

# Structural Variation and Supramolecular Isomerism in the *C*-Methylcalix[4]resorcinarene/Bipyridine System

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**ABSTRACT:** Five supramolecular compounds [CMCR·2bipy] **1**, [CMCR·3bipy] **2**, [CMCR·2bipy·2H<sub>2</sub>O] **3**, [2CMCR]·1.5bipy·5H<sub>2</sub>O **4**, and [CMCR·bipy]·3.5ethanol·H<sub>2</sub>O·bipy **5** (where the square brackets enclose framework components, CMCR = *C*-methylcalix[4]resorcinarene, bipy = 4,4'-bipyridine), prepared hydrothermally and from solution, are described. CMCR adopts a chair conformation in **1** and **2**, and a flattened cone conformation in **3–5**. The framework structures vary from 2D stepped-sheet (**1**), 3D stepped sheet (**2**), brick-wall (**3** and **5**) to a network consisting of perpendicular nonintersecting ribbons of CMCR molecules (**4**). The supramolecular architectures found in the current study are compared with those of other multicomponent CMCR/bipy system reported in the literature. The nature of the enclosed cavities in the brick-wall type structures is a function of the number of phenoxy OH groups not involved in the framework hydrogen bonding, and thus available for bonding to guest molecules. The number of solvent-binding phenoxy groups per CMCR ranges from two to zero in the brick-wall structures surveyed here.

## Introduction

Crystal engineering is continuing to attract attention due to its relevance to molecular recognition, ion exchange, small molecule inclusion, and, in general, the rational design of new materials.<sup>1–3</sup> Numerous functional host–guest complexes have been prepared through metal–ligand and hydrogen bonding or  $\pi$ – $\pi$  interactions. Our initial interest in the supramolecular solids formed by *C*-methylcalix[4]resorcinarenes (CMCR) and bifunctional “pillar” molecules such as bipyridine (bipy) and *trans*-bis(4-pyridyl)ethylene (bpe) was motivated by their capability to include photoactive molecules, leading to diluted but often ordered solids, suitable for the time-resolved photocrystallographic studies.<sup>4–6</sup>

In previous work, we have reported a flattened-cone conformation of CMCR, giving a CMCR/bipy *brick-wall* framework that can accommodate the large decamethylruthenocene molecule.<sup>4</sup> The first crystallographic observations of the CMCR chair-conformation were made on samples prepared by hydrothermal methods,<sup>5</sup> which also yielded three other frameworks with guest benzophenone molecules.<sup>6</sup>

Because of its conformational flexibility, first observed by solution NMR methods,<sup>7</sup> and a large number of OH groups, CMCR is an unusual versatile building block for supramolecular assemblies. Frameworks based on CMCR and bipyridine have been shown to contain large cavities capable of accommodating organic or inorganic guests, including a 0D carcerand-like capsule,<sup>6,8</sup> a 1D wavelike polymer,<sup>9,10</sup> a 1D linear structure,<sup>11</sup> a 2D brick-wall-like sheet,<sup>4</sup> and a 3D stepped network.<sup>5</sup>

We describe here a number of CMCR/bipy supramolecular solids: [CMCR·2bipy] **1**, [CMCR·3bipy] **2**, [CMCR·2bipy·2H<sub>2</sub>O] **3**, [2CMCR·1.5bipy]·5H<sub>2</sub>O **4**, and [CMCR·bipy]·3.5ethanol·H<sub>2</sub>O·bipy **5** and discuss their structures in view of the known CMCR/bipy structural chemistry.

Table 1. Summary of Hydrothermal Syntheses

sample	CMCR molar	bipy molar	additive	resulting CMCR/bipy ratio in solid
I	0.025	0.05	benzil 0.05	<b>1</b> : 1:2
II	0.025	0.05	benzil 0.05	<b>2</b> : 1:3
III	0.025	0.05	benzil 0.05	<b>3</b> : 1:2
IV	0.025	0.05	benzophenone 0.05	<b>4</b> : 1:0.75
A	0.05	0.025		<b>4</b> : 1:0.75, <b>1</b> : 1:2
B	0.05	0.05		<b>2</b> : 1:3
C	0.05	0.1		<b>2</b> : 1:3
D	0.05	0.2		<b>2</b> : 1:3, <b>3</b> : 1:2
E	0.05	0.4		<b>2</b> : 1:3, very small crystals only

## Experimental Procedures

**Synthesis.** Compound **1** was prepared as follows. An aqueous solution (4 mL) of *C*-methylcalix[4]resorcinarene (0.025 mmol), bipyridine (0.05 mmol), and benzil (0.05 mmol) was mixed and sealed in a heavy walled Pyrex glass tube (ca. 6 mL). The mixture was maintained at 140 °C for 1 day in an oven, and subsequently cooled to room temperature at a rate of 20°/day. Light yellow crystals were collected. Compounds **2**, **3**, and **4** were prepared under nominally identical conditions in different runs in the presence of either benzophenone or benzil.

In a second run, using the same hydrothermal procedure, five tubes were loaded with aqueous solution (4 mL) of *C*-methylcalix[4]resorcinarene (0.05 mmol) and bipyridine (0.025(A), 0.05(B), 0.1(C), 0.2(D) and 0.4(E) mmol). Compounds **1** and **4** were found in tube A; compound **2** was found in tubes B and C; compound **2** and **3** were found in tube D. Thus, though the phases with the highest CMCR/bipy ratio (**1**: 1:2, **4**: 1:0.75) were obtained from A as might be expected, and the 1:3 ratio phases from solutions B–D, the 1:2 ratio phase **3** was also obtained from the bipy-rich solution D. Very small crystals of **2**, identified at the SUNY X3 beamline at NSLS, were obtained from tube E. The hydrothermal syntheses are summarized in Table 1.

Complex **5** was prepared under moderate conditions by addition of bipy (0.1 mmol) to a 97% hot ethanol solution (5 mL) of CMCR (0.05 mmol) in the presence of benzil (0.5 mmol). Colorless needle-shaped single crystals were obtained by slow evaporation. **5** appears as the dominant phase also when benzophenone or decamethylruthenocene rather than benzil

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**Table 2. Crystallographic Data for 1–5**

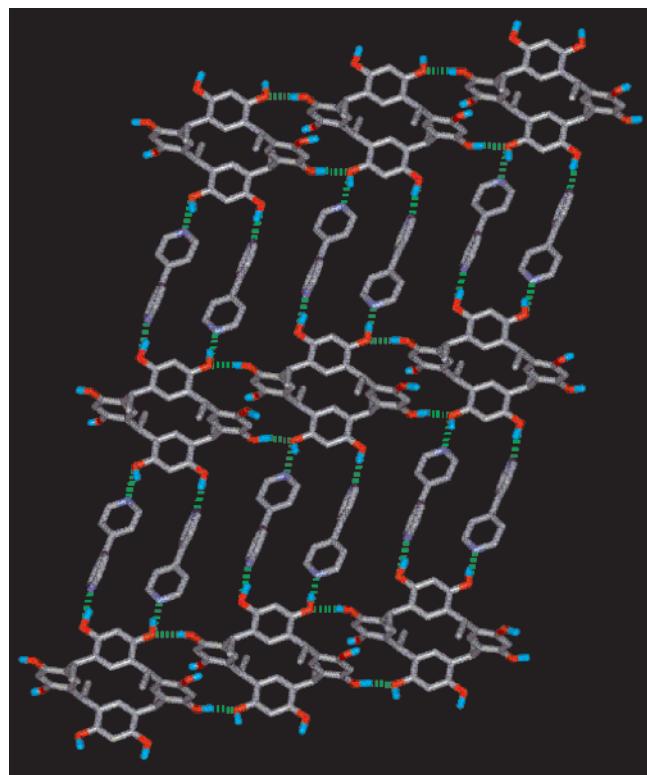
compound	CMCR·2bipy <b>1</b>	CMCR·3bipy <b>2</b>	CMCR·2bipy·2H <sub>2</sub> O <b>3</b>
empirical formula	C <sub>52</sub> H <sub>48</sub> N <sub>4</sub> O <sub>8</sub>	C <sub>62</sub> H <sub>56</sub> N <sub>6</sub> O <sub>8</sub>	C <sub>52</sub> H <sub>52</sub> N <sub>4</sub> O <sub>10</sub>
fw	856.94	1013.13	892.98
crystal size (mm)	0.28 × 0.24 × 0.14	0.30 × 0.18 × 0.10	0.34 × 0.18 × 0.14
T (K)	90(1)	90(1)	90(1)
λ (Å)	0.71073	0.71073	0.71073
space group	P-1	P-1	P-1
a/Å	6.9270(11)	9.8060(6)	13.0965(11)
b/Å	10.8968(18)	10.8427(6)	13.8019(13)
c/Å	14.735(2)	13.0429(8)	13.9915(12)
α/deg	101.312(6)	74.672(2)	63.410(2)
β/deg	100.335(6)	73.633(2)	84.946(4)
γ/deg	95.999(4)	89.016(2)	75.216(3)
V(Å <sup>3</sup> )	1061.6(3)	1280.78(13)	2185.7(3)
Z	1	1	2
D <sub>c</sub> (Mg/m <sup>3</sup> )	1.340	1.314	1.357
μ (mm <sup>-1</sup> )	0.091	0.088	0.095
F(000)	452	534	944
GoF	1.060	0.951	0.934
R1, [I > 2σ(I)]	0.0669	0.0550	0.0415
wR2,	0.1889	0.1378	0.0914
[I > 2σ(I)]			
compound	2CMCR·1.5bipy·5H <sub>2</sub> O <b>4</b>	CMCR·2bipy·3.5ethanol·H <sub>2</sub> O <b>5</b>	
empirical formula	C <sub>79</sub> H <sub>86</sub> N <sub>3</sub> O <sub>21</sub>	C <sub>59</sub> H <sub>71</sub> N <sub>4</sub> O <sub>12.5</sub>	
fw	1413.51	1036.20	
crystal size (mm)	0.18 × 0.08 × 0.05	0.20 × 0.10 × 0.10	
T (K)	90(1)	90(1)	
λ (Å)	0.71073	0.71073	
space group	P2(1)/n	C2/c	
a/Å	13.735(2)	30.608(3)	
b/Å	27.419(6)	16.861(2)	
c/Å	18.398(4)	22.005(2)	
α/deg	90	90	
β/deg	109.087(7)	105.517(2)	
γ/deg	90	90	
V(Å <sup>3</sup> )	6548(2)	10942.2(18)	
Z	4	8	
D <sub>c</sub> (Mg/m <sup>3</sup> )	1.434	1.258	
μ (mm <sup>-1</sup> )	0.104	0.088	
F(000)	2996	4424	
GoF	0.970	0.935	
R1, [I > 2σ(I)]	0.0937	0.0587	
wR2,	0.2526	0.1492	
[I > 2σ(I)]			

are added to the reaction mixture. No evidence for inclusion of guest molecules was found in any of these cases.

**X-ray Diffraction and Structure Solution.** X-ray data were collected with the SMART program on a Bruker SMART1000 CCD diffractometer installed at a rotating anode source (Mo K $\alpha$  radiation  $\lambda = 0.71073 \text{ \AA}$ ), and equipped with an LN<sub>2</sub> Oxford Cryostream Cooler. To avoid loss of solvent of crystallization, the mounted crystal was put into the cold stream immediately after being removed from its mother liquor. The program SAINT<sup>12</sup> was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined with SHELXL.<sup>13</sup> Hydrogen atoms of the CMCR, ordered bipy, and water molecules in **2** and **3** were located in difference Fourier maps and refined without constraints. The other hydrogen atoms were positioned at calculated locations. Crystallographic data for complexes **1–5** are given in Table 2.

## Results and Discussion

**Description of the Structures.** In compound **1** (Figure 1), the CMCR molecules are located on inversion centers and have the chair conformation of C<sub>2h</sub> sym-

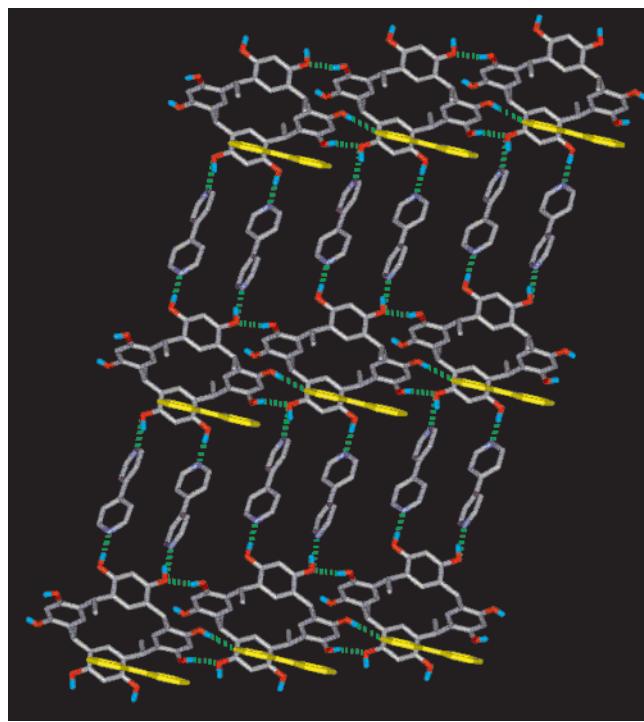


**Figure 1.** The two-dimensional stepped sheet hydrogen-bonded CMCR/bipy network of **1**.

metry, in which two of the opposite aryl rings are coplanar but rotated by 180° with respect to each other, and the other two rings are at an angle of 91.8° almost perpendicular to this plane. The four methyl groups lie in axial positions and have the *rctt* (reference–cis–trans–trans) arrangement of the chair conformer, as in [CMCR·3bipy·2H<sub>2</sub>O]·benzophenone,<sup>5</sup> rather than the more common crown-shaped, or the “flattened cone” conformation recently observed for several CMCR complexes.<sup>4,14</sup>

As shown in Figure 1, in **1** each CMCR is linked to adjacent CMCR molecules by four phenoxyl O–H…O hydrogen bonds to form columns parallel to the crystallographic [010] direction [O3…O1a = 2.765(3) Å, O3–H3…O1a = 165(4)°; a: x, y – 1, z]. O–H…N hydrogen bonds between the axial phenoxyl groups and bipyridine molecules link the columns into stepped stair-like sheets parallel to the (011) plane [O1…N2b = 2.699(4) Å, O1–H1…N2b = 166(4)°; O2…N1c = 2.800(3) Å, O2–H2…N1c = 165(4)°; b: x, y + 1, z, c: –x + 2, –y + 3, –z + 2] (Figure 1). Adjacent sheets are connected through interlayer hydrogen bonding between CMCRs [O4…O4d = 2.798(4) Å, O4–H4…O4d = 131(8)°; d: –x + 1, –y + 2, –z + 1], leading to a three-dimensional framework.

**2** (Figure 2), described previously,<sup>5</sup> has a structural motif similar to that of **1**. The CMCR molecules adopt the chair conformation and are linked laterally with adjacent CMCR molecules into extended columns. Hydrogen bonded bipy “pillar” molecules connect the columns into stepped sheets. In this structure, adjacent sheets are connected by a second set of bipy spacer molecules, to yield a bipy-supported 3D stepped network.



**Figure 2.** The three-dimensional stepped sheet CMCR/bipy hydrogen-bonded network of **2**.

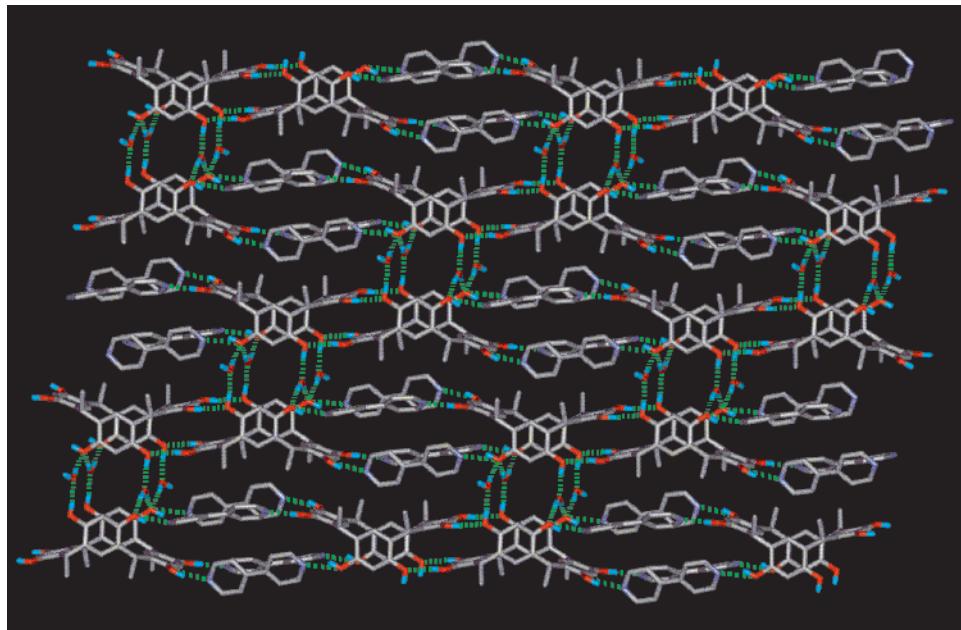
**1** and **2** are solvent-free despite being crystallized from aqueous solution in which hydrogen bonding must be prominent. It is commonly assumed that the nature of the solvent and templating function of the guest molecules, in which the size, functionality, and shape of guest favor a particular assembly process, play an important role in determining the host framework. Nevertheless, no guest molecules were included in the bulk of **1** and **2**, even when benzil was present in the reaction mixture.

Although **1** and **2** contain no open channels, the ability of the stepped-sheet framework to accommodate

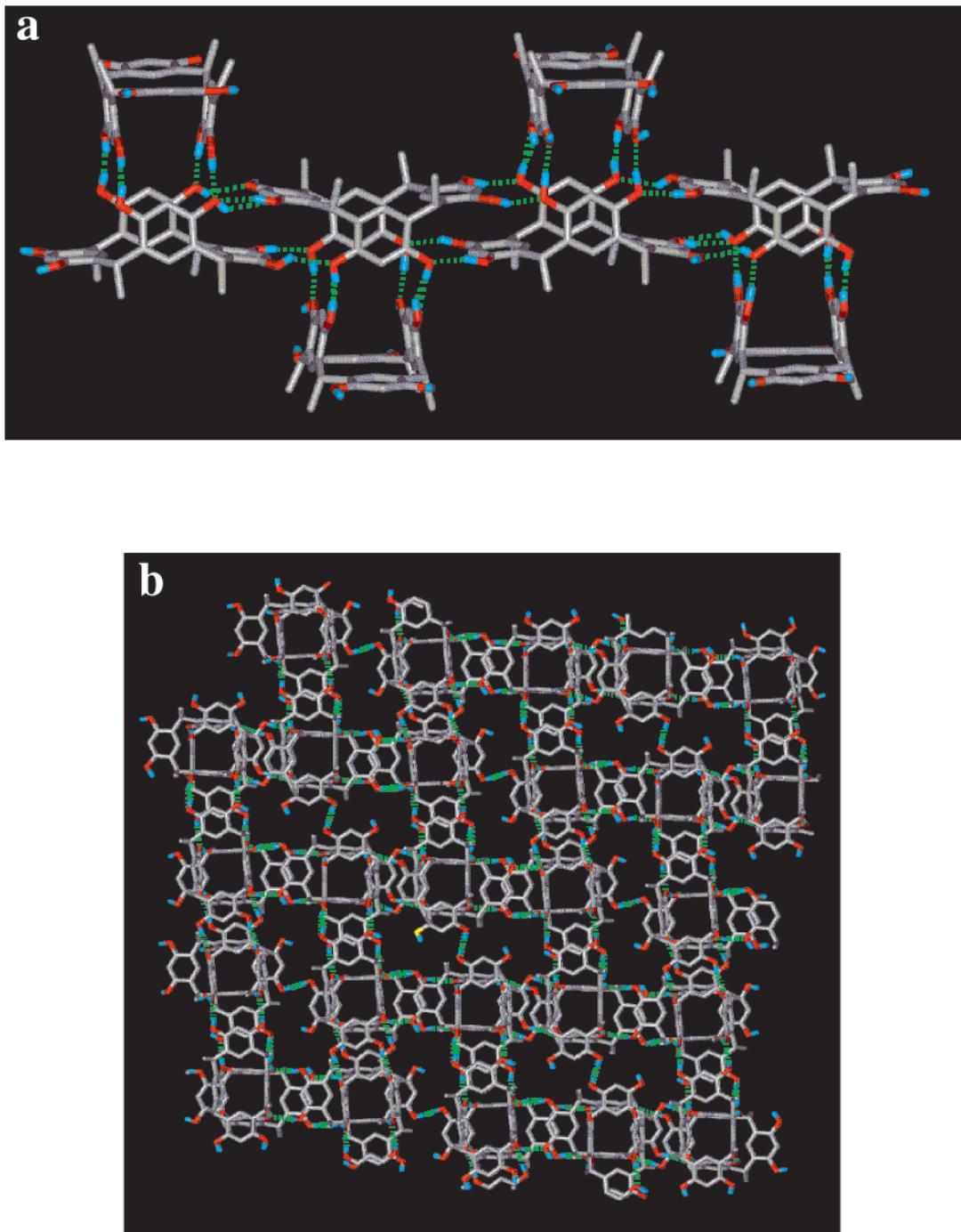
guest molecules is demonstrated by  $[\text{CMCR}\cdot 3\text{bipy}\cdot 2\text{H}_2\text{O}]\text{-benzophenone}$ ,<sup>5</sup> which has the architecture of **2**, except that hydrogen-bonded water molecules are interspersed between adjacent CMCR molecules in the same column, such as to extend the size of cavity and allow inclusion of bulkier guest molecules.

In compound **3** (Figure 3), two adjacent CMCR molecules with the flattened-cone conformation form a side-to-side hydrogen-bonded dimer [ $\text{O}7\cdots\text{O}1\text{a} = 2.856(2)$  Å,  $\text{O}7-\text{H}7\cdots\text{O}1\text{a} = 163(2)$ °;  $\text{O}8\cdots\text{O}6\text{a} = 2.890(2)$  Å,  $\text{O}8-\text{H}8\cdots\text{O}6\text{a} = 177(2)$ °;  $\text{a}: -x, -y + 2, -z + 1$ ]. The dimers are connected along the equatorial direction of CMCR through hydrogen bonding with two pairs of stacked bipy molecules [ $\text{O}2\cdots\text{N}3\text{b} = 2.739(2)$  Å,  $\text{O}2-\text{H}2\cdots\text{N}3\text{b} = 149(2)$ °;  $\text{O}3\cdots\text{N}1\text{c} = 2.759(2)$  Å,  $\text{O}3-\text{H}3\cdots\text{N}1\text{c} = 172(2)$ °;  $\text{O}4\cdots\text{N}4 = 2.797(2)$  Å,  $\text{O}4-\text{H}4\cdots\text{N}4 = 164(2)$ °;  $\text{O}5\cdots\text{N}2\text{d} = 2.707(2)$  Å,  $\text{O}5-\text{H}5\cdots\text{N}2\text{d} = 153(2)$ °;  $\text{b}: -x + 1, -y + 4, -z$ ;  $\text{c}: x, y + 1, z$ ;  $\text{d}: -x + 1, -y + 3, -z$ ] to form ribbons parallel to the [101] direction. Four water molecules, related by a center of symmetry, serve as bridges to link the ribbons into a two-dimensional brick-wall-like sheet. One water molecule ( $\text{O}10$ ) acts as double hydrogen bonding donor to bridge two phenoxyl oxygen atoms of one CMCR and forms a third H-bond by accepting a hydrogen from a CMCR in an adjacent ribbon [ $\text{O}10\cdots\text{O}5 = 2.774(2)$  Å,  $\text{O}10-\text{H}12\cdots\text{O}5 = 177(2)$ °;  $\text{O}10\cdots\text{O}2 = 2.866(2)$  Å,  $\text{O}10-\text{H}11\text{c}\cdots\text{O}2 = 177(2)$ °;  $\text{O}1\cdots\text{O}10\text{e} = 2.659(2)$  Å,  $\text{O}1-\text{H}1\cdots\text{O}10\text{e} = 173(2)$ °;  $\text{e}: -x, -y + 3, -z + 1$ ]. A second water molecule ( $\text{O}9$ ) bridges the CMCRs as a hydrogen donor and acceptor [ $\text{O}6\cdots\text{O}9 = 2.692(2)$  Å,  $\text{O}6-\text{H}6\cdots\text{O}9 = 170(2)$ °;  $\text{O}9\cdots\text{O}2\text{e} = 2.892(2)$  Å,  $\text{O}9-\text{H}10\cdots\text{O}2\text{e} = 172(2)$ °].

Thus, the four bipy spacers and four water connectors assemble the CMCR dimers along equatorial and axial directions, respectively, leading to a brick-wall architecture (Figure 3). The remaining hydrogen atom, attached to  $\text{O}9$ , hydrogen bonds with a CMCR molecule from a neighboring sheet [ $\text{O}9\cdots\text{O}3\text{f} = 2.861(2)$  Å,  $\text{O}9-$



**Figure 3.** The two-dimensional CMCR/bipy/water hydrogen-bonded brick-wall sheet of **3**.



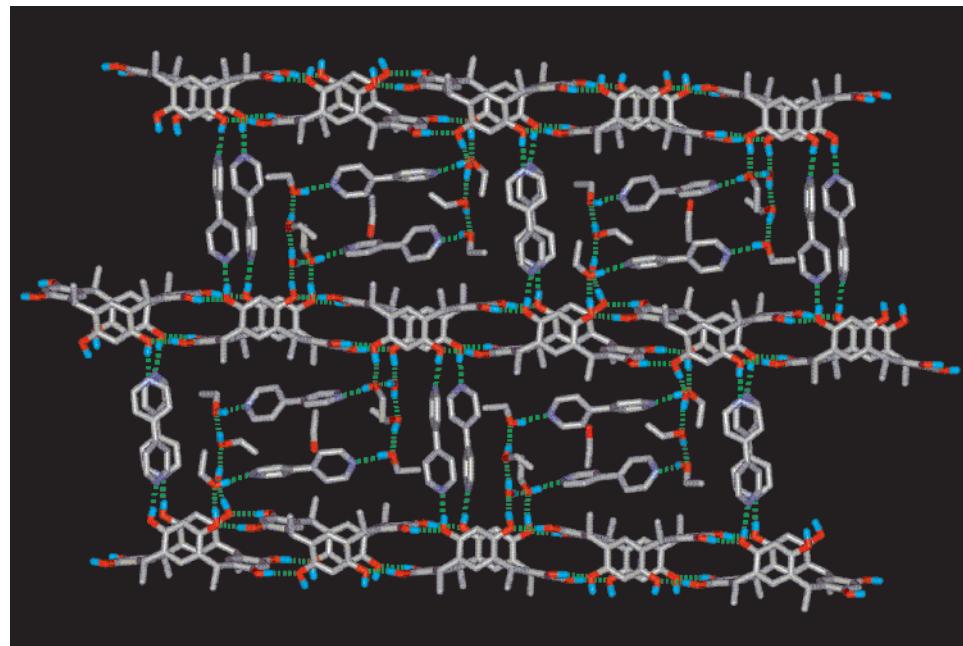
**Figure 4.** (a) View along one of the mutually perpendicular CMCR columns of **4**. (b) View perpendicular to the nonintersecting, mutually perpendicular CMCR columns.

$H9\cdots O3f = 162(2)^\circ$ ;  $f: [x - 1, y, z]$ , giving rise to a three-dimensional network. In the other known brick-wall structures, bipy “pillars” are oriented along the axial direction of the CMCR molecules, to yield a large cavity capable of accommodating guest molecules. The equatorial connection mode in **3** is unusual and presents a novel host framework. A very large cavity could be generated if, while preserving the equatorial bipy connectors, the water-molecule bridges in the axial direction could be replaced by bipy pillars in the presence of suitable guests.

The structure of compound **4** (Figure 4) contains two CMCR molecules in the asymmetric unit, both with the

flattened-cone conformation. Adjacent CMCRs are connected by equatorial hydrogen bonds to form nonintersecting molecular columns along the  $a$  and  $c$  directions. The perpendicular columns are connected into a 3D network through hydrogen bonding between the building blocks. The bipy molecules connect the CMCR molecular columns through hydrogen bonding to stabilize the network.

In compound **5** (Figure 5), the flattened-cone CMCR molecules are linked into columns by intermolecular hydrogen bonds [ $O3\cdots O2a = 2.870(2)$  Å,  $O3-H3\cdots O2a = 172(3)^\circ$ ;  $O4\cdots O5a = 2.710(2)$  Å,  $O4-H4\cdots O5a = 166(4)^\circ$ ;  $O7\cdots O1b = 2.746(2)$  Å,  $O7-H7\cdots O1b = 174(3)^\circ$ ;



**Figure 5.** The two-dimensional hydrogen-bonded CMCR/bipy brick-wall sheet of **5**, showing the bipy and disordered ethanol and water molecules inside the cavity.

**Table 3. Supramolecular Solids Based on CMCR and bipy**

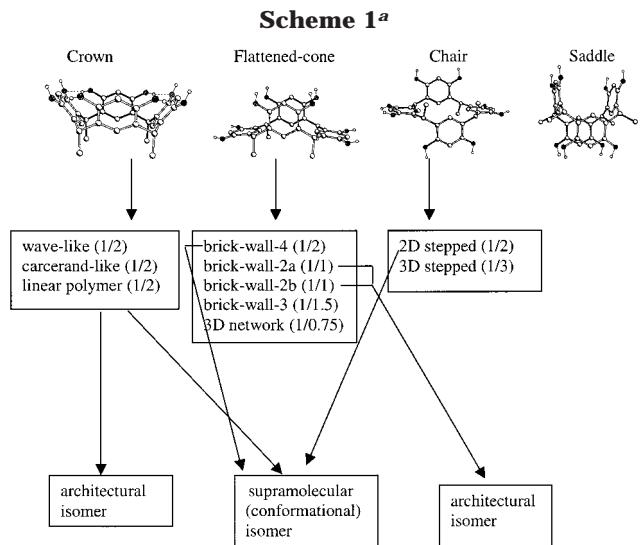
compounds	conformation of CMCR	framework	ref
[CMCR·2bipy]·MeCN	bowl	wavelike	18, 10
[CMCR·2bipy]·ferrocene	bowl	wavelike	8
[CMCR·2bipy]·acetyl ferrocene	bowl	wavelike	8
[CMCR·2bipy]·chlorotoluene	bowl	wavelike	17
[CMCR·2bipy]·adamantanone	bowl	wavelike	17
[CMCR·2bipy]·[2.2]paracyclophane	bowl	wavelike	17
[CMCR·2bipy]·MeNO <sub>2</sub>	bowl	wavelike	18
[CMCR·2bipy]·2THF	bowl	wavelike	19
[CMCR·2bipy]·THF·MeCN	bowl	wavelike	19
[CMCR·2bipy]·4nitrobenzene	bowl	carcerand	9
[CMCR·2bipy]·benzophenone	bowl	carcerand	6
[CMCR·2bipy]·2butanol	bowl	carcerand	20
[CMCR·2bipy]·4-brbp	bowl	linear	11
[CMCR·2bipy]·DMR·2EtOH <sup>a</sup>	flattened-cone	brick-wall	4
[CMCR·2bipy]·4m-xylene	flattened-cone	brick-wall	14
[CMCR·bipy]·benzophenone·H <sub>2</sub> O	flattened-cone	brick-wall	6
[CMCR·bipy]·benzil	flattened-cone	brick-wall	21
[CMCR·1.5bipy]·benzophenone·3EtOH·H <sub>2</sub> O	flattened-cone	brick-wall	21
[CMCR·2bipy]·2H <sub>2</sub> O <b>3</b>	flattened-cone	brick-wall	this work
[CMCR·0.75bipy]·4H <sub>2</sub> O <b>4</b>	flattened-cone	3D network	this work
[CMCR·bipy]·3.5EtOH·bipy H <sub>2</sub> O <b>5</b>	flattened-cone	brick-wall	this work
[CMCR·3bipy]·2H <sub>2</sub> O·benzophenone	chair	3D stepped	5
[CMCR·3bipy] <b>2</b>	chair	3D stepped	this work
[CMCR·2bipy] <b>1</b>	chair	2D stepped	this work

<sup>a</sup> DMR = decamethylruthenocene; 4-brbp = 4-bromobiphenyl.

O8···O6b = 2.905(2) Å, O8–H8···O6b = 174(4)°; a:  $-x + 1, y, -z + 1/2$ ; b:  $-x + 3/2, -y + 3/2, -z$ . In this structure, the columns are linked through O–H···N hydrogen bonding with pairs of stacked bipy dimers to give “skewed-brick” sheets parallel to the (011) plane [O2···N1c = 2.710(3) Å, O2–H2···N1c = 171(4)°; O1···N2 = 2.673(3) Å, O1–H1···N2 = 170(3)°; c:  $-x + 3/2, -y + 3/2, -z + 1$ ]. The dimers are stabilized by  $\pi$ – $\pi$  interactions between the pyridyl groups (with center-to-center and interplanar distances of 4.246 and 3.537 Å, respectively). The two pyridyl groups of the bipy molecules are twisted by 35.8° around the central bond. Successive CMCR/bipyridyl layers are offset with respect to each other, such that cavities rather than channels are formed. Compound **5** is an architectural

isomer of previously reported [CMCR·bipy]·benzophenone·H<sub>2</sub>O.<sup>6</sup> This is the first example of architectural isomerism involving the flattened-cone conformation of CMCR.

In contrast to [CMCR·2bipy]·DMR·2EtOH,<sup>4</sup> in which CMCRs in adjacent columns are connected by two pairs of stacked bipy dimers, in **5** only one pair of dimers connect the CMCR molecules, resulting in a larger cavity. The remaining two phenoxy groups of CMCR are hydrogen-bonded with the water and ethanol solvent molecules [O1···O10c = 2.707(3) Å, O1–H1···O10c = 171(4)°; O6···O40 = 2.683(3) Å, O6–H6···O40 = 171(3)]. Two bipy molecules, oriented approximately perpendicular to the framework bipys, are incorporated within the cavities. The bipy guest molecules form

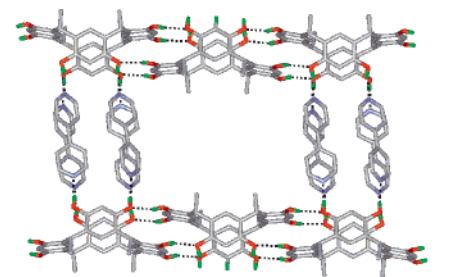


<sup>a</sup> Ratios do not include bipy guest molecules.

hydrogen bonds with ethanol molecules [ $O10\cdots N3 = 2.697(3)$  Å,  $O10-H10\cdots N3 = 170(4)^\circ$ ;  $O9\cdots N4d = 2.785(3)$  Å,  $O9-H9\cdots N4d = 162(5)^\circ$ ; d: x, y, z - 1]. The inclusion of a bipy as a guest rather than a pillar molecule of the CMCR/bipy host framework is unusual.

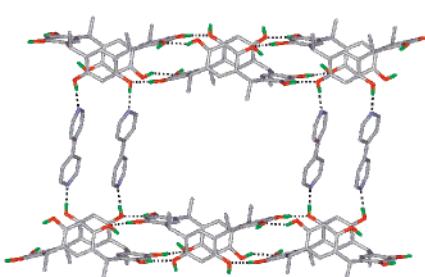
**Synthesis and Reaction.** Hydrothermal methods have been used widely in the preparation of quartz, zeolites, and inorganic–organic hybrid open frameworks,<sup>15</sup> and increasingly also for the synthesis of supramolecular organic systems.<sup>16</sup> The chair conformation of CMCR was first observed in solids after application of hydrothermal synthesis, illustrating that the synthetic method plays an important role in the search for novel structures. Compounds **1–4**, though obtained under similar reaction conditions, exhibit diverse structural character with CMCR/bipy ratios varying from 4/3 to 1/3. It is plausible that conditions vary during the successive steps of the hydrothermal procedure. The nature of the products correlates somewhat with the ratio of CMCR/bipy in solution, as phases with a higher ratio of CMCR/bipy were seldom found in tubes containing lower CMCR/bipy ratios, and vice versa.

**Supramolecular Isomerism.** The reported supramolecular solids based on CMCR and bipy are listed in Table 3, while the dependence of structural type on CMCR conformation and structural relations among the solids are illustrated in Scheme 1. A total of 10 distinct frameworks have been identified so far. The brick-wall nomenclature used in Scheme 1 is further explained in the following section.



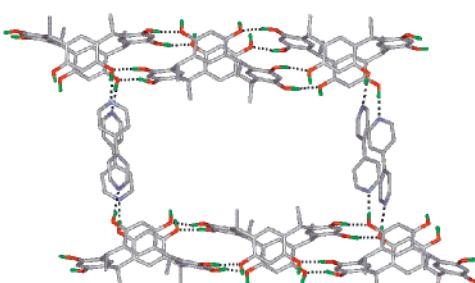
CMCR/bipy = 1/2

BW4



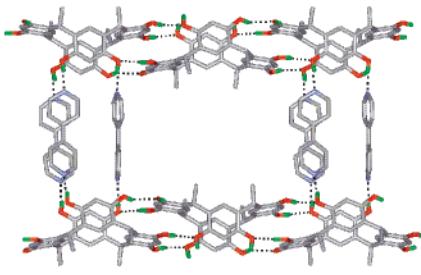
CMCR/bipy = 1/1

BW2a



CMCR/bipy = 1/1

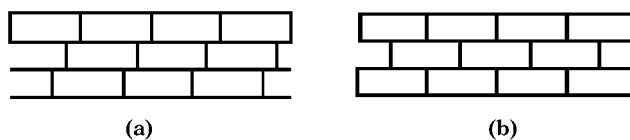
BW2b



CMCR/bipy = 1/1.5

BW3

**Figure 6.** Four different hydrogen-bonded CMCR/bipy brick-wall motifs. Ratios given exclude guest bipy molecules. Examples are as follows, BW4: [CMCR·2bipy]·DMR·2EtOH and [CMCR·2bipy]·4m-xylene, BW2a: [CMCR·bipy]·benzophenone·H<sub>2</sub>O and [CMCR·bipy]·benzil, BW2b: [CMCR·bipy]·bipy·3.5EtOH·H<sub>2</sub>O (5). BW3: [CMCR·1.5bipy]·benzophenone·3EtOH·H<sub>2</sub>O.

**Scheme 2.** Asymmetric Brick-Wall (a) and Regular Brick-Wall (b) Architectures

Compound **1**, in which CMCR adopts the less common chair conformation, displays a novel two-dimensional stepped framework, and is a conformational isomer of the other solids with the 1:2 CMCR/bipy ratio. Though the CMCR/bipy ratio is 1:2 in compounds **3** and **5**, the water molecule participates in the framework in the former, while half the bipy molecules occur as guests in the latter. Thus, they are not supramolecular isomers of the other solids with the 1:2 ratio.

None of compounds **1–5** are supramolecular isomers of each other, as their framework stoichiometries differ, even though the building blocks are the same, with the exception of the incorporation of water molecules in the framework of **4**. However, compound **5** is an architectural isomer of [CMCR·bipy]·benzophenone·H<sub>2</sub>O,<sup>6</sup> in which the brick-wall is constructed from two juxtaposed bipy monomers supporting the CMCR columns, and CMCR similarly has the flattened-cone conformation. A group of five supramolecular isomers with the 1:2 CMCR/bipy framework ratio is identified in Scheme 1.

**Brick-Wall Frameworks.** Among the many structural architectures exhibited by CMCR and bipy, the brick-wall structure occurs commonly when CMCR is in the flattened-cone conformation. While the brick-wall structures are topologically identical, the number and the mode of arrangement of pillars are different among the structures, as illustrated in Figure 6. The frameworks are formed by two pairs of stacked bipy dimers (BW4), two juxtaposed bipy monomers (BW2a), a pair of stacked bipy dimers (BW2b), and a combination of a pair of stacked dimer and a monomer (BW3), with framework CMCR/bipy ratios of 1/2, 1/1, 1/1, and 1/1.5, respectively. In this nomenclature, the number following BW indicates the number of phenoxy groups of each CMCR molecule involved in the H-bonding with the bipyridine pillars. As the other four phenoxy OH groups participate in the equatorial H-bonding, the cavity in the BW4 structure is hydrophobic, while H-donor atoms are available for bonding to solvent molecules in the BW2 and BW3 frameworks.

The brick-wall framework of **3** differs from the others listed in Table 3 in that the CMCR molecules are connected equatorially through bipy molecules and also in that a water molecule is an integral part of the framework. The brick-wall scheme of **3** lacks the mm symmetry characteristic for most of the other frameworks as illustrated in Scheme 2.

## Conclusions

The already impressive variety of CMCR/bipy-based frameworks with composition ratios varying from 4/3

to 1/3 (Table 3) is likely to increase with further exploration of the system. The existence of *multi-frameworks* based on the same building blocks, with the occasional incorporation of water molecules, illustrates the potential of CMCR based solid-state chemistry in particular and supramolecular chemistry in general. The use of longer spacer molecules such as bispyridylethylene (bpe) and higher homologues, already explored in some studies,<sup>5,21</sup> is likely to lead to the discovery of new solids capable of including considerably larger guest molecules.

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