Metal–Organic Materials

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The asc Trinodal Platform: Two-Step Assembly of Triangular, Tetrahedral, and Trigonal-Prismatic Molecular Building Blocks**

*Alexander Schoedel, Amy J. Cairns, Youssef Belmabkhout, Lukasz Wojtas, Mona Mohamed, Zhenjie Zhang, Davide M. Proserpio, Mohamed Eddaoudi, and Michael J. Zaworotko**

Metal–organic materials (MOMs) assembled from metal-based or organic molecular building blocks (MBBs) and organic linkers have attracted increasing scientific interest during the past decade.[1] Their structure (especially their modularity) and properties (especially extra-large surface area) have made them an attractive class of porous materials for applications including gas purification and storage, catalysis, small molecule separations, and chemical sensing. In comparison to their purely inorganic analogues (for example, zeolites), their surface areas and their amenability to fine tuning of composition affords an exceptional level of control over physicochemical properties.

In the context of MOMs, the application of crystal engineering,[2] the rational design and assembly of functional crystalline solids, has afforded a large variety of 2D and 3D networks. MBBs most typically consist of metal carboxylate or metal pyridine clusters where the peripheral points of extension dictate the respective geometrical building units, corresponding to a vertex figure that can be reduced to a single vertex. Uninodal nets with one kind of vertex are well represented and include those sustained by 3- (**srs,**[3] **ths**[4]), 4- (**dia,**[5] **nbo**[6]), 6- (**pcu,**[1d,4b,7] **acs**[8]), 8- (**bcu**[9]), or 12- (**fcu**[10]) connected nodes. These high-symmetry nets are typically fine-tuned through the organic linker(s) and have spawned the concept of isoreticular chemistry.[11] High-symmetry MBBs have also been exploited to generate binodal nets with one kind of edge (edge-transitive)[12] in which the second node is a 3-connected organic moiety, as exemplified by the following nodes: copper-paddlewheel $[Cu_2(CO_2)_4]$ (3,4-c, **tbo,**[13] **pto**[14]) square MBBs; basic zinc acetate $[Zn_4(\mu_4\text{-}O)\text{-}(CO_2)_6]$ octahedral MBBs (6,3-c, **qom**).[15] However, only a handful of these nets might be described as platforms for which the underlying topology can serve as a blueprint for the generation of families of related materials through judicious selection of the MBBs, as exemplified by uninodal 6-c **pcu** (IRMOFs)[11a] and binodal 3,24-c **rht**[16] platforms.

In contrast, high-symmetry trinodal nets (edge-two-transitive) sustained by three different polygons or polyhedra remain rare despite their potential to afford new topologies,[17] and to the best of our knowledge, none are versatile enough to serve as platforms. We believe that this is largely related to the difficulties associated with controlling the stoichiometry and order of self-assembly of three or more different MBBs in a one-pot reaction. We address these handicaps herein by applying our recently reported two-step crystal engineering strategy[18] to generate the first trinodal MOM platform.

The two-step approach relies upon first preparing a trigonal-prismatic primary molecular building block (tp-PMBB) based on $[Cr_3(\mu_3\text{-}O)(CO_2)_6]$ clusters decorated with six coordinating ligands (Figure 1).[19] The hexapyridyl variant, tp-PMBB-1, is soluble, cheap, and robust and can subsequently be used for the preparation of binodal nets.[18] Herein, we describe how tp-PMBB-1 can be reacted with tetrahedral (Zn^{2+}, Cd^{2+}) and three triangular MBBs (1,3,5-benzenetricarboxylic acid, H_3btc; 1,3,5-tris(4-carboxyphenyl) benzene, H_3btb; 4,4′,4″-[1,3,5-benzenetriyltris(carbonylimino)] trisbenzoic acid, H_3btctb) in *N*,*N*-dimethylformamide (DMF; see the Supporting Information for further details) to afford the first four examples of trinodal networks involving triangular, tetrahedral, and trigonal-prismatic building blocks.

The prototypal compound, tp-PMBB-1-**asc**-1, is based upon trigonal-prismatic clusters $[Cr_3O(isonic)_6(H_2O)_3]^+$ (isonic = pyridine-4-carboxylate) coordinated to six tetrahedral Zn^{2+} cations that are in turn coordinated to two triangular btc^{3-} anions. The resulting tetrahedral MBB, $Zn(CO_2)_2(py)_2$, is well known for its role in sustaining hydrogen-bonded[20] and diamondoid networks.[21] The D_{3h} symmetry of btc^{3-} complements that of tp-PMBB-1 (also D_{3h}) and the tetrahedral $Zn(CO_2)_2(py)_2$ nodes to form the first example of a MOM with **asc** topology. The novelty of the underlying net topology was assessed using TOPOS[22] in conjunction with the RCSR[23] database (the unique three-letter code **asc** has been assigned in the RCSR database and is used herein). Attempts to synthesize tp-PMBB-1-**asc**-1 in a one pot reaction were unsuccessful.

$[Zn_3btc_2\{Cr_3O(isonic)_6(H_2O)_2(OH)\}]\cdot x\,DMF$ (tp-PMBB-1-**asc**-1) crystallized in the hexagonal space group $P\bar{6}2m$ with one formula unit per unit cell. Six crystallographically equivalent tetrahedral Zn^{2+} nodes are each coordinated by

[*] A. Schoedel, Dr. L. Wojtas, M. Mohamed, Z. Zhang, Prof. Dr. M. J. Zaworotko
Department of Chemistry, University of South Florida
4202 East Fowler Ave., CHE205, Tampa, FL 33620 (USA)
E-mail: xtal@usf.edu
Homepage: http://chemistry.usf.edu/faculty/zaworotko/
Dr. A. J. Cairns, Dr. Y. Belmabkhout, Prof. Dr. M. Eddaoudi
Chemical Science
King Abdullah University of Science and Technology
Thuwal 23955-6900 (Kingdom of Saudi Arabia)
Prof. D. M. Proserpio
Università degli Studi di Milano, Dipartimento di Chimica
Via Golgi, 19, 20133 Milano (Italy)

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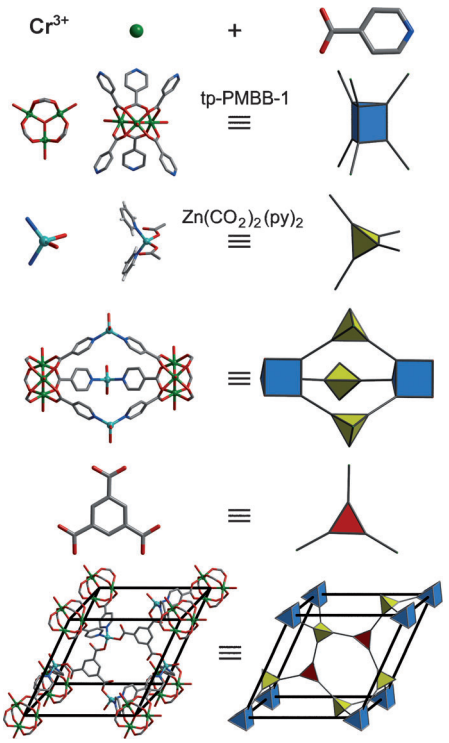

Figure 1. Self-assembly of molecular building blocks (pyridine (py), pyridine-4-carboxylate (isonic), 1,3,5-benzenetricarboxylic acid (H_3btc)) to afford the trinodal net tp-PMBB-1-**asc**-1. Selected fragments from the crystal structure are shown: C gray, O red, N blue, Cr green, Zn cyan. Synthesis of tp-PMBB-1 then reaction with Zn^{2+} and H_3btc yields a hexagonal-symmetry open-framework structure (bottom). Hydrogen atoms have been omitted for clarity.

two 1,3,5-benzenetricarboxylate ligands in a monodentate fashion, which are in turn coordinated to three Zn^{2+} cations, resulting in an overall honeycomb-like 2-periodic layered structure. The resulting layers are pillared by tp-PMBB-1 moieties by the remaining binding sites of the Zn^{2+} cations to form the 3-periodic **asc** framework with cavities of around 22×13 Å and circa 10 Å windows (Figure 2a). The open hexagons in each layer are capped on both sides by two tp-PMBBs resulting in a cage with dimensions of around 14×10 Å. This assembly is composed of edge shared 4-c and face shared 6-c secondary molecular building blocks (SMBBs; Figure 2b). The framework-accessible free volume was calculated to be 64.8% using PLATON.[24] An isostructural network, tp-PMBB-1-**asc**-1-Cd, was obtained under similar reaction conditions (see the Supporting Information) and thus validates that the tetrahedral Zn-node can be replaced by another divalent metal cation.

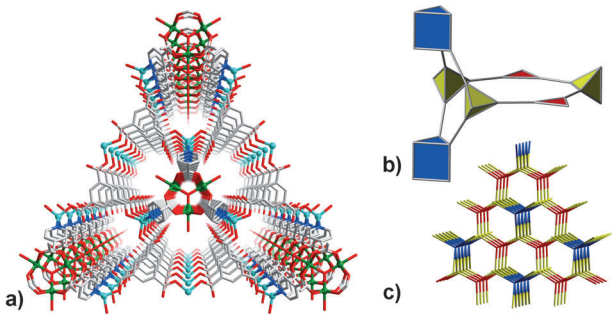

Figure 2. a) Representation of tp-PMBB-1-**asc**-1 along [001] (hydrogen atoms omitted for clarity). b) The 4- and 6-connected ring SMBBs (trigonal prisms: blue, tetrahedra: yellow, triangles: red). c) Topological representation of the new trinodal (3,4,6)-c net.

The modular nature of tp-PMBB-1-**asc**-1 prompted us to use expanded (btb^{3-}) and functionalized ($btctb^{3-}$) variants of btc^{3-}. $[Zn_3btb_2\{Cr_3O(isonic)_6(H_2O)_2(OH)\}]\cdot x$DMF (tp-PMBB-1-**asc**-2) and $[Zn_3btctb_2\{Cr_3O(isonic)_6(H_2O)_2(OH)\}]\cdot x$DMF (tp-PMBB-**asc**-3) also crystallize in the hexagonal space group $P\bar{6}2m$ and exhibit **asc** topology (Figure 3). The angle between the pyridine moieties at the Zn^{2+}centers is more acute because of bidentate coordination by the carboxylate moieties. This results in a slightly shorter *c* dimension in comparison to tp-PMBB-1-**asc**-1. The increased lengths of the triangular ligands enables large nanocages of 39×19 Å (btb^{3-}) and 47×23 Å ($btctb^{3-}$) with 14–15 Å windows (Figure 3) and a free volume of more than 80%.

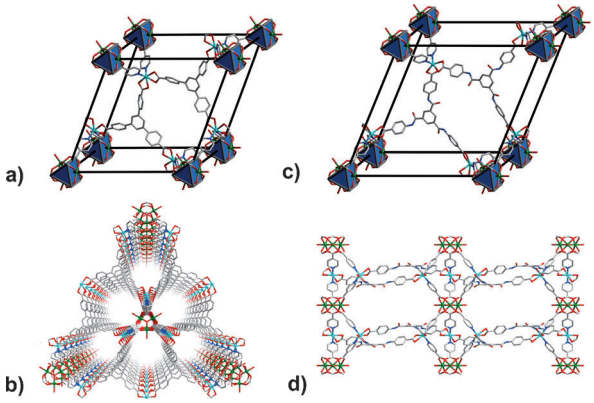

Figure 3. a) Unit cell of tp-PMBB-1-**asc**-2. b) View along [001] the btb^{3-} linker showing the formation of circa 15 Å channels. c) Unit cell of tp-PMBB-1-**asc**-3. d) The triangular linker provides amide functionalization to the large nanocages, which are viewed along [010]. Hydrogen atoms and ligand disorder have been omitted for clarity.

Trigonal-prismatic and $Zn(CO_2)_2(py)_2$ MBBs form robust networks, which prompted us to evaluate the gas sorption behavior of tp-PMBB-1-**asc**-1. Crystals of tp-PMBB-1-**asc**-1 were activated by soaking in hot DMF overnight,[25] followed by immersion in hot acetonitrile before degassing at room temperature for 16 h under dynamic vacuum. The N_2 adsorption at 77 K exhibits a type I isotherm characteristic of microporous materials and reveals an overall uptake of 428 cm^3g^{-1} near 1 bar. The apparent surface corresponds to a Brunauer–Emmet–Teller (BET) surface area of 1671 m^2g^{-1} and a Langmuir surface area of 1861 m^2g^{-1} (for details, see the Supporting Information). Hydrogen (77 K) and CO_2 (273 K, 298 K) adsorption isotherms were also recorded and are presented in Figure 4. tp-PMBB-1-**asc**-1 exhibits CO_2 uptake of 136 cm^3g^{-1} (21.1 wt%) at 273 K, which is relatively high compared to other classes of porous materials.[26] The isosteric heat of adsorption (Q_{st}) for CO_2 was calculated to be

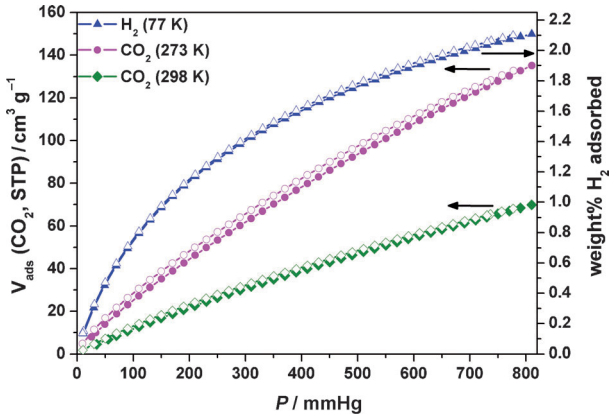

Figure 4. Reversible carbon dioxide (273 K, 298 K) and hydrogen (77 K) gas adsorption isotherms for tp-PMBB-1-**asc**-1.

about 26 kJ mol^{-1} at low loading and remains relatively steady to higher loadings (for details, see the Supporting Information). The hydrogen uptake at 77 K of tp-PMBB-1-**asc**-1 is 2.1 wt% at 1 bar, which is high in the context of MOMs without open metal sites.[27] We refer to compounds without open metal sites as H_2O removal at Cr^{3+} trimeric clusters requires temperatures of more than 200 °C.[28] Therefore, coordinated water molecules should remain bound at the Cr^{3+} sites in the as-tested material as suggested by weight loss in the thermogravimetric analysis at around 200 °C (see the Supporting Information). Gas adsorption studies conducted upon tp-PMBB-1-**asc**-1-Cd revealed a similar surface area and gas uptakes to those of tp-PMBB-1-**asc**-1 (for details, see the Supporting Information).

The chemical stability of tp-PMBB-1-**asc**-1 was addressed by immersing crystals in neat pyridine at 105 °C for 24 h. The crystal structure of the exchanged compound, tp-PMBB-1-**asc**-1-py (Figure 5), revealed that terminal water ligands at

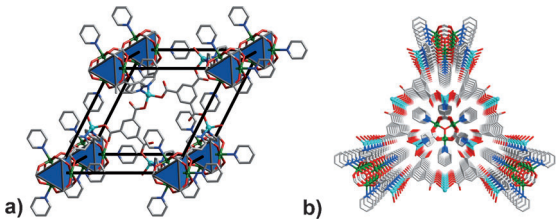

Figure 5. a) tp-PMBB-1-**asc**-1 after treatment in hot pyridine. Water molecules at the Cr^{3+} coordination sites have been fully replaced in a single-crystal to single-crystal exchange process. b) Representation of tp-PMBB-1-**asc**-1-py along [001]. Hydrogen atoms have been omitted for clarity.

Cr^{3+} had been replaced by pyridine in a single-crystal to single-crystal process with retention of structure. This observation is in contrast to the MIL-88 family of frameworks,[29] which exhibit breathing behavior. We believe that breathing is restricted because of the rigidity of the hexagonal Zn_3btc_2 layer, which in turn means that crystallinity is maintained (see the Supporting Information). Water stability was evaluated by immersing the as-prepared compound in H_2O for 24 and 48 h. The powder X-ray diffraction patterns (see supporting information) match closely. Gas adsorption studies of the water-exchanged sample after 48 h, followed by activation, resulted in no loss of surface area (see the Supporting Information).

In summary, we have demonstrated that a new trinodal MOM platform comprised of simple and inexpensive triangular, tetrahedral, and trigonal-prismatic nodes can be prepared using a two-step synthetic process. This process facilitates control over the underlying network of the trinodal system and offers many potential variations of nodes, thereby rendering the **asc** topology into a fine-tunable platform that is well-suited to target specific properties. The prototype, tp-PMBB-1-**asc**-1, exhibits chemical stability (organic solvents, including bases, and water) and relatively high uptake of carbon dioxide and hydrogen in the context of MOMs that are based upon saturated metal centers. These features are highly desirable in the context of the cost/performance ratio that will be needed to develop MOMs for industrial applications.[30]

Experimental Section

tp-PMBB-1-**asc**-1: $[Cr_3O(isonicH)_4(isonic)_2(H_2O)_3](NO_3)_5{\cdot}2H_2O$ (tp-PMBB-1, 1.42 mmol, 2.00 g) was dissolved in 100 mL of *N*,*N*-dimethylformamide (DMF) for 15 min in an ultrasonic bath. The solution was filtered and a 5 mL aliquot was placed in a 20 mL scintillation vial. A solution of zinc nitrate hexahydrate (1.08 mmol, 0.322 g) and 1,3,5-benzenetricarboxylic acid (0.86 mmol, 0.180 g) in 3 mL of DMF was added, and the mixture was heated to 70 °C for 4 days. A dark green crystal of tp-PMBB-1-**asc**-1 was harvested and used for single-crystal X-ray crystallographic study. The remaining crystalline product was washed with DMF (3 × 5 mL) and MeCN (2 × 5 mL) and dried in air for 1 hour (yield: ca. 47% based on Cr).

tp-PMBB-1-**asc**-1-py: As-synthesized tp-PMBB-1-**asc**-1 was placed in pyridine (20 mL) at 105 °C for 24 h. A light purple single crystal was harvested and used for the single-crystal X-ray crystallographic study.

Experimental details on the other structures reported herein can be found in the Supporting Information.

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