

Three-fold interpenetrating three-dimensional networks based on *C*-methylcalix[4]resorcinarene incorporating benzophenone guest molecules

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Received (in Columbia, MO, USA) 11th October 2002, Accepted 13th December 2002

First published as an Advance Article on the web 15th January 2003

A new solid based on *C*-methylcalix[4]resorcinarene and the linker molecule bis(4-pyridylmethylidene)hydrazine (bpmh) has been prepared, in which brick-wall sheets are linked in the third dimension to give networks with three intersecting perpendicular channels; the networks interpenetrate three-fold, but nevertheless leave cavities capable of including sizable guest molecules.

Solid-state dilution of photoactive species plays an important role in time-resolved diffraction studies of excited state structures.^{1,2} Molecular dilution without sacrificing the three-dimensional crystalline periodicity achieved by the supramolecular method has the advantage over amorphous mixtures that precise information on the molecular geometry can be obtained by conventional diffraction methods.³ *C*-Methylcalix[4]resorcinarene (CMCR) is a versatile building block that has significant application in constructing supramolecular frameworks capable of accommodating molecules of interest.^{4,5} A remarkable variety of different frameworks with spacers (pillars) such as 4,4'-bipyridine and the 4,4'-bis(pyridyl)ethylene have been generated based on the flexibility of conformation of CMCR. They include the 0D capsule, 1D wave-like, 2D brick-wall and 2D and 3D stepped networks.^{6–8} To incorporate large guest molecules, the size of cavity must be extended. One strategy is to employ longer spacers, the other is to insert a linker molecule in between neighboring CMCRs within the CMCR columns as in CMCR-3bipy·2H₂O·Ph₂CO, in which water molecules are interspersed within the CMCR column, extending the cavity.⁹

A third strategy is extension of the cavity or channel by judicious choice of pillars that can connect the basic structural units (BSUs) in the third dimension. Among the structural architectures exhibited by CMCR and pyridyl ligands, the brick-wall BSUs show four types of patterns with different number and arrangement of pillars.¹⁰ With the exception of BW4, which has four pillars per CMCR molecule so that all OH donor groups of CMCR are involved in the two-dimensional framework structure, the other three frameworks retain free hydroxyl groups accessible to hydrogen bond acceptors, which can increase the structural dimensionality, given the larger flexibility of hydrogen bonds compared with covalent bonding.

We have synthesized such a three-dimensional network by use of the longer spacer bis(4-pyridylmethylidene)hydrazine (bpmh). A phase with three-fold interpenetrating 3D networks of composition CMCR·2bpmh·Ph₂CO **1** was obtained. While a doubly interpenetrating network based on CMCR has been described very recently,¹¹ this is the first solid with three-fold interpenetrating supramolecular frameworks based on either calixerenes or calixresorcinarenes. Notwithstanding the interpenetration of three frameworks the cavities are sufficiently large to include a pair of benzophenone molecules. In contrast to almost all known CMCR-based frameworks which are formed by connecting CMCR molecules with pillars along the axial direction of CMCR, the framework of **1** is supported by pillars in both axial and equatorial directions.

Good quality crystals of **1** were obtained by slow evaporation of an ethanol solution of CMCR–bpmh–benzophenone with 1:2:2 ratio of the components.¹² Low-temperature X-ray

diffraction analysis shows that **1** consists of a three-dimensional hydrogen bonded network.¹³ The CMCR molecules adopt a boat-like (flattened cone) conformation and form molecular columns through intermolecular hydrogen bonding along the equatorial direction [O1...O7a = 2.718(3) Å, O1–H1...O7a = 150(4)°; O2...O4b = 2.698(3) Å, O2–H2...O4b = 149(3)°; O3...O5b = 2.837(3) Å, O3–H3...O5b = 176(3)°; O8...O6a = 2.737(3) Å, O8–H8...O6a = 177(3)°; a: $-x + 1, -y + 2, -z$; b: $-x + 1, -y + 1, -z + 1$]. These columns are connected by bpmh spacers into brick-wall sheets of the BW2a type (two

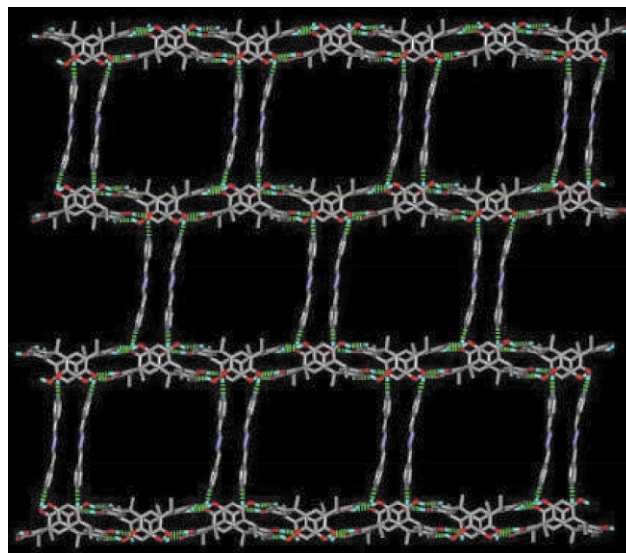


Fig. 1 Brick-wall sheet formed by bpmh and CMCR in **1**.

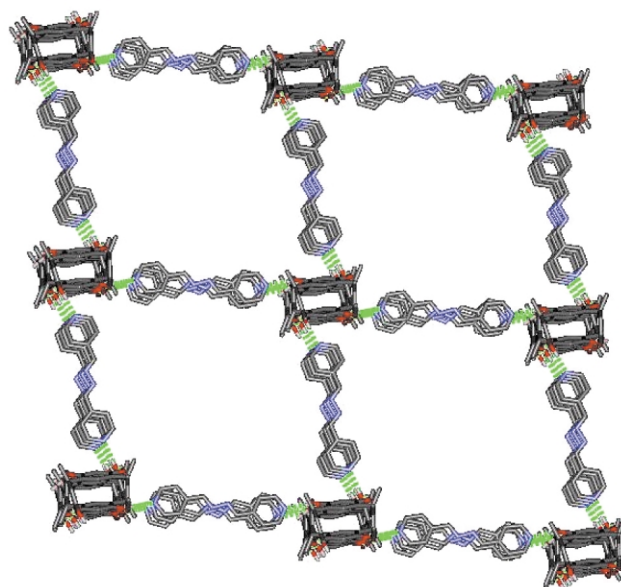


Fig. 2 3D framework formed by bpmh pillars connecting the 2D brick-wall sheet in **1**.

juxtaposed spacer molecules per CMCR) through O–H...N hydrogen bonding [O5...N2 = 2.672(3) Å, O5–H5...N2 = 174(4)°; O6...N1c = 2.731(4) Å, O6–H6...N1c = 169(5)°; c: $-x, -y + 1, -z$] as illustrated in Fig. 1. The remaining two hydroxyl groups of each CMCR are oriented such that the O–H bonds point outward and are nearly orthogonal to the plane of the brick-wall sheet, so that they can form O–H...N hydrogen-bonds in the third direction to additional bpmh pillars [O4...N7d = 2.678(4) Å, O4–H4...N7d = 140(5)°; O7...N5e = 2.688(4) Å, O7–H7...N5e = 164(5)°; d: $-x, -y + 1, -z + 1$; e: $x, y + 1, z$]. This gives rise to a three-dimensional network with 3D interlinked channels with approximate dimensions of 16.6 × 16.0 Å, 16.6 × 16.5 Å and 16.5 × 10.0 Å, one of which is illustrated in Fig. 2. The large channels have a strong tendency to being filled by self-inclusion. A view depicting the 3-fold interpenetration is shown in Fig. 3(a). The double bpmh linkers in the third dimension are threaded through the voids of two successive brick-walls.

Two benzophenone guests related by an inversion center are located within the cavity left after interpenetration, such that two phenyl rings from different benzophenones form strong π – π interactions [inter-planar and center to center distances are

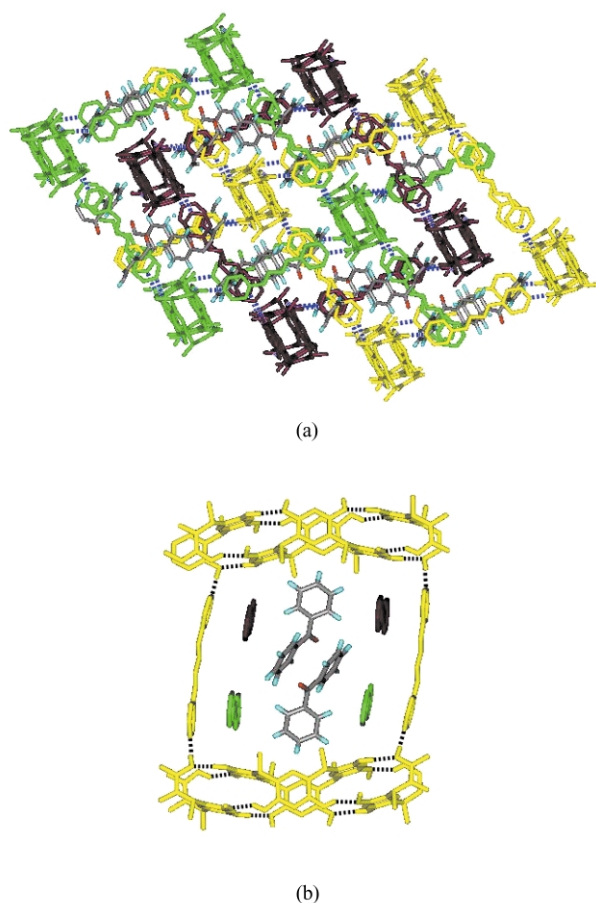


Fig. 3 (a) View of the 3-fold interpenetrating networks of **1**. (b) View showing the arrangement of the guests within the cavity remaining after interpenetration of the networks. The bpmh linker molecules of the two other networks are seen edge on in the figure.

3.381 and 3.675 Å, respectively] (Fig. 3(b)). The twist angles between the C(C=O)C plane and the two phenyl ring planes of benzophenone are 23.9 and 43.3°, significantly different from those in neat benzophenone crystals and benzophenone supramolecular compounds,³ indicating the effect of the host framework on the conformation of the guest molecules. As expected, an appreciable dilution of the photoactive guest is achieved in the host–guest crystal (1.16 vs. 6.64 M/L in the neat solid). However, preliminary spectroscopic examination at room and low (25 K) temperatures indicates that the luminescence of benzophenone in **1** is quenched, an observation that requires further exploration.

In summary, a novel framework with a unique 3D structure has been prepared. A large cavity capable of including two benzophenone guest molecules remains in spite of the 3-fold interpenetration that occurs in the solid. In the new solid CMCR connects into a framework along both the axial and the equatorial directions, providing a new pathway to CMCR-based materials with large microporous structures. Suppression of the interpenetration by inclusion of a suitable guest has the potential of generating a framework with exceptionally large cavities.

Support of this work by the National Science Foundation (CHE9981864) and the Petroleum Research Fund of the American Chemical Society (PRF37614-AC3) is gratefully acknowledged.

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- CMCR (0.05 mmol, 27.2 mg), bis(4-pyridylmethylidene)hydrazine (0.1 mmol, 20.8 mg) and benzophenone (0.1 mmol, 18.2 mg) were mixed in 5 mL ethanol solution and heated until the solution became clear. The solution was cooled and some orange precipitate (identified as CMCR-2bpmh-EtOH) was filtered off. Yellow prismatic crystals of **1** were obtained from the filtrate at room temperature after 5 days.
- Crystal data*: compound **1**: C₆₉H₆₂N₈O₈; *M*_r = 1147.27, triclinic, space group *P* $\bar{1}$, *a* = 13.810(6), *b* = 14.509(5), *c* = 15.157(6) Å, α = 89.123(11), β = 73.006(14), γ = 81.958(12)°, *U* = 2875(2) Å³, *Z* = 2, *D*_c = 1.325 Mg m⁻³, crystal size 0.32 × 0.18 × 0.10 mm³, μ (Mo-K α) = 0.089 mm⁻¹, *F*(000) = 1208, *GoF* = 1.029. Among 35257 reflections, 15638 reflections are unique (*R*_{int} = 0.0318). The final *R*₁ and *wR*₂ are 0.0830 and 0.1835, respectively, for 1024 parameters and 7631 reflections [*I* > 2 σ (*I*)]. The data were collected on a Bruker SMART1000 CCD with Mo-K α radiation (λ = 0.71073 Å) at 150(1) K. Reflections were reduced by the SAINT program. The structures were solved by direct methods and refined by a full matrix least squares technique based on *F*² using the SHELXL 97 program. CCDC 195326. See <http://www.rsc.org/suppdata/cc/b2/b209989f/> for crystallographic data in CIF or other electronic format.