A metal–organic framework with three cavities based on three-coloured square tiling derived from a cyclobutane constructed in the solid state[†]

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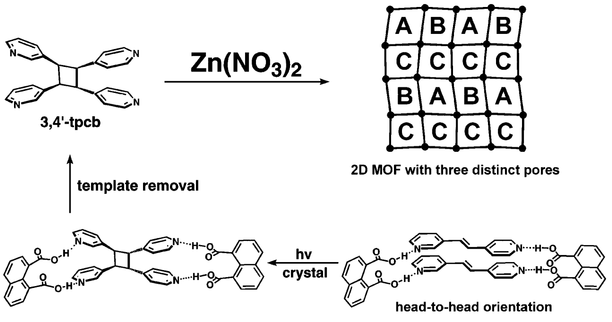
Received (in Victoria, Australia) 14th May 2010, Accepted 29th June 2010
DOI: 10.1039/c0nj00367k

The unsymmetrical tetratopic ligand *rctt*-1,2-bis(3-pyridyl)-3,4-bis(4-pyridyl)cyclobutane self-assembles with zinc(II) nitrate to form a 2D metal–organic framework with three distinct cavities.

Metal–organic frameworks (MOFs) are one of the most studied class of compounds in the area of materials science and supramolecular chemistry.[1] Tremendous interests in MOFs are attributed to scientific and technological applicability (*e.g.* gas storage,[2–4] catalysis,[5] anion[6] and guest[7] exchange, drug delivery).[8–10] Recent studies have reported biporous MOFs (*i.e.* MOFs with two distinct pores) being able to accommodate different guest molecules in different channels.[11–18] A very rare example of a triporous MOF supported by calix[4]arenes has just been reported.[19] Indeed, MOFs with more than one type of cavity can be considered to represent an entry to a new generation of MOF-based materials with applications in areas such as separation processes that, in principle, allow the recognition and storage of compounds unable to coexist (*e.g.* acid/base, oxidizers/reducers).[11] Understanding how to design molecular building units that self-assemble to form MOFs with more than one cavity type can, thus, be considered to represent an important area of development in the advancing field.

In recent years, we have demonstrated how [2 + 2] photodimerisations can be engineered in the organic solid state.[20] Specifically, we have shown that molecular cocrystals can be utilized as reaction media wherein synthetic templates arrange olefins for intermolecular [2 + 2] photodimerisations using principles of hydrogen-bond-driven self-assembly. The cocrystals react to form cyclobutanes lined with pyridyl groups that form stereospecifically, in quantitative yield, and in gram amounts. We have also shown that the resulting cyclobutanes can be utilised as polytopic ligands[21] to form MOFs with up to two different cavities,[15] helical coordination polymers,[22] MOFs with functionalized pores,[23] as well as related metal–organic polygons[24] and polyhedra.[25–27]

Herein, we report a MOF with three different cavities;[28] namely, $[\mathrm{Zn_2}(\mathbf{3,4'\text{-}tpcb})_2(\mathrm{NO_3})_4(\mathrm{H_2O})_4]_\infty$ (**1**) (where **3,4′-tpcb** = *rctt*-1,2-bis(3-pyridyl)-3,4-bis(4-pyridyl)cyclobutane). The ligand **3,4′-tpcb** has been prepared in a templated solid-state synthesis stereospecifically and in quantitative yield (Scheme 1).[29] In the MOF, the cyclobutane, which is unsymmetrical, binds four metal atoms *via* the two different pyridyl groups to give a 2D MOF based exclusively on 4-connected nodes. The formation of three different cavities arises from an ability of the different pyridyl groups to sustain tiling of square cavities wherein the walls of the cavities consist of combinations of 3- and 4-pyridyl groups. The resulting 2D framework exhibits a topology that corresponds to uniform 3-coloured tiling of squares wherein each colour, *de facto*, represents a chemically distinct cavity. Although square tiling is a well-documented target in MOF chemistry, the framework **1** represents, to our knowledge, the first example of a 2D MOF based on 3-coloured uniform tiling. Uniform *n*-coloured tilings (where *n* > 1) are Archimedian tilings that involve *n*-coloured polygons surrounding each identical vertex (Fig. 1).[30,31] MOFs with topologies that correspond to *n*-coloured tilings have, to our knowledge, not been addressed yet, and as we will demonstrate, are attractive models to develop 2D frameworks based on multiple cavities.



Scheme 1

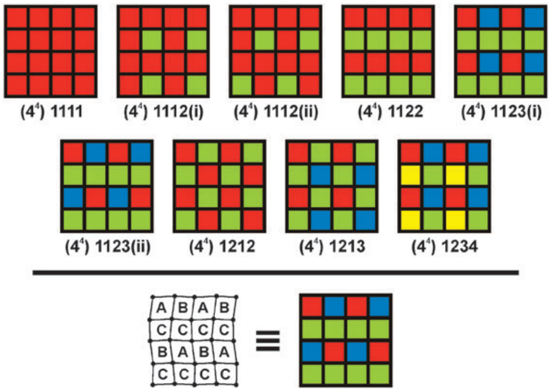


Fig. 1 Uniform colourings of square tiling [(4^4) indicates the vertex configuration,[30,31] whereas each of the four subsequent numbers symbolizes a tile of a distinct colour surrounding a vertex; (i) indicates a simple reflection symmetry, (ii) indicates a glide reflection symmetry].

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[†] CCDC 776968. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0nj00367k

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Compound **1** was prepared by combining acetonitrile solutions of **3,4′-tpcb** (0.025 g, 0.068 mmol) and $Zn(NO_3)_2 \cdot H_2O$ (0.014 g, 0.068 mmol) (25 mL total). A 5 mL aliquot of the colourless solution was layered with 10 mL diethyl ether in a test tube and allowed to sit for approximately one week, which resulted in the formation of colourless single crystals of $\mathbf{1}\cdot 4(H_2O)\cdot(CH_3CN)\cdot[(CH_3CH_2)_2O]$ (**1a**) suitable for X-ray diffraction (yield: 0.030 g, 77%).

X-Ray diffraction studies§ revealed that **1a** crystallises in the monoclinic space group $P2_1/n$. The asymmetric unit contains two **3,4′-tpcb** ligands, two Zn(II) cations, four NO_3^- anions, eight H_2O molecules, one acetonitrile molecule, and one diethyl ether molecule. The components self-assemble into a 2D MOF wherein each ligand and metal ion act as a 4-connected node (Fig. 2). Each Zn(II) ion lies in an octahedral coordination environment, with two 3-pyridyl groups and two 4-pyridyl groups in equatorial positions and water molecules in the axial positions [Zn(II)–N bond distances: 2.124(7)–2.238(7) Å; Zn(II)–O bond distances: 2.113(6)–2.176(6) Å]. As a consequence of the self-assembly process, the components form a 2D MOF based on tiling of approximate square cavities. The opposite corners of each cavity are defined by two Zn(II) ions and two cyclobutane rings, with the walls being composed of the 3- and 4-pyridyl groups. Importantly, that the cyclobutane possesses two different pyridyl groups means that the grid consists of three chemically distinct cavities. In particular, the walls of Cavity A are defined by four 4-pyridyl units, the walls of Cavity B are defined by two 4-pyridyl and two 3-pyridyl units at opposite walls, and the walls of Cavity C are defined by one 4-pyridyl and three 3-pyridyl units. Cavity A is, thus, defined by two acute angles provided by **3,4′-tpcb**, Cavity B is defined by two obtuse angles, and Cavity C is defined by combinations of acute and obtuse angles. The cavities alternate along the crystallographic *b* axis in an ACBC manner and through a 2-fold roto-inversion axis in an ABAB manner. Each vertex is, thus, identical being surrounded by one Cavity A, one Cavity B, and two Cavities C's. As a result of the arrangement, the 2D framework constitutes a 4-connected uninodal net with a $(4^4 \times 6^2)$ topology (*i.e.* Shubnikov tetragonal plane net).[32,33]

The framework **1** self-assembles as stacked layers that are held together by a network of hydrogen bonds. The network involves 16 water molecules, eight NO_3^- ions, and two molecules of diethyl ether (Fig. 3a). The solvent water and ether molecules, as well as included acetonitrile, occupy lacunae between the stacked layers. The hydrogen bonding involving the components can be considered to be composed of one major and two minor subunits. The major subunit lies on a center of inversion and is composed of four NO_3^- ion and six water molecules sustained by 12 hydrogen bonds (Fig. 3b). Four of the water molecules belong to (H_2O)–Zn moieties of adjacent frameworks. The two minor subunits consist of one NO_3^- ion, five water molecules, and one diethyl ether molecule held together by eight hydrogen bonds, with two of the five water molecules belonging to a (H_2O)–Zn moiety (Fig. 3c). The hydrogen bonding serves to link stacked layers (Fig. 3d and e).

An analysis of the structure of **1** using SOLVE subroutine in PLATON[34] revealed that each of the three different cavities do not exhibit solvent-accessible voids. Despite a lack of sizable pores, however, **1** exhibits intriguing structural features that require further comment. Specifically, the MOF **1** is a unique example of a 2D framework with three chemically distinct cavities, or in the mathematical language, a uniform 3-coloured (4^4) 1123(ii) tiling of squares (where (ii) is glide reflection symmetry).[30] More specifically, the different coloured tiles correspond to the three different cavities of **1**

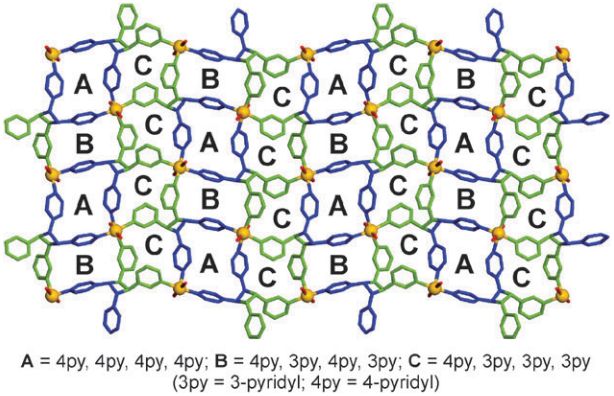


Fig. 2 Crystal structure of **1** showing three different cavities (A, B, C) along the crystallographic *c*-axis (colour scheme: Zn, orange; O, red; 3-pyridyl, green; 4-pyridyl, blue). Cavity dimensions (corner-to-corner distances) and angles: Cavity A: 7.2 × 6.9 Å, 99° and 80°; Cavity B: 7.2 × 6.2 Å, 94° and 85°; Cavity C: (a) 6.9 × 6.6 × 6.2 × 6.6 Å, 92°, 87°, 99° and 82° and (b) 6.9 × 6.6 × 6.1 × 6.6 Å, 85°, 94°, 92° and 88°.

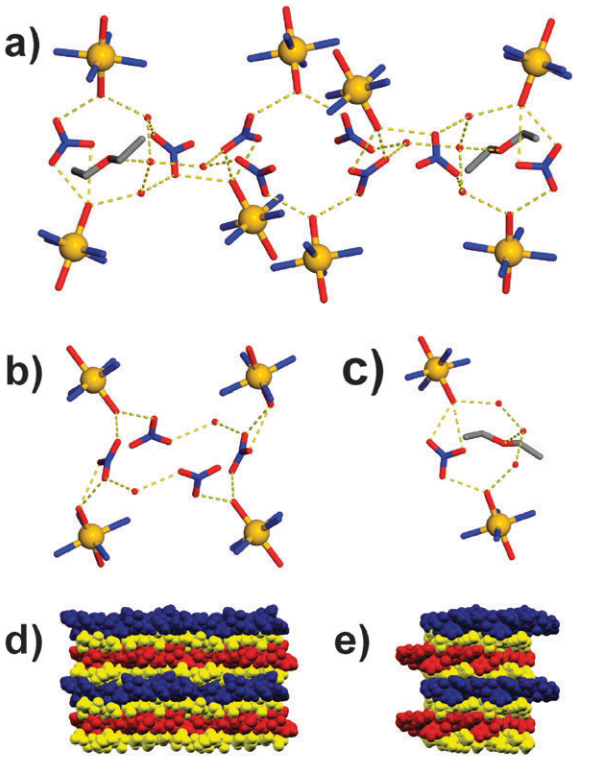
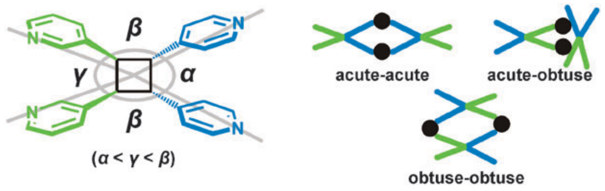


Fig. 3 Crystal structure of (a) hydrogen-bonding involving the NO_3^- ions, H_2O, and ether molecules, (b) major subunit, (c) minor subunit, stacked layers of **1** along the crystallographic axis *c* (d), and *b* (e).



Scheme 2

(Cavity A = red; Cavity B = blue, Cavity C = green) with metal ions and cyclobutane rings as vertices. From a mathematical standpoint, there are only three ways to form uniform square tiling with three distinct colours (Scheme 1). That the components of **1** afford (4^4) 1123(ii) tiling of squares can be attributed to both the presence of the two different pyridyl groups attached to the cyclobutane ring, which defined a total of three different angles, and the flexibility of cavity formation (*e.g.* coordination geometry of Zn(II) ion) to support combinations of acute and obtuse corners (Scheme 2). Moreover, it is likely that other *n*-uniform coloured tilings can be accessible using similar unsymmetrically substituted ligands, which suggests that such coloured tilings can serve as models to develop 2D MOFs based on more than one cavity type.[35]

In summary, we have presented a 2D MOF with three chemically distinct cavities based on an unsymmetrical and rigid tetratopic ligand derived from a solid-state synthesis. The structure of the 2D MOF is based on uniform three-coloured square tiling. Studies are underway to prepare unsymmetrical ligands in the solid state involving pyridyl functionalities that exhibit longer bridge lengths, which would be expected to support MOFs that accommodate different guest species and take advantage of the unusual topologies that can be achieved by stereocontrolled solid-state syntheses.

Notes and references

§ Crystal data for **1a**: $C_{54}H_{69}N_{13}O_{21}Zn_2$, M_r = 1366.96, monoclinic, a = 13.0139(13) Å, b = 27.361(3) Å, c = 17.7274(18) Å, α = 90.00°, β = 90.687(5)°, γ = 90.00°, V = 6311.8(11) Å^3, T = 183(2) K, space group $P2_1/n$, Z = 4, μ(MoKα) = 0.844 mm^{-1}, 40 470 reflections measured, 11 091 independent reflections (R_{int} = 0.1121). The final R_1 values were 0.0901 ($I > 2\sigma(I)$). The final w$R(F^2)$ values were 0.2344 ($I > 2\sigma(I)$). The final R_1 values were 0.1438 (all data). The final w$R(F^2)$ values were 0.2624 (all data). The goodness of fit on F^2 was 1.079. The investigated crystal exhibited pseudo-merohedral twinning that precluded the modeling of the hydrogen atoms belonging to water molecules.

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35 We expect that 3,4′-tpcb, for example, can support 2D tiling of other *n*-uniform coloured tilings.