

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

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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 long luminescence lifetimes,⁵ as well as the significant geometry change upon excitation established by spectroscopic experiments and theoretical calculations.^{6–9} Because of the molecular dilution achieved such complexes are potential candidates for time-resolved photocrystallography.¹⁰ Surprisingly, though many examples of ferrocene inclusion compounds, such as (DCA)₂·Fe(C₅H₅)₂ (DCA = deoxycholic acid),¹¹ 2(α-CD)·Fe(C₅H₅)₂,¹² CMCR·*m*bipy·*n*Fe(C₅H₅)₂^{13,14} (*m* = 2, *n* = 1; *m* = 1.5, *n* = 0.85) and Pd₆(tpt)₆(2,2'-bipy)₆[Fe(C₅H₅)₂]₄¹⁵ (tpt = 1,3,5-tri(4-pyridyl)-2,4,6-triazine) have been described, the only report on inclusion of ruthenocene or its derivatives in a supramolecular framework is that on the CMCR·2bipy·decamethylruthenocene complex.¹⁶

We report here the first example of a transformation from a wave-like to a not previously observed triangular brick-wall structure, which is accompanied by a conformational change of CMCR from a bowl to a boat-like (flattened cone) structure, leading to a supramolecular isomer of identical framework composition, but different structural connectivity. *trans*-1,4-Bis(pyridyl)ethylene (bpe), a longer spacer than bipy, is used to assemble a host–guest complex in the presence of ruthenocene. Two novel complexes of composition CMCR·2bpe·ruthenocene-ethanol **1** and CMCR·2bpe·ruthenocene **2** have been prepared as follows.

A clear solution obtained by heating a mixture of CMCR (0.05 mmol, 27.2 mg), *trans*-1,4-bis(pyridyl)ethylene (0.1 mmol, 18.2 mg) and ruthenocene (0.1 mmol, 23.1 mg) in 3 ml ethanol solution was kept at room temperature. Yellow block-shaped crystals of **1** were obtained within 1 day. They converted to yellow prismatic crystals of **2** after being kept in solution for one week,[†] indicating compounds **1** and **2** to be kinetically-controlled and thermodynamically-stable phases, respectively.

X-Ray diffraction analysis revealed that the framework of **1** consists of a wave-like polymer as depicted in Fig. 1.‡ CMCR adopts a bowl-like conformation with four intramolecular hydrogen bonds [O3···O2 = 2.938(6) Å, O3–H3···O2 = 171(5)°; O4···O1^a = 2.774(6) Å, O4–H4···O1^a = 165(6)°; ^a –*x*, *y*, –*z* + 3/2] along the upper rim of CMCR. Four O–H···N

hydrogen bonds [O1···N2 = 2.695(5) Å, O1–H1···N2 = 126(6)°; O2···N1^b = 2.757(5) Å, O2–H2···N1^b = 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^a = 2.764(3) Å, O1–H1···O3^a = 169(4)°; O2···O4^b = 2.755(3) Å, O2–H2···O4^b = 163(4)°; ^a –*x* – 1/2, –*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^c = 2.766(4) Å, O4–H4···N2^c = 161(5)°; ^c *x* – 1/2, –*y* + 1/2, *z* – 1/2]. 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

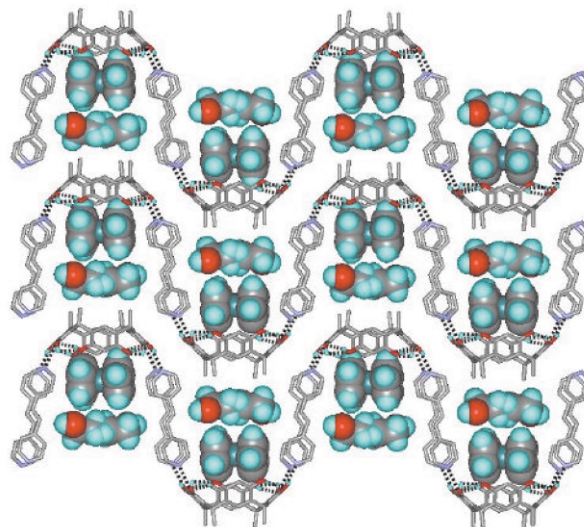


Fig. 1 Crystal structure of **1**.

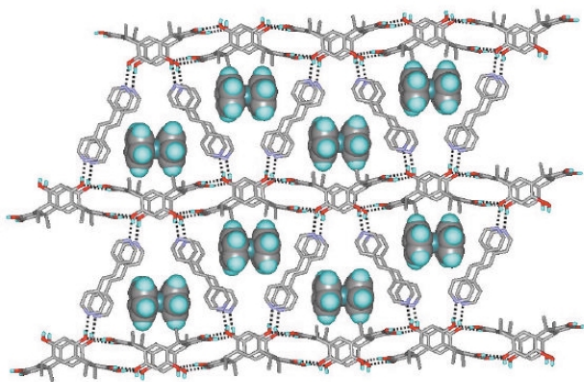


Fig. 2 Crystal structure of **2**.

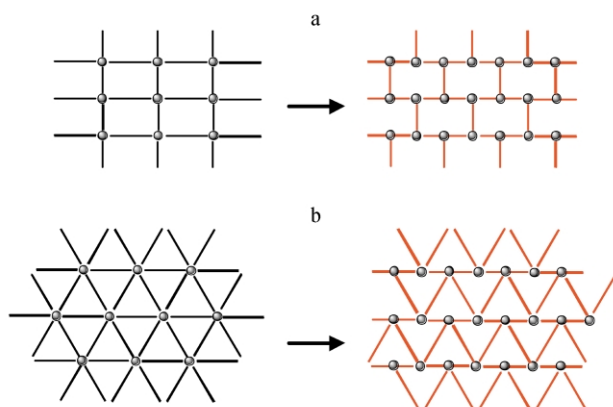


Fig. 3 Relation between the rectangular and triangular nets (left) to the rectangular and triangular brick-wall structures (right). Every second row shifts by half a translation period, reducing the connectivity at each of the nodes from 4 to 3 in the rectangular case (a) and from 6 to 4 in the triangular networks (b).

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 completing the transformation from the wave-like to the triangular brick-wall architecture. As a consequence of this transformation, the cavity of **1** shrinks and the ethanol molecule is squeezed out. At the same time the ruthenocene molecules move from the rim of the CMCR bowl to the opposite site of the cavity, previously occupied by the ethanol molecules. In both **1** and **2** the ruthenocene guest is entrapped within the cavity in such a way that its principal rotation axis is approximately perpendicular to that of CMCR. The molecule adopts an eclipsed D_{5h} conformation, similar to that observed in neat ruthenocene.²⁰ No significant difference between the Cp–Ru distances in **1** and **2** and that in neat ruthenocene was found.

Due to numerous hydroxy groups and the conformational flexibility of CMCR, CMCR-based systems exhibit a very opulent supramolecular diversity.²¹ The frameworks of **1** and **2** are supramolecular (conformational) isomers. This is the first observation of supramolecular isomers in CMCR/bpe systems.

In summary, respectively kinetically-controlled and thermodynamically-stable conformational isomers **1** and **2** have been identified. They are related by an unusual transformation of a

supramolecular framework into a structure with different conformation and connectivity of the main component. The transformation provides guidance for the rational design of new supramolecular solids and the prediction of structural motifs. The observation of the novel triangular architecture of **2** once again demonstrated the versatility of CMCR-based frameworks.

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Notes and references

† The possibility that the conversion represents solution of **1** and simultaneous crystallization of **2**, rather than a novel solid state transformation is being investigated.

‡ Crystal data: Compound **1**: $C_{68}H_{68}N_4O_9Ru$; $M_r = 1186.33$, monoclinic, space group $C2/c$, $a = 15.0614(18)$, $b = 14.6928(18)$, $c = 26.775(4)$ Å, $\beta = 95.622(5)^\circ$, $U = 5896.7(13)$ Å³, $Z = 4$, $D_c = 1.336$ Mg m⁻³, crystal size $0.21 \times 0.16 \times 0.10$ mm³, $\mu(\text{Mo-K}\alpha) = 0.328$ mm⁻¹, $F(000) = 2480$, $GoF = 1.012$. Among 51747 reflections, 8818 reflections are unique ($R_{\text{int}} = 0.0804$). The final $R1$ and $wR2$ are 0.0703 and 0.1906, respectively, for 449 parameters and 4015 reflections [$I > 2\sigma(I)$]. Crystal data: Compound **2**: $C_{66}H_{62}N_4O_8Ru$; $M_r = 1140.27$, monoclinic, space group $C2/c$, $a = 23.9761(12)$, $b = 17.1389(9)$, $c = 15.5942(8)$ Å, $\beta = 121.336(2)^\circ$, $U = 5473.3(5)$ Å³, $Z = 4$, $D_c = 1.384$ Mg m⁻³, crystal size $0.26 \times 0.22 \times 0.18$ mm³, $\mu(\text{Mo-K}\alpha) = 0.349$ mm⁻¹, $F(000) = 2376$, $GoF = 1.033$. Among 42681 reflections, 7979 reflections are unique ($R_{\text{int}} = 0.0637$). The final $R1$ and $wR2$ are 0.0568 and 0.1639, respectively, for 450 parameters and 5332 reflections [$I > 2\sigma(I)$]. The data were collected on a Bruker SMART1000 CCD with MoK α radiation ($\lambda = 0.71073$ Å) at 293(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 196014 and 196015. See <http://www.rsc.org/suppdata/cc/b2/b212548j/> for crystallographic files in CIF or other electronic format.

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