Metal–Organic Frameworks

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Formation of a Metal–Organic Framework with High Surface Area and Gas Uptake by Breaking Edges Off Truncated Cuboctahedral Cages**

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Metal–organic frameworks (MOFs) with their intriguing structures and high surface areas are widely considered as promising materials for gas storage.[1] Of high interest are particularly MOFs that are based on coordination polyhedra , such as H_4Ls (di-isophthalate linkers) studied by Schröder,[2] the (3,24)-net series initially reported by Eddaoudi and Zaworotko[3] and further explored by Zhou,[4] Hupp,[5] and our group,[6] zeolitic imidazolate frameworks (ZIFs) designed by Yaghi,[7] metal–azolate frameworks (MAFs) synthesized by Chen,[8] and networked molecular cages assembled by Fujita.[9] These kinds of MOFs generally consist of face-sharing or vertex-sharing regular polyhedra. But might there be another way of assembling MOF networks? The breaking of networks that are based on truncated cubocthedral cages with the lowest connected polybenzene (pbz) topology was initially predicted twenty years ago by Keeffe and, until now, has never been found in carbon materials and MOF materials.[10] The preparation of such structures is still a great challenge. In addition, three-dimensional MOFs with three-connected topologies represent the lowest connected networks and are thus exceedingly pursued.[11]

We are interested in the formation of coordination nanocages and MOFs from rigid and flexible multidentate ligands that contain both a homodonor and a heterodonor.[6,12] To design discrete Archimedean-solid-type cages, rigid multidentate ligands, such as fullerene-like molecules based on *cyclo*-P_5 and Cu^{I},[12a] are generally preferred.[9a,13] Interestingly, Fujita recently expanded coordination nanocages into networked octahedral cages.[9b] A similar structure, formed by a different tridentate heterodonor ligand (5-(pyridin-4-yl-)-isophthalic acid) was also reported by our group.[14] In order to further extend our work, we used a flexible heterodonor linker (3,5-bis[4-carboxyanilino-carbonyl]pyridine (BCP)), which contains acylamide groups, to successfully synthesize a highly mesoporous three-connected MOF ($\{[Zn(BCP)\cdot H_2O]\cdot 3.5\,H_2O\cdot DMF\}_\infty$; DMF = *N*,*N*-dimethylformamide; NJU-Bai9, NJU-Bai for Nanjing University Bai's group) with pbz topology based upon breaking the edges off truncated cuboctahedra. This is the first example of a well-characterized three-dimensional MOF obtained by breaking edges off Archimedean-solid-type cages. As expected, the lowest connectivity provides NJU-Bai9 with a high Brunauer–Emmett–Teller (BET) surface area (4258 $m^2\,g^{-1}$), a rather low density of the dehydrated framework (0.403 $g\,cm^{-3}$), and a high capacity for the adsorption of H_2, CH_4, and CO_2.

The solvothermal reaction of $Zn(NO_3)_2\cdot 6\,H_2O$ with BCP in DMF that contains fluoroboric acid afforded colorless cuboctahedral crystals of $\{[Zn(BCP)\cdot H_2O]\cdot 3.5\,H_2O\cdot DMF\}_\infty$ (NJU-Bai9), which crystallizes in the centrosymmetric cubic space group $Fd\bar{3}c$. In this structure, free solvent molecules were removed using the SQUEEZE[15] routine of PLATON[16] and the structure was then refined again using the data generated.

The single-crystal X-ray analysis of NJU-Bai9 showed that each Zn^{II} center is four-coordinated, binding two oxygen atoms from two BCP ligands with monodentate coordination mode, one nitrogen atom from a third BCP ligand, and one oxygen atom from a water molecule. Because of the rotating nature of the acylamide groups in the BCP ligands, the twisting of the ligands makes the Zn atoms chiral centers (Figure 1 a). Two kinds of enantiotropic Zn atom centers connect with ligands of the same shape to generate a large merohedral distorted truncated cuboctahedron (MDTC) cage with a diameter of 3.4 nm, which further assembles to a three-dimensional network. For easy comprehension, we simplified both the ligands and Zn atoms to three kinds of three-connected nodes (Figure 1), and the topology of NJU-Bai9 is assigned with the reticular chemistry structure resource (RCSR) symbol pbz. NJU-Bai9 is the first well-characterized pbz-type metal–organic framework ever reported. After simplification, a pair of enantiotropic MDTC cages is discovered in NJU-Bai9: MDTC-Λ and MDTC-Δ (Figure 1 b, violet and purple, respectively; blue or orange dash lines should be ignored when considering MDTC cages). This kind of nonhelical chiral cages has never been reported in MOFs. Every MDTC cage consists of 12 Λ-Zn centers, 12 Δ-Zn centers, and 24 ligand centers. After complementing the missed facets by linking the nearest Λ-Zn (or Δ-Zn) centers in the MDTC-Δ (or MDTC-Λ) cage with blue (or orange) dash lines (Figure 1 b), the MDTC cage becomes a complete distorted truncated cuboctahedron (consisting of six curved octagons, twelve curved quadrangles, four small curved hexagons, and four big planar hexagons). Notably, if all the Λ-Zn (or Δ-Zn) atoms coordinate in the same mode as their enantiotropic counterpart Δ-Zn (or Λ-Zn) atoms, missed facets will be restored, thus making the whole cage an isolated

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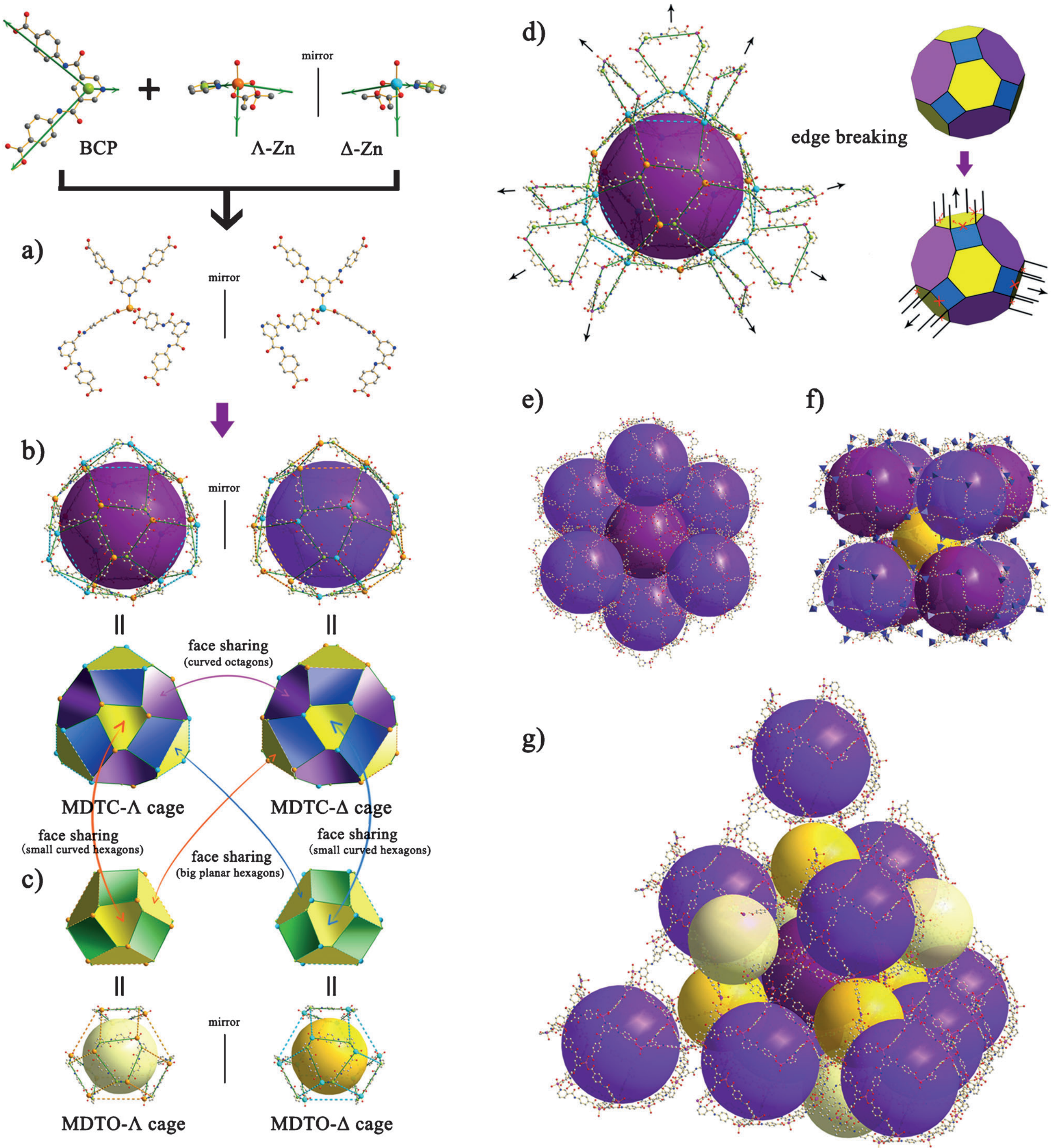

Figure 1. Assembly of NJU-Bai9. a) A pair of enantiotropic Zn centers, each coordinated with three BCP ligands. b) A pair of enantiotropic MDTC cages constructed by 12 Λ-Zn centers, 12 Δ-Zn centers, and 24 ligands centers. c) A pair of enantiotropic MDTO cages abstracted from the space between MDTC cages. The scheme from b to c shows how these four kinds of cages (MDTC-Λ, MDTC-Δ, MDTO-Λ, MDTO-Δ) are assembled. d) Edge breaking off an MDTC cage, which is illustrated by a regular truncated cuboctahedron. e) Every MDTC-Λ cage shares facets with six MDTC-Δ cages. f) Every MDTO cage shares facets with four MDTC-Λ and four MDTC-Δ cages. g) The overall packing mode of these four kinds of cages.

truncated cuboctahedron with three-connected nodes (Figure S1). Thus, the existence of Λ-Zn/Δ-Zn atoms is the key factor to break the edges off big planar hexagons in complete distorted truncated cuboctahedra to further extend to a three-dimensional network, while causing the sound truncated cuboctahedra to become merohedral.

As illustrated by a MDTC-Λ cage in Figure 1d, the breaking of the edges off all big planar hexagons connected by Δ-Zn centers results in the formation of three small curved hexagons with Δ-Zn centers (the edge breaking process is also illustrated by an analogous regular truncated cuboctahedron). These 12 small curved hexagons provide six MDTC-Δ cages around this MDTC-Λ cage by sharing six curved octagons (Figure 1 e). Similarly, every MDTC-Δ cage is surrounded by six MDTC-Λ cages. With this kind of packing mode, another pair of enantiotropic merohedral distorted truncated octahedral (MDTO-Δ and MDTO-Λ) cages with a diameter of 2.6 nm are abstracted from the space between MDTC-Δ and MDTC-Λ cages (Figure 1 c). The metal centers in every MDTO cage are unichiral. Each MDTO cage features four small curved hexagons, four big planar hexagons, and six curved quadrangles. It shares two kinds of hexagon facets with two kinds of MDTC cages (Figure 1 b and c) and is thus surrounded by eight MDTC cages (Figure 1 f). The overall packing of these two pairs of enantiotropic cages (MDTC-Δ and MDTC-Λ, MDTO-Δ and MDTO-Λ) in NJU-Bai9 is shown in Figure 1 g. The even dispersal of these chiral cages makes the whole network achiral, which is confirmed by the CD spectrum of NJU-Bai9 (Figure S2). NJU-Bai9 is a double interpenetrated network, and the stabilization of the two isolated networks is mainly attributed to the intermolecular π–π interactions between six pairs of phenyl–pyridyl rings in each small curved hexagon of MDTC or MDTO cages (centroid–centroid distance: 3.646 Å; Figure S3). Because of the interpenetration, the sizes of the inner cavities in the MDTC and MDTO cages are decreased to a diameter of 2.6 nm and 1.6 nm, respectively. Nevertheless, a diameter of 2.6 nm still makes NJU-Bai9 a mesoporous MOF. As is expected, this three-connected pbz-topological NJU-Bai9 exhibits a quite low density of the dehydrated framework (0.403 g cm^{-3}), which is lower than that of the well-known MOF-177 (0.427 g cm^{-3}).[1c] If the interpenetration could be avoided, the density of the dehydrated framework of NJU-Bai9 could be decreased to 0.202 g cm^{-3}, which may be one of the lowest values in MOFs. The free volume in fully desolvated NJU-Bai9 is 78.1 % (calculated by the PLATON program), while that of NJU-Bai9 without interpenetration may reach up to 89.1 %, which may be one of the highest values in MOFs.

To confirm the permanent porosity of NJU-Bai9, the as-synthesized sample was treated with supercritical carbon dioxide (SCD) and then degassed under high vacuum at room temperature for 12 h to obtain the evacuated framework. The N_2 adsorption for NJU-Bai9 at 77 K exhibits a reversible pseudo-type-I isotherm with stepwise adsorption behavior (Figure 2 a), which is characteristic for MOFs with hierarchically assembled micro- and mesopores.[17] Significantly, NJU-Bai9 can take up large amounts of N_2 (1062 cm^3 g^{-1} at 1 bar and 77 K) and exhibits a high apparent Brunauer–Emmett–Teller (BET) surface area of around 4258 m^2 g^{-1} (Langmuir surface area $\approx$ 4645 m^2 g^{-1}). To the best of our knowledge, NJU-Bai9 possesses the highest surface area among the interpenetrated porous MOFs reported to date. The pore–size distribution (PSD) for NJU-Bai9 was determined by analyzing the Ar isotherm at 87 K using nonlocal density functional theory (NLDFT) implementing a hybrid kernel based on a zeolite–silica model containing cylindrical pores. The distribution calculated by fitting the Ar adsorption data for NJU-Bai9 showed two types of pores with estimated diameters of 2.2 and 1.4 nm (Figure S4), consistent with the dimensions (2.6 and 1.6 nm) of the two different cages as

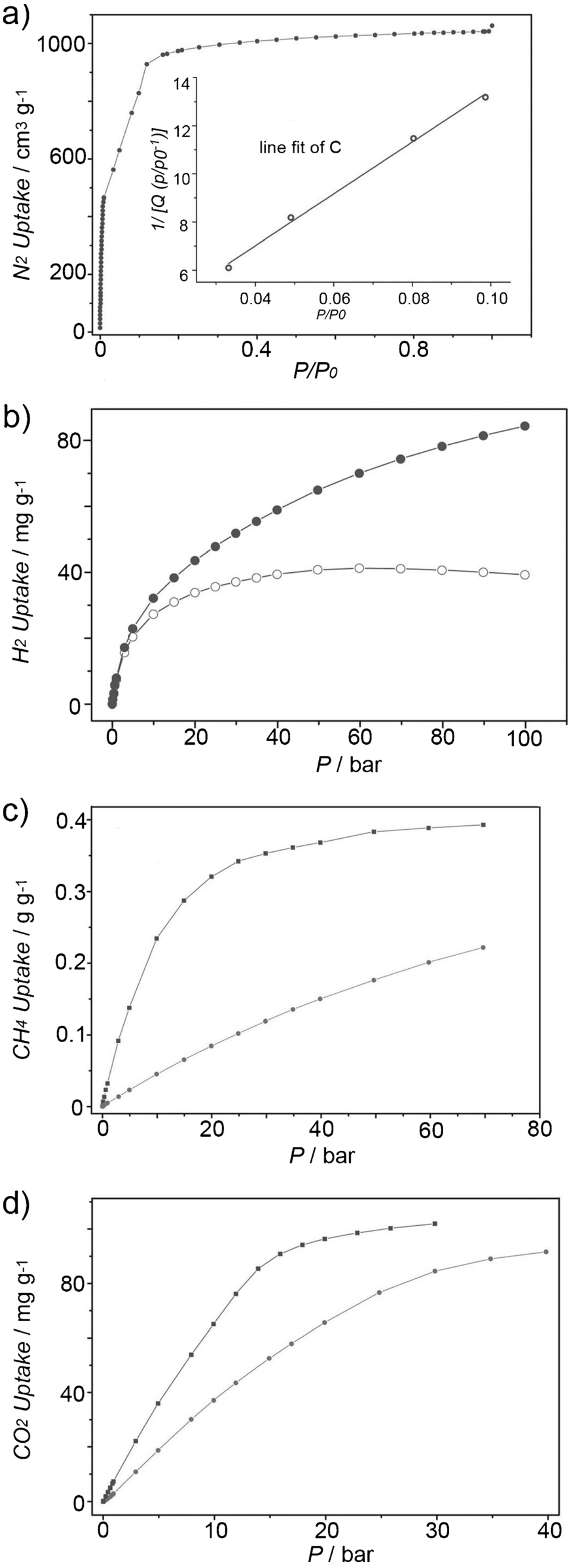

Figure 2. Gas adsorption data for NJU-Bai9. a) Low-pressure N_2 adsorption (77 K), b) high-pressure H_2 adsorption (77 K), c) high-pressure CH_4 adsorption (squares: 273 K, circles: 298 K), d) high-pressure CO_2 adsorption (squares: 273 K, circles: 298 K).

determined for the crystal structure of NJU-Bai9, thus confirming the presence of two distinct cages in the bulk porous material. On the basis of the N_2 sorption isotherm, NJU-Bai9 has a calculated total pore volume of 1.64 cm^3 g^{-1}, which represents the largest value among the interpenetrated MOFs.[18] NJU-Bai9 keeps its crystal lattice after gas adsorption studies, as confirmed by powder X-ray diffraction patterns (Figure S5).

The large surface area and pore volume of NJU-Bai9 prompted us to further investigate its gas storage capacities. Adsorption data were collected up to 100 bar at 77 K for H_2, 70 bar at 298 K for CH_4, and 40 bar at 298 K for CO_2. At 77 K, the total H_2 uptake of NJU-Bai9 is 8.4 wt% (92.2 mg g^{-1}) at 100 bar (Figure 2b), making NJU-Bai9 one of the best MOFs for H_2 storage, comparable to NU-100 (99.5 mg g^{-1}), which is the benchmark of MOFs for H_2 storage.[1a,19] The CH_4 adsorption of NJU-Bai9 at 298 K is 0.21 g g^{-1}, which is about 42% of the US Department of Energy's (DOE) new target of 0.5 g g^{-1}. Interestingly, at 273 K, the CH_4 adsorption of NJU-Bai9 is 0.40 g g^{-1}, which is almost 80% of the DOE's new target and is larger than those of well-known MOFs, such as PCN-14[20a] and USTA-20.[20b] In addition, the CO_2 uptake of NJU-Bai9 (total = 1070 mg g^{-1}) is among the highest uptakes reported for MOF materials.[19c,21]

In conclusion, we utilized a heterodonor linker containing flexible acylamide groups and synthesized a highly mesoporous interpenetrated three-coordinated MOF (NJU-Bai9) with pbz topology. This MOF is the first fully characterized MOF with lowest connectivity and an unprecedented example of breaking edges off truncated cuboctahedral cages to assemble a three-dimensional network. It has the largest BET surface area among interpenetrated MOFs and higher uptakes of H_2, CH_4, and CO_2. Attempts to obtain the non-interpenetrated NJU-Bai9 are undergoing. Nevertheless, our work provides a new strategy to synthesize metal–organic frameworks with high porosity and low density. We believe that it will facilitate the exploration of more MOFs with amazing structures and properties.

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