Transformation of a C-methylcalix[4]resorcinarene-based host-guest complex from a wave-like to a novel triangular brick-wall architecture

Bao-Qing Ma and Philip Coppens*
Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14260-3000, USA.
E-mail: coppens@acsu.buffalo.edu

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A novel 2D triangular brick-wall framework based on CMCR and bpe with included ruthenocene guest molecules is formed with time by conversion of a 1D wave-like polymer structure with an accompanying bowl-to-boat conformational change of the CMCR molecules.

Solid state host–guest assembly has attracted intensive interests because of its applications in fields as diverse as nonlinear optics, sensors and micro-reaction vessels.1,2 Guests in host materials like cyclodextrins, clathrates and zeolites may exhibit photophysical properties significantly different from those of neat crystals. It has recently been demonstrated that C-methylcalix[4]resorcinarene (CMCR) forms supramolecular frameworks with bifunctional pillars such as 4,4′-bipyridine, capable of including molecular guests of interest. The various frameworks show great diversity and include capsule, brick-wall, wave-like and stepped networks,3,4 which allow guests of different size and shape to be entrapped.

The major impetus for the inclusion of ruthenocene and decamethylruthenocene within the host framework are their hydrogen bonds [O1⋯N2 = 2.695(5) Å, O1⋯H1⋯N2 = 126(6)°; O2⋯N1b = 2.757(5) Å, O2⋯H2⋯N1b = 162(6)°; c –x, -y + 2, -z + 1] between hydroxy groups and two stacked bpe dimers link the CMCR molecules into a 1D wave-like polymer. Adjacent polymers arrange in a tongue-in-groove way, leaving a cavity in between juxtaposed CMCRs, in which one ruthenocene and one ethanol molecule guest, located across a crystallographic two-fold axis, are accommodated.

The CMCRs in compound 2 adopt a boat-like conformation and form typical molecular columns through complementary intermolecular hydrogen bonds [O1⋯O3 = 2.764(4) Å, O1⋯H1⋯O3 = 169(4)°; O2⋯O4b = 2.755(3) Å, O2⋯H2⋯O4b = 163(4)°; -x + 1, -y + 1/2, -z; b x + 1/2, -y – 1/2, z + 1/2]. Two stacked bpe dimers are hydrogen-bonded in diagonal directions to the upper rims of two non-adjacent (1,3) CMCRs in adjacent columns [O3⋯N1 = 2.716(4) Å, O3⋯H3⋯N1 = 162(4)°; O4⋯N2 = 2.766(4) Å, O4⋯H4⋯N2 = 161(5)°; x – 1/2, -y + 1/2, z – 1/2], forming a two-dimensional sheet as illustrated in Fig. 2. It is comparable with the rectangular brick-wall framework BW4,17 in which two stacked bpe dimers connect columns in the perpendicular direction. The new architecture relates to a triangular net in the same way the brick wall structure relates to a rectangular net (Fig. 3) and can be described as triangular brick wall. This unique architecture with a (4,4) net18 has not been realized before in supramolecular chemistry, though other four-connected networks such as the 2D grid, the kagome, diamond and NbO architectures, have been observed frequently.19

A clear relationship between the two structures exists. Compound 2 can virtually be viewed as an evolution from 1. When the CMCR conformation converts from bowl to boat, the intramolecular hydrogen bonds within the upper rim of CMCR are broken and change their orientation to the axial direction. This allows hydrogen bonding with the bpe dimers which reorient toward cavity to facilitate formation of the bonds. The

Fig. 1 Crystal structure of 1.
intermolecularly hydrogen bonded hydroxy groups of CMCR in 1 are linked to bpe spacers, but also have a close contact (O–O distance 4.1 Å) with those from an adjacent wave-like polymer. The flattening of the CMCR phenyl rings previously attached to the bpe spacers shortens the intermolecular distances between the hydroxy groups in adjacent waves leading to the formation of columns of hydrogen-bonded CMCR molecules, thus shrinking and the ethanol molecule...