-immersion experiments, **1** had a flexible structure, which was strongly influenced by the presence of guest molecules (Figs. S4-6). In order to determine the effects of different types of guest molecules on the structural changes, guest exchange experiments were conducted. When single crystal **1** was immersed in benzene, hexane, and methanol, in which **1** was insoluble, its crystallinity was retained to result in **1**$_{benzene}$, **1**$_{hexane}$, and **1**$_{MeOH}$, respectively, which were suitable for SCD analysis. The exchange process was traced by Fourier transform nuclear magnetic resonance (FT-NMR), and the result revealed the exchange was terminated in three days (Fig. S7). After solvent-exchange, Fourier transform infrared (FT-IR) spectroscopy (Fig. S8) revealed that the C=O stretching vibration of DMF molecules at 1661 cm^{-1} in **1** clearly disappeared. Instead, new peaks corresponding to the exchanged guest molecules appeared at ~3090 cm^{-1} for benzene ($\nu_{C-H(benzene)}$), ~2990 cm^{-1} for *n*-hexane ($\nu_{C-H(hexane)}$), and ~3340 cm^{-1} for methanol ($\nu_{O-H(methanol)}$). During the guest-exchange, possibility of dissolution and recrystallization of **1** in the new solvents was excluded by photographs obtained with an optical microscope during the immersion of the crystals, which also indicated the preservation of single-crystallinity of **1** during the exchange process (Fig. S9).

Table 1. Selected crystal parameters for **1**, **1**$_{benzene}$, **1**$_{hexane}$, and **1**$_{MeOH}$.

	$a = b$ (Å)	c (Å)	Cell volume (Å³)	Void volume (Å³)[a]	Intraframework O···O distance (Å³)[b]			Interframework O···O distance (Å³)[b]		Desolvating temperature (°C)[c]	Boiling point (°C)
					①-②	②-③	①-④	④-⑤	①-⑤		
1 (DMF)	18.985(3)	68.340(14)	21331(6)	10333.5 (48.4%)	15.539	16.080	33.794	12.104	21.690	150	152
1$_{benzene}$	19.168(3)	67.695(13)	21540(6)	10814.4 (50.2%)	15.582	16.029	33.535	12.519	21.016	100	80.1
1$_{hexane}$	18.653(3)	65.066(13)	19605(6)	8301.0 (42.3%)	15.283	15.283	32.533	11.000	21.533	170	68.5
1$_{MeOH}$	18.118(3)	67.542(14)	19202(5)	7865.3 (41.0%)	15.367	15.367	33.771	11.119	22.652	60	64.7

[a] Calculated by *PLATON*
[b] The numbering was indicated in the right figure.
[c] The desolvating temperature of guest molecules from MOF **1** was determined by TGA.
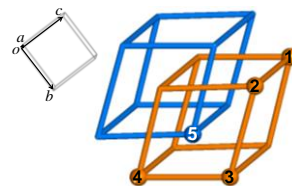
SCD analysis revealed the dynamic movement of the interpenetrated nets (Fig. 2) upon the guest-exchange. In the structure of **1**, the adjacent interpenetrated nets created two interesting spaces, which were composed of two phenyl rings from each net (Fig. 2a). In the A site, a pair of two phenyl rings had an edge-to-edge geometry with a dihedral angle of 64.07°, but in the B site the phenyl rings were parallel to each other with a dihedral angle of 5.06°, creating a face-to-face geometry with an offset angle of 29.30°. These sites subsequently acted as important spaces for exchanged guest molecules to selectively fit into, depending on the preferred interactions. In **1**$_{benzene}$, benzene molecules were located in A sites with edge-to-face π−π interactions with two phenyl rings from CPMA ligands (Fig. 2b) (shortest C···C distances, 3.883 Å; dihedral angles, 47.99°). Meanwhile, the dihedral angle between two phenyl rings of the framework showed minor changes as 66.36°. This was sufficient for the guest molecules to form the strongest π−π interactions without significant alteration of the host framework because edge-to-face π-π interactions are more stable than face-to-face interactions.[17] In **1**$_{hexane}$, the included *n*-hexane molecules formed CH−π interactions with two phenyl rings of CPMA^{2-} ligands in the B sites (shortest C···C distances, 3.919, and 4.016 Å) (Fig. 2c). The space between the parallel phenyl rings in the B sites provided the hexane molecules with the proper environment for effective CH−π interactions with both phenyl rings. Moreover, the offset angle of two phenyl rings changed from 29.30° (θ) to 20.02° (θ'), and the distance between the two phenyl rings became longer from 7.668 to 8.062 Å, which provides enough space to accommodate hexane molecules and constructs CH−π interactions more efficiently (Fig. 2c). This offset angle change is closely related with the cell parameter changes. However, in **1**$_{MeOH}$, there were no significant interactions between the MeOH molecules and the host framework except for a hydrogen bond of one methanol molecule with a carboxylate oxygen atom (Fig. 2d). Instead, the

included methanol molecules participated in guest-guest interactions with water molecules via hydrogen bonding, thus forming stronger host-host interactions via the π−π interactions between the phenyl rings (Fig. S10). TGA data of the guest-exchanged compounds also reflected the strength of the host-guest interaction depending on the guest molecules. The temperature at which the host lost its guest molecules was shifted from their boiling point depending on the strength of host-guest interactions (Fig. S11 and Table 1); in **1**$_{benzene}$, the included benzene molecules were liberated at 100 °C while the boiling point of neat benzene is 80.1°C. **1**$_{hexane}$ showed much larger difference between those temperatures, 170 *vs.* 68.5 °C. In contrast, methanol molecules in **1**$_{MeOH}$ evaporated completely at 60 °C, near the boiling point of MeOH, indicating its weak host-guest interactions.

After guest exchange, the space groups remained as *R32* for **1**$_{benzene}$ and changed to *R-3c* for **1**$_{hexane}$ and **1**$_{MeOH}$, and the dimensions of the unit cells changed significantly (Table 1 and S1-4). This was primarily due to the interframework sliding, which was triggered by the newly formed host-guest, host-host, or guest-guest interactions upon guest-exchange, as described previously. The cell volume of **1** slightly increased from 21331(6) to 21540(6) Å³ for **1**$_{benzene}$, and significantly reduced to 19605(6) and 19202(5) Å³, for **1**$_{hexane}$ and **1**$_{MeOH}$, respectively. Specially, the guest molecule exchange from DMF to MeOH led to the greatest changes in the cell parameters, which corresponded to reduction of a cell volume by 10%, accompanied by a decrease in the void volume by 23.9%. The changes in the cell parameters were attributed to the compression of the individual **pcu** nets and the sliding motion between the interframework along the *c* axis as shown in the figure under Table 1. Since each edge of the **pcu** net conformed to the flexible CPMA ligand linking the oxo clusters (Fig. 1b), new interactions altered the degree of framework compression, which can be expressed by the distances between

oxo centres in the intraframework (Table 1). Consequently, since the oxo centres in positions O1 and O4 were located along the *c* axis, this framework compression directly changed the length of the c parameter. In addition, the sliding motion led to effective host-guest or host-host interactions, as described previously, and changed the interframework O···O distances between O4 and O5 as well and O1 and O5. Accordingly, 1_{hexane} and 1_{MeOH} experienced intraframework compression as well as the sliding motion, while in $1_{benzene}$ those movements did not occur significantly, because the benzene molecules fit into the A site and did not require significant structural changes. On the other hand, the offset change in 1_{hexane} led to a larger c axis compression than in other compounds, owing to CH−π interactions between hexane and the phenyl rings on the c axis (Fig. S12). In 1_{MeOH}, the major changes were in the reduction of the *a* and *b* parameters, which were due to strong host-host interactions. The peak positions of the measured XRPD patterns for **1** and the guest-exchanged products coincided with those of the simulated patterns derived from the X-ray single-crystal data, except that the XRPD pattern of 1_{MeOH} was somewhat different from the simulated pattern (Fig. S13). This may be because 1_{MeOH} rapidly lost MeOH molecules during the measurements. The compression of the lattice plane of 1_{hexane} and 1_{MeOH} was confirmed by the shift of the XRPD peaks to the higher angle region than those of **1** or $1_{benzene}$ (Fig. S13).

Conclusions

A Zn₄O-containing doubly interpenetrated MOF with a *pcu* net, [Zn₄O(CPMA)₃]₂•12DMF (**1**) underwent single-crystal to single-crystal transformations upon guest exchange of DMF molecules with benzene, *n*-hexane, and methanol. SCD analysis revealed that the structural transformations involving sliding motions of the interpenetrating networks as well as dynamic movements of the molecular components were triggered by the host-guest interactions. The π−π interactions in $1_{benzene}$ and CH−π interactions in 1_{hexane} between the introduced solvent molecules and the phenyl rings of the CPMA²⁻ ligand in the host framework were discussed with respect to the resulting structures. Interestingly, **1** showed a significant decrease in cell volume from 21331 to 19202 $Å^3$ (10%) upon guest exchange with methanol, which indicated that in 1_{MeOH} the dominant force which determined the structure was the interframework interactions rather than the host-guest interactions. In order to facilitate potential applications of MOFs in molecular sensing, separation, catalysis, and storage, it is essential to understand how MOFs respond to external stimuli and to determine the host-host, host-guest, and guest-guest interactions involved in the responses via X-ray single crystal structural analysis.

Acknowledgements

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