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EDGE ARTICLE

Vertex-directed self-assembly of a high symmetry supermolecular building block using a custom-designed porphyrin†

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Metal–organic materials that are constructed from polyhedral supermolecular building blocks, SBBs, can offer exquisite control over structure and afford useful features such as multiple cage types and relatively narrow pores. This contribution describes how a custom-designed porphyrin, tdcpp, self-assembles with M(II) (M = Zn, Cd) cations to generate the first examples of SBBs that are uniform polyhedra based upon a porphyrin molecular building block, MBB. The faces of tdcpp moieties link triangular $M_2(CO_2)_3$ or $M(CO_2)_3$ moieties to form *small cubicuboctahedral* SBBs that are in turn fused to adjacent SBBs at the opposite face of each tdcpp moiety. The resulting high symmetry augmented **pcu** topology networks, MMPF-4 (M = Zn) and MMPF-5 (M = Cd), exhibit two distinct polyhedral cages and are permanently microporous with selective CO_2 uptake.

Introduction

Metal–Organic Materials (MOMs) are typically comprised of a metal or metal cluster (*i.e.* the "node") that is coordinated to a multi-functional organic ligand(s) (*i.e.* the "linker").[1] MOMs represent a powerful paradigm for crystal engineering because there are numerous pre-existing metal clusters or molecular building blocks, MBBs, that can serve as nodes.[2] The inherent modularity of MOMs means that they might even be described as platforms or blueprints because if structure can be controlled then so can scale, composition and properties.[3] However, this does not mean that all MBBs are amenable to control. For example, "square paddlewheel" MBBs that are linked by benzenedicarboxylate moieties can self-assemble into numerous motifs that in turn afford several supramolecular isomers for a given combination of MBBs.[4] Furthermore, functionalized porphyrins, which would be desirable MBBs because of their catalytic, molecular recognition and light harvesting properties,[5] are generally difficult to control as linkers (bifunctionalized)[6] or nodes (typically tetrafunctionalized).[7] Indeed, to our knowledge there are very few porphyrin-based MOFs with surface areas of >1000 m^2 g^{-1}.[8]

A design approach that can offer exquisite control over structure and also provide advantageous structural features is to build MOMs from high connectivity, high symmetry supermolecular building blocks, SBBs, that are based upon uniform polyhedra.[9] Such an approach complements the parallel development of the chemistry of discrete nanoscale molecular polygons and polyhedra.[10] Indeed, the same MBBs can be used for both discrete and infinite structures since directionality, rigidity and established chemistry are desirable features.[9,10e,11]

Molecular polyhedra represent ideal blueprints for SBBs and related structures since they delineate the geometric features required to generate curvature around a point in space.[9,12] Particularly attractive subsets of polyhedra are those that are *uniform polyhedra i.e.* they are constructed from regular polygons, their vertices are identical (congruent) and they are highly symmetric in terms of reflective and rotational symmetry. There already exists a library of MBBs that can serve as the polygonal components needed to build the types of SBBs that can support high symmetry, high connectivity nets.[13] Further, there are 80 uniform polyhedra but not all are suited to serve as blueprints for MOMs. *Platonic solids*, *Archimedean solids* and *faceted polyhedra* represent the three subsets of uniform polyhedra, 27 in total, that are most practically suited to serve as blueprints and, given the ubiquity of square and triangular MBBs, the polyhedra illustrated in Fig. 1 represent appropriate targets for self-assembly.[9,14] The *rhombicuboctahedron* or its edge skeleton are targets for *face-directed* (*i.e. molecular paneling*)[10c] or *edge-directed* self-assembly, respectively, whereas the two faceted polyhedra are accessible by *vertex-directed* self-assembly of squares and triangles or squares only. We report herein that a custom-designed porphyrin, tetrakis(3,5-dicarboxyphenyl)porphine (tdcpp) (Fig. 2a) can serve as square MBBs that connect triangular $Zn_2(CO_2)_3$[15] or

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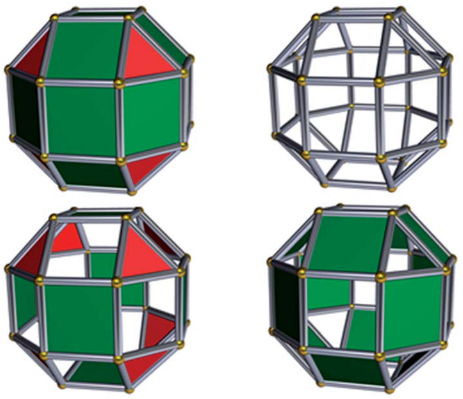

Fig. 1 The rhombicuboctahedron (above left) and its edge skeleton (above right). Two faceted polyhedra share the same edge skeleton: small cubicuboctahedron (below left) and small rhombihexahedron (below right).

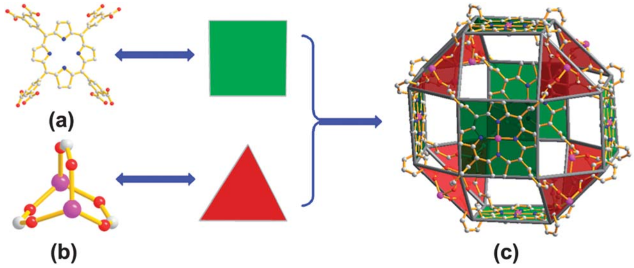

Fig. 2 (a) Tdcpp serves as a square MBB; (b) $Zn_2(CO_2)_3$ paddlewheel moiety serves as a triangular MBB; (c) the *small cubicuboctahedron* in MMPF-4 is formed by 6 square Zn–tdcpp MBBs and 8 triangular $Zn_2(CO_2)_3$ MBBs and exhibits an internal diameter of 21.528 Å with window dimensions of 7.831 Å × 8.048 Å (atom to atom distance).

$Cd(CO_2)_3$ moieties. Zn(II) was initially selected because its affinity for tetrahedral geometry is long known to favor the formation of triangular "paddlewheel" moieties,[15c,d] unlike metals such as Cu(II), which is predisposed to form the ubiquitous $Cu(CO_2)_4$ "square paddlewheel". The *small cubicuboctahedral* SBB that are thereby generated are the first SBBs that are uniform polyhedra based upon porphyrin MBBs. The resulting MOMs are termed MMPF-4 (Zn) and MMPF-5 (Cd) (MMPF denotes metal–metalloporphyrin framework) (Fig. 2 or Fig. S1, ESI†).

Results and discussion

Single crystals of MMPF-4 (formula: $[Zn_{19}(tdcpp)_3][(NO_3)_8]\cdot(DMSO)_{61}\cdot(H_2O)_{25}$) and MMPF-5 (formula: $[Cd_{11}(tdcpp)_3][(H_3O)_8]\cdot(DMSO)_{36}\cdot(H_2O)_{11}$) were prepared by solvothermal reaction of H_{10}tdcpp ligand with $Zn(NO_3)_2$ and $Cd(NO_3)_2$ respectively in dimethylsulfoxide (DMSO) at 135 °C. Single-crystal X-ray crystallographic studies conducted using synchrotron radiation at the Advanced Photon Source, Argonne National Laboratory, revealed that MMPF-4 crystallized in cubic space group $Ia\bar{3}$ with $a = 43.030(2)$ Å whereas MMPF-5 crystallized in cubic space group $Pm\bar{3}m$ with $a = 22.521(15)$ Å. The higher symmetry observed for MMPF-4 can be attributed to the mirror plane in the $Zn_2(CO_2)_3$ paddlewheel moieties. The $(Zn_2)_8(Zn\text{–}tdcpp)_6$ SBB of MMPF-4 is illustrated in Fig. 2, which reveals how one face of each tdcpp moiety is metallated with Zn(II) *in situ*. Although each Zn–tdcpp is 8-connected in the context of the MOM, in the context of the SBB it serves as a 4-connected node that is linked by $Zn_2(CO_2)_3$ triangular paddlewheel moieties. The resulting SBB is a *small cubicuboctahedron* composed of the faces of six Zn–tdcpp moieties that are linked by eight $Zn_2(CO_2)_3$ moieties. The crystal structure of MMPF-4 reveals that the SBB exhibits window dimensions of 7.831 Å × 8.048 Å and its internal diameter is 21.528 Å (atom to atom distance). Similarly (Fig. S1, ESI†), MMPF-5 is also based upon a *small cubicuboctahedron* SBB composed of the faces of six Cd–tdcpp moieties that are linked by eight $Cd(CO_2)_3$ moieties. Window dimensions of 8.004 Å × 8.195 Å and an internal diameter of 22.521 Å (atom to atom distance) are observed in the SBB of MMPF-5.

Fig. 3a reveals how the opposite face of each Zn–tdcpp moiety in MMPF-4 serves as the face of an adjacent SBB, thereby making it a 6-connected node that supports an augmented **pcu** network[16] (Fig. S2, ESI†). The cage formed between the SBBs can be described as an octahemioctahedron, and it is enclosed by eight triangular $Zn_2(CO_2)_3$ paddlewheel MBBs from eight different SBBs (Fig. 3b). The eight triangular $Zn_2(CO_2)_3$ paddlewheel MBBs are bridged through 12 isophthalate moieties from 12 tdcpp ligands, and the resulting octahemioctahedral cage has an internal diameter of 11.189 Å with window dimensions of 8.048 Å × 8.048 Å (atom to atom distance). Similarly, in MMPF-5 (Fig. S3, ESI†), SBBs are fused with six adjacent SBBs through six Cd–tdcpp moieties to support an augmented **pcu** network. The corresponding octahemioctahedral cage exhibits an internal diameter of 11.589 Å and window dimensions of 8.195 Å × 8.195 Å. Alternatively, MMPF-4 and MMPF-5 can be described as 8-connected networks through the octahemioctahedron, which connects 8 *small cubicuboctahedra* through eight triangular MBBs (Fig. S4, ESI†). If one assumes the tdcpp ligands are 8-connected nodes and the triangular MBBs are 3-connected nodes, MMPF-4 and MMPF-5 can then be described as (8,3)-connected networks with **the** topology (Fig. S5, ESI†).[17] MMPF-4 and MMPF-5 represent rare examples of

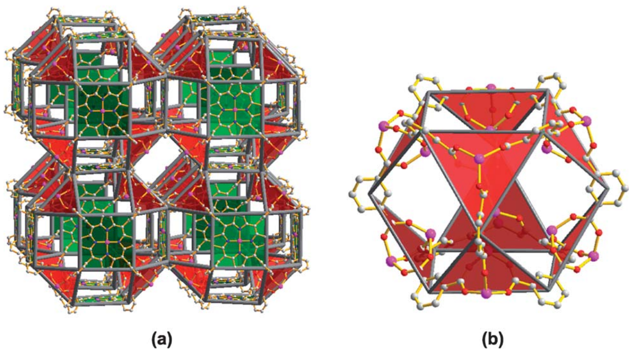

Fig. 3 (a) Zn–tdcpp ligands fuse the square faces of *small cubicuboctahedra* to afford an augmented *pcu* network with two types of cavity in MMPF-4; (b) the cage formed between the SBBs can be described as octahemioctahedron and has an internal diameter of 11.189 Å with window dimensions of 8.048 Å × 8.048 Å (atom to atom distance).

networks for which where there are no supramolecular isomers,[2b] as is also the case for certain other high connectivity 12-connected (**fcu**)[12a,18] and 24 connected nets (**rht**).[19] The high symmetry of the *small cubicuboctahedron* SBBs distinguishes MMPF-4 and MMPF-5 from other types of networks reported for porphyrin-based MOFs, *e.g.* 1D or 3D channelled nets reported by Robson,[20] Suslick[6,21] and Goldberg;[7c,22] pillared nets reported by Choe[23] and Hupp.[8c,d,24] They also differ from MMPF-1,[25] in which cages are formed by pillaring two sets of four copper paddlewheel moieties through eight-closely contacted porphyrin ligands. The cages in MMPF-1 therefore possess much lower symmetry compared to those in MMPF-4 and MMPF-5. To our knowledge these high-symmetry porphyrin-based *cubicuboctahedral* cages are unprecedented in metalloporphyrin containing MOMs.[5b,c,d]

MMPF-4 and MMPF-5 possess solvent accessible volumes of 70.4% and 75.5% respectively, as calculated using PLATON.[26] The phase purities of bulk MMPF-4 and MMPF-5 were confirmed by powder X-ray diffraction studies (Fig. S6, ESI†). Thermogravimetric analysis (TGA) revealed a continuous weight loss of ~50% for MMPF-4 (~40% for MMPF-5) from 25 to ~200 °C corresponding to loss of guest solvent molecules, which is closely followed by the loss of tdcpp ligands leading to the collapse of the frameworks (Fig. S7, ESI†).

A major challenge for porphyrin-based MOMs lies with preservation of porosity upon removal of guest solvent molecules.[7,8] To assess their permanent porosities, freshly prepared samples of MMPF-4 and MMPF-5 were activated according to procedures reported in the literature[27] before gas sorption measurements. As shown in Fig. 4a, the Ar adsorption isotherm at 87 K reveals that MMPF-4 exhibits an uptake capacity of 376 cm^3 g^{-1} at the saturation pressure with typical type-I sorption behavior, as expected for microporous materials. Derived from the Ar adsorption data, MMPF-4 has a Langmuir surface area ($P/P_0 = 0.9$) of 1205 m^2 g^{-1} (BET surface area (P/P_0 = 0.01–0.15), 958 m^2 g^{-1}), which to the best of our knowledge, is the second highest yet reported for porphyrin-based MOMs.[8g] N_2 adsorption at 77 K (Fig. S8, ESI†) and O_2 adsorption at 87 K (Fig. S9, ESI†) reveal similar surface area values for MMPF-4, further validating its permanent porosity in the absence of guest solvent molecules. MMPF-5 does not exhibit significant uptake of Ar, N_2, and O_2 at either 77 K or 87 K; however, it demonstrates a substantial CO_2 adsorption capacity of 67 cm^3 g^{-1} (or 3.0 mmol g^{-1}) at 273 K (Fig. S10, ESI†), which corresponds to a NLDFT (non-local density functional theory)[28] surface area of ~740 m^2 g^{-1}. The significant lower surface area of MMPF-5 *vs.* MMPF-4 might be a result of partial framework collapse after removal of the guest solvent molecules, as observed in other porphyrin-based MOFs.[8c,d]

We also investigated CO_2 uptake performance of MMPF-4. The CO_2 adsorption isotherm measured at 273 K indicates that MMPF-4 has an uptake capacity of 124 cm^3 g^{-1} (or 5.54 mmol g^{-1}, or 24.4 wt%) (Fig. 4b), which is among the highest yet reported for porous MOMs under the same conditions.[29] Indeed, it outperforms the best performing ZIF (ZIF-20, 70 cm^3 g^{-1})[29b,30] and porous organic polymer material (PPN-6-SO_3Li, ~110 cm^3 g^{-1}).[31] It also surpasses the high surface area polyhedral cage-containing **rht**-type MOF (**rht**-MOF-1, 98 cm^3 g^{-1}) under the same conditions.[19g] We also measured the CO_2 adsorption isotherm at 298 K, revealing a capacity of 67 cm^3 g^{-1} (or 3.0 mmol g^{-1}, or 13.2 wt%) for MMPF-4 (Fig. 4b), which is again among the highest yet reported for porous MOMs under the same conditions[29] and also surpasses the best performing ZIF (ZIF-78, 9.1 wt%).[29d]

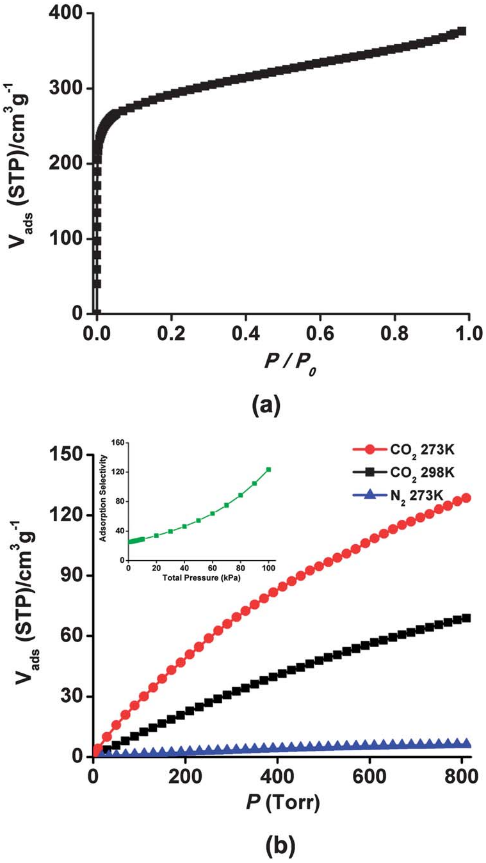

Fig. 4 (a) Ar adsorption isotherm of MMPF-4 at 87 K; (b) CO_2 adsorption isotherms at 273 K (red) and 298 K (black), N_2 adsorption isotherm (blue) at 273 K, and IAST-predicted adsorption selectivity (inset green) for MMPF-4 at 273 K.

To assess the potential of MMPF-4 for possible post-combustion CO_2 capture applications, we also measured N_2 adsorption isotherms. As shown in Fig. 4b, MMPF-4 adsorbs a relatively small amount of N_2 (~3.0 cm^3 g^{-1} or 0.13 mmol g^{-1} at 1 bar), meaning a selective uptake capacity of 41 for CO_2/N_2 at 273 K and 1 bar. Given that our attempts to measure the low-pressure N_2 adsorption isotherms at 298 K could not generate meaningful data points because of the extremely low N_2 uptake capacity, we decided to utilize the adsorption isotherms at 273 K for the assessment. We employed the ideal adsorption solution theory (IAST), which has been shown to be valid for calculating the gas selectivity of MOFs,[32] to estimate the adsorption selectivity of MMPF-4 for CO_2/N_2 in post-combustion flue-gas streams which are typically composed of 15% CO_2 and 85% N_2. As shown in Fig. 4b (inset), MMPF-4 is calculated to exhibit an adsorption selectivity of 123 for CO_2 over N_2 at 273 K and 1 bar. Both the selective uptake capacity observed experimentally and the adsorption selectivity estimated from IAST of MMPF-4 for CO_2 over N_2 are among the highest yet reported for porous MOFs,[29b,33] ZIFs,[30,34] and porous organic polymer materials.[30,35]

Conclusions

In summary, the linkage of a custom designed tdcpp porphyrin ligand by triangular MBBs that are generated *in situ* results in the formation of the high symmetry *small cubicuboctahedron* SBBs that are the result of vertex-directed self-assembly. These SBBs are the key to the generation of two isostructural porphyrin-based MOMs, MMPF-4 and MMPF-5, that are permanently porous, and MMPF-4 exhibits the second highest surface area yet seen for porphyrin-based MOFs. MMPF-4 also demonstrates selective CO_2 uptake. Considering the modularity of the high symmetry *small cubicuboctahedron* SBBs that are prepared *via* the crystal engineering approach described herein, MMPF-4/5 may serve as blueprints for the design of a range of highly porous MOFs. In addition, given the versatility of metalloporphyrins, this work also lays a solid foundation for the construction of functional porous porphyrin-based MOMs for applications in CO_2 capture, gas storage, catalysis, sensing, light-harvesting, *etc.* These goals are currently being addressed in our laboratory with new variants of functional porphyrin ligands.

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