Electronic Supplementary Information

Visualizing the distinctly different crystal-to-crystal structural dynamism and sorption behaviors of interpenetration-direction isomeric coordination networks

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Experimental section

Materials and measurements.

The ligand H₂mpba was synthesized according to the literature.^{S1} Other chemicals were analytical reagents and used without purification. Elemental analyses (EA) were performed on a Vario EL elemental analyzer. PXRD data were obtained by a Bruker D8 ADVANCE X-ray powder diffractometer (Cu K α). Thermogravimetry analyses were conducted on a TA Q50 instrument under N₂ atmosphere with a heating rate of 5.0 °C/min. Gas sorption isotherms were measured by a Micromeritics ASAP 2020M instrument. Before gas sorption experiments, the as-synthesized samples were placed in sample tubes and dried under high vacuum at 200 °C for more than 10 h to remove the remnant solvent molecules.

Crystal structure analyses.

Single-crystal diffraction data for 1-3 were collected using a Bruker Apex CCD area-detector diffractometer (Mo-K α). The structures were solved by the direct method and refined with the full-matrix least-squares method on F^2 by the SHELXTL package.^{S2} Hydrogen atoms were placed geometrically. Anisotropic thermal parameters were used for all non-hydrogen atoms of the host frameworks. The relatively large R factors of **2** should arise from its very complicated structure containing many seriously disordered guest molecules. The reflection spots in the diffraction pattern were seriously overlapped and dispersed. If we omit the disordered solvent molecules by the SQUEEZE routine of PLATON, the R factors of **2** can be largely decreased. Crystal data and details of data collections and refinements of the compounds were listed in Table S1. CCDC 1004621-1004623 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.

PXRD data for Pawley and Rietveld refinement for **1'** and **2'** were collected on a Bruker D8 Advance X-ray powder diffractometer (Cu K α_1) with a scanning speed of 0.02°/step and 10 seconds/step. The generator was operated at 40 kV and 40 mA. The powder samples were packed in a borosilicate glass capillary ($\Phi = 0.8$ mm) and then the capillary was sealed by a

torch. All the indexing and refinement of the PXRD patterns were carried out by the Reflex module of Material Studio 5.0.^{S3} Rietveld refinements were performed to the structures obtained from computational calculations, in which the pseudo-Voigt profile parameters, zero-shift, background, March–Dollase preferred orientation correction parameters and Berar–Baldinozzi asymmetry correction parameters were optimized step by step till to meet good agreement between the calculated and the experimental powder diffraction patterns, while the atomic coordinates and unit-cell parameters were fixed. It should be noted that, if the atomic coordinates were not fixed, as does by conventional Rietveld refinements, the agreement factors can be further decreased but the resultant crystal structures are chemically unreasonable, which should be mainly attributed to the intrinsic difficulty of solving complicated crystal structures from PXRD data (the relatively low-quality data obtained by an in-house PXRD instrument, instead of high-quality data obtained by the highly intense and highly monochromatized synchrotron radiation, should be also important).

Computational details.

The potential surface of the torsion between the pyrazol ring and phenyl ring of H₂mpba were calculated by the "scan" algorithm in Gaussian 03 with a step-width of 2.5 degree, in which the density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level. MM, periodic-density functional theory (PDFT), simulated annealing and GCMC simulations were all performed through the Materials Studio 5.0 package. Concretely, PDFT calculations for optimizations of the desolvated structures were carried out by the Dmol³ module. The widely used generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function and the double numerical plus d-functions (DND) basis set as well as the DFT Semi-core Pseudopots (DSPP) were used. MM calculations for the framework energy and geometry optimizations of the structures during adsorption and desorption processes were performed with the smart algorithm based on the universal forcefield (UFF) in the Forcite module. The Mulliken charges and ESP charges calculated by DFT were employed to the framework atoms and guest atoms, respectively. The convergence tolerances were set as: energy, 2×10^{-5} kcal/mol; force, 1.0×10^{-3} kcal/mol/Å;

displacement, 1.0×10^{-5} Å. Simulated annealing for the sorption processes before the MM optimizations were calculated by the Adsorption Locator module with automated temperature control and 5 annealing cycles (5×10^4 steps per cycle). The GCMC simulations for the adsorption isotherms were carried out by the Sorption module adopting the Metropolis method based on the UFF and both the host frameworks and the guest molecules were regarded as rigid. The cutoff radius was chosen as 15.5 Å for the Lennard-Jones (LJ) potential, and 5×10^6 equilibration steps were followed with 5×10^6 production steps.

Syntheses.

 $[Zn(Hmpba)_2]$ ·C₄H₈O₂ (1): A mixture of H₂mpba (0.022 g, 0.1 mmol), Zn(NO₃)₂·6H₂O (0.030 g, 0.1 mmol), EtOH (4 mL), H₂O (1 mL), DMA (0.1 mL) and dioxane (2.0 mL) was sealed in a 10-mL Teflon-lined stainless container and kept at 100 °C for 3 days, and then cooled to ambient temperature at a rate of 10 °C/h to form light yellow rodlike crystals (yield ca. 0.026 g, 89% based on H₂mpba). EA calcd (%) for $[Zn(C_{12}H_{11}N_2O_2)_2]$ ·C₄H₈O₂ (C₂₈H₃₀N₄O₆Zn): C 57.59, H 5.18, N 9.59; Found: C 57.36, H 5.16, N 9.64.

 $[Zn(Hmpba)_2] \cdot 0.5C_2H_5OH \cdot H_2O$ (2): The same reaction method for 1 was used except that dioxane was not added. Colorless block crystals were obtained (yield ca. 0.022 g, 85% based on H₂mpba). EA calcd (%) for $[Zn(C_{12}H_{11}N_2O_2)_2] \cdot 0.5C_2H_5OH \cdot H_2O$ ($C_{50}H_{53}N_8O_{11}Zn_2$): C 55.98, H 4.98, N 10.45; Found: C 56.04, H 4.87, N 10.52.

 $[Zn(Hmpba)_2]$ (3): The same reaction method for 1 was used except that the solvents were replaced by H₂O (5 mL). Colorless block crystals were obtained (yield ca. 0.023 g, 93% based on H₂mpba). EA calcd (%) for $[Zn(C_{12}H_{11}N_2O_2)_2]$ (C₂₄H₂₂N₄O₄Zn): C 58.13, H 4.47, N 11.30; Found: C 57.96, H 4.46, N 11.20.

Complex	1	2	2 (SQUEEZE)	3
Formula	C ₂₈ H ₃₀ N ₄ O ₆ Zn	$C_{50}H_{53}N_8O_{11}Zn_2$	$C_{48}H_{44}N_8O_8Zn_2$	C ₂₄ H ₂₂ N ₄ O ₄ Zn
Formula weight	583.95	1073.79	991.65	495.85
Temperature (K)	123(2)	123(2)	123(2)	123(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Tetragonal
Space group	Pba2	Fdd2	Fdd2	I4 ₁ /acd
a/Å	11.2987(7)	22.694(2)	22.694(2)	15.2355(8)
b/Å	14.6667(9)	29.694(3)	29.694(3)	15.2355(8)
c/Å	8.2144(5)	33.408(3)	33.408(3)	39.1054(19)
$V/\text{\AA}^3$	1361.25(14)	22513(4)	22513(4)	9077.2(11)
Ζ	2	16	16	16
$D_{\rm c}/{\rm g~cm^{-3}}$	1.425	1.267	1.170	1.451
reflns coll.	7872	21424	21424	21550
unique reflns	2569	9823	9823	2352
R _{int}	0.0391	0.0915	0.0848	0.0373
$R_1 \left[I > 2\sigma(I)\right]^{[a]}$	0.0559	0.0825	0.0638	0.0382
$wR_2 \left[I > 2\sigma(I)\right]^{[b]}$	0.1237	0.1963	0.0985	0.1055
R_1 (all data)	0.0588	0.1414	0.1093	0.0486
wR_2 (all data)	0.1253	0.2396	0.1097	0.1135
GOF	1.032	1.000	0.978	1.010
Flack	0.05(3)	0.07(3)	0.06(2)	

 Table S1 Crystallographic data and structure refinement details.

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|. {}^{b}wR_{2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$



Fig. S1. Perspective view of coordination environments of **1**. Symmetric codes: A = 0.5-x, 0.5+y, 1+z; B = 0.5-x, -0.5+y, -1+z; C = 0.5+x, 1.5-y, -1+z, D = 1-x, 1-y, z, E = 1-x, 2-y, z. Dihedral angle between plane 1 and plane 2 is 74.4°. According to Figure 2, the corresponding conformational energy can be calculated as 5.40 kJ/mol.



Fig. S2. Perspective view of coordination environments of **2**. Symmetric codes: A = 1-x, -y, z; B = 1.25-x, -0.25+y, -0.25+z; C = -0.25+x, 0.25-y, -0.25+z, D = 0.75-x, -0.25+y, 0.25+z, E = 1.5-x, 0.5-y, z, F = 1.75-x, 0.25+y, -0.25+z. Dihedral angle between plane 1 and plane 2 is 70.4°, between plane 3 and plane 4 is 59.1°, between plane 5 and plane 6 is 45.3°, between plane 7 and plane 8 is 44.3°, and the average dihedral angle is 54.8°. According to Figure 2, the corresponding conformational energies are calculated as 4.63, 2.18, 0.20 and 0.13 kJ/mol, respectively (average energy is 1.79 kJ/mol).



Fig. S3. Perspective view of coordination environments of **3**. Symmetric codes: A = 0.75-x, 0.25-y, -0.25+z; B = 1-x, 0.5-y, z; C = 0.25-x, 0.75-y, 0.25+z, D = 0.25+x, 0.25+y, 0.25+z. Dihedral angle between plane 1 and plane 2 is 45.2°. According to Figure 2, the corresponding conformational energies are calculated as 0.19 kJ/mol.



Fig. S4. (a) Comparison of the dimensions of the diamondoid cages of **1-3** by superposition of the simplified structures. (b) Comparison of the interpenetration directions of **1-3** by atomic structures (only two of the four interpenetrated cages are shown, and hydrogen atoms are omitted for clarity). One can see that the ligand directions of the green cages are the same among **1-3**, indicating that the supramolecular isomerism is not based on structural differences of individual nets. On the other hand, those of the blue ones are different among **1-3**, indicating that supramolecular isomerism is based on the interpenetration direction of coordination networks.



Fig. S5. Dioxane guests in the pore of 1 (the methyl groups are highlighted in orange).



Fig. S6. Thermogravimetry curves for 1, 2 and 3.



Fig. S7. PXRD patterns for (a) 1 and (b) 2.



Fig. S8. PXRD patterns for 1 and 2 after immersed in MeOH or H₂O.



Fig. S9. PXRD patterns for 1, 2 and 3 immersed into different solvents.



Fig. S10. (a) Final Rietveld refinement result of **2'**, (b) pore surface structure of **2'**, and (c) comparison of the **dia** networks of **2** and **2'** (the dash line indicates the unit cell edge).



Fig. S11. Perspective view of coordination environments of **1**'. Symmetric codes: A = 1.5-x, -0.5+y, 0.5+z; B = 0.5-x, 0.5+y, 0.5+z; C = 1.5-x, 0.5+y, -0.5+z, D = 0.5-x, -0.5+y, -0.5+z. Dihedral angle between plane 1 and plane 2 is 72.4°, between plane 3 and plane 4 is 52.6°, and the average dihedral angle is 62.5° . According to Figure 2, the corresponding conformational energies are calculated as 5.03 and 1.07 kJ/mol, respectively (average energy is 3.05 kJ/mol).



Fig. S12. Perspective view of coordination environments of **2'**. Symmetric codes: A = 1-x, -y, z; B = 1.25-x, -0.25+y, -0.25+z; C = -0.25+x, 0.25-y, -0.25+z, D = 0.75-x, -0.25+y, 0.25+z, E = 1.5-x, 0.5-y, z, F = 1.75-x, 0.25+y, -0.25+z. Dihedral angle between plane 1 and plane 2 is 54.3°, between plane 3 and plane 4 is 67.5°, between plane 5 and plane 6 is 46.2°, between plane 7 and plane 8 is 54.1°, and the average dihedral angle is 55.5°. According to Figure 2, the corresponding conformational energies are calculated as 1.33, 3.95, 0.26 and 1.30 kJ/mol, respectively (average energy is 1.71 kJ/mol).



Fig. S13. Comparison of the interpenetration classes and interpenetration modes of polar **dia** networks in (a) **1** and (b) **1'**. It can be seen that they are not only topologically equivalent (with the same catenation pattern) but also identical in the orientations of the polar networks. However, the four **dia** networks in **1** are related by a simple translation operation (class Ia), whereas those in **1'** are related by more complicated operations (both translation and screw axis 2_1 , class IIIa). See highlighted (black ellipsoid) parts for the differences.





Fig. S14. The intermediate structures of (a) 1a (unit-cell parameters: a = 10.065 Å, b = 16.088 Å, c = 15.715 Å, V = 2544.7 Å³), (b) 1b (unit-cell parameters: a = 11.482 Å, b = 14.634 Å, c = 7.938 Å, V = 1333.8 Å³) and (c) 2a (unit-cell parameters: a = 22.263 Å, b = 30.153 Å, c = 32.905 Å, V = 22089 Å³) derived by MM simulation.

References

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