Hydrogen-bonded Supramolecular Solids of Resorcinarenes with 4,4′-Bipyridine and 1,4-Bis(4-pyridyl)butadiyne

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The self-assembly of the bifunctional 4,4′-bipyridine (bipy) with bowl-shaped C-iso-butyl-resorcinarene (1) under two different conditions was investigated. The 0D carcerand-like capsule complex \(1 \cdot 2(bipy) \cdot 0.5\text{EtOH} \cdot 4\text{H}_2\text{O}\) (3) with four stacked bipys was formed in 95 % ethanol solution. The 2D wave-like layered sheet complex \(1 \cdot 2(bipy) \cdot \text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}\) (4) constructed by bipy bridging 1D wave-like ribbons with hydrogen-bonded planar hexagonal rings was obtained from a wet acetonitrile solution. The multicomponent complexes \(2 \cdot 2(bpb) \cdot \text{MeCN}\) (5) and \(1 \cdot (bpb) \cdot 2\text{MeOH}\) (6) formed from self-assembly of 1,4-bis(4-pyridyl)butadiyne (bpb) with C-methyl-resorcinarene (2) in acetonitrile and 1 in methanol, respectively. The structure of 5 reveals four symmetrical intermolecular O–H···N hydrogen bonds between 2 and bpb with two slightly distorted pyridine molecules, forming a wave-like chain polymer. A large extended cavity is built up to give a multicomponent molecular host which is filled with a solvent- and self-inclusion molecule as guests. The structure of 6 exhibits a pair of resorcinarene molecules side-connected to each other by two intermolecular O–H···O hydrogen bonds to form a 1D wave-like tape, which is further bridged by bpb with two perpendicular pyridines to form a 2D sheet.

Key words: Resorcinarene, Hydrogen Bonding, Host-Guest Chemistry, Supramolecular Chemistry

Introduction

A program of study has been aimed at the design of multicomponent hosts held together by non-covalent forces [1]. The typical C-methyl-resorcinarene, which has eight pendant hydroxyl functional groups readily available, may be chosen as a platform for the assembly process [2]. The notable hexameric capsule \([C\text{-methyl-resorcin}[4]arene]_6(\text{H}_2\text{O})_8\), as a large multicomponent host, provides an experimental and structural proof for self-assembling processes found in nature [3], which can bear relevance in understanding related biological phenomena such as reversible interconversions and virus formations [4]. Studies of solid state structures along with multinuclear magnetic resonance investigations have revealed that resorcinarenes may adopt four different conformers, crown \((rccc, C_{4v})\), boat \((rect, C_{2v})\), chair \((rectt, C_{2h})\) and saddle \((rect, D_{2d})\), of which the bowl-like crown conformation has a cavity due to its upper rim hydroxy groups pointing upward [5–7]. It is therefore possible to use resorcinarene as a multiple hydrogen-bond donor in the exploitation of various hydrogen-bonded networks. Indeed, the cavity of resorcinarene has been deepened by hydrogen bonding self-assembly with pyridine and other N-based heterocycles [8]. The known structures of this class of multicomponent molecular solids include a 0D carcerand capsule [9, 10], 1D wave-like [11, 12], 2D brick wall-like [13], 2D stepped [14, 15], 3D stepped [16], and 3D network patterns [17, 18]. Moreover, a variety of guest molecules were encapsulated in the resorcinarene-polypyridine networks as host molecules [2, 19]. The notable studies of Atwood, MacGillivray and Coppens have revealed the ability of the combination of C-methyl-resorcinarene and 4,4′-bipyridine (bipy) to organize, upon crystallization with a suitable guest, into different supramolecular frameworks that may be grouped according to the conformation of C-methyl-resorcinarene [7–16].

With the realization of the interesting multicomponent host-guest behavior with different structural types, we are interested in the hydrogen-bonded assembly of the substituted resorcinarenes with bowl-shaped conformation. Our initial choice of C-iso-butyl-resorcinarene (1) was guided by the retained
C₄₆ symmetric structure of the bowl-shaped conformer which may provide the highest ability to form supramolecular capsules [6]. It is also noted that the high solubility of 1 due to its iso-butyl groups offers a choice of co-crystallization solvents, which brings chances for an unpredictable framework. In studies contributing to the supramolecular chemistry of the host-guest complexes based on resorcinarenes, the hydrogen-bonded supramolecular solids isolated from the self-assembly of substituted resorcinarenes with polypyridines have been studied along with their structural characterization. In this paper, the syntheses and crystal structures of four multicomponent complexes 1·2(bipy)·0.5EtOH·4H₂O (3), 1·2(bipy)·CH₃CN·2H₂O (4), 2·2(bpb)·MeCN (5), and 1·(bpb)·2MeOH (6) (2 = C-methyl-resorcinarene, bpb = 1,4-bis(pyridyl)butadiyne) are presented in this paper.

**Experimental Section**

**General**

All solvents were commercial products of high purity and used as received. Resorcinarenes 1 and 2 were prepared according to procedures described in the literature [20]. 1,4-bis(pyridyl)butadiyne (bpb) was synthesized according to a published method [21]. 4,4'-Bipyridine was purchased from Aldrich Ltd. ¹H NMR spectra were recorded on a Bruker DPX-300 instrument with tetramethylsilane as internal standard.

**Preparation of complex 1·2(bipy)·0.5EtOH·4H₂O (3)**

A mixture of 1 (35 mg, 0.05 mmol) and bipy (15.6 mg, 0.10 mmol) in acetonitrile (5 mL) was gently warmed while stirring until a clear yellow solution was obtained. The solution was covered and allowed to cool slowly to r.t. A mixture of 1 (35 mg, 0.05 mmol) and bipy (15.6 mg, 0.10 mmol) in acetonitrile (5 mL) was gently warmed while stirring until a clear yellowish-orange solution was obtained. The solution was covered and allowed to cool slowly to r.t. Orange crystals of 4 suitable for X-ray diffraction formed, upon cooling, within approximately a week at 4 °C. The crystals were isolated and dried in air at r.t. M.p. 265–270 °C. – ¹H NMR (300 MHz, [D₆]DMSO, ppm): δ = 1.02 (d, J = 6.8 Hz, 24H, CH₃), 1.51 (br, 4H, H₂O), 1.58 (m, 4H, CH(CH₃)₂), 2.02 (t, J = 7.4 Hz, 8H, CH₂), 2.22 (s, 3H, CH₃CN), 4.51 (t, 4H, Ar₂CHCH₂), 7.05 (s, 4H, ArH, ortho to OH), 7.24 (s, 4H, ArH, meta to OH), 7.91 (dd, 4H, J = 7.2 Hz, H in py), 8.49 (bs, 8H, ArOH), 9.12 (dd, 4H, J = 7.2 Hz, H in py). Based on the intensities of the signals, the ratio of resorcinarene to bipy was shown to be 1:1, and the amount of included water and acetonitrile solvents was calculated to be respective two and one molecules for each resorcinarene. – Anal. for (C₉₃H₄₆N₄O₄)·(C₁₄H₈N₂)·(C₂H₃N)·2(H₂O): calcd. C 72.5, H 6.32, N 6.41; found C 73.1, H 6.26, N 6.37. This result indicated no loss of water and acetonitrile molecules.

**Preparation of complex 2·2(bpb)·MeCN (5)**

A mixture of 2 (26 mg, 0.05 mmol) and bpb (22 mg, 0.10 mmol) in acetonitrile (5 mL) was gently warmed while stirring until a clear yellow solution was obtained. The solution was covered and allowed to cool slowly to r.t. Yellow crystals of 5 suitable for X-ray diffraction formed, upon cooling, within approximately two days at 4 °C. The crystals were isolated and allowed to dry for 1 d in air. M.p. 290–300 °C. – ¹H NMR (300 MHz, [D₆]DMSO, ppm): δ = 1.27 (s, 12H, CH₃), 2.21 (s, 6H, 3CH₂CN), 4.42 (t, 4H, Ar₂CHCH₂), 6.26 (s, 4H, ArH, ortho to OH), 6.83 (s, 4H, ArH, meta to OH), 8.05 (dd, 8H, J = 7.2 Hz, H in py), 8.52 (bs, 8H, ArOH), 9.13 (dd, 8H, J = 7.2 Hz, H in py). In these data, we arbitrarily normalized the peaks corresponding to 2 and bpb. The ratio of 2 to bpb is 1:2, and the amount of included acetonitrile solvent was calculated to be one molecule for each resorcinarene. – Anal. for (C₉₃H₄₆N₄O₄)·(C₁₄H₈N₂)·(C₂H₃N)·2(H₂O): calcd. C 74.8, H 5.13, N 7.04; found C 73.1, H 6.26, N 6.37. This result indicated no loss of acetonitrile.

**Preparation of complex 1·(bpb)·2MeOH (6)**

A mixture of 1 (35 mg, 0.05 mmol) and bpb (22 mg, 0.10 mmol) in methanol (5 mL) was gently warmed while stirring until a clear orange solution was obtained. The warm solution was allowed to cool slowly to r.t. Yellowish-orange crystals of 6 suitable for X-ray diffraction appeared after 1 d at 4 °C. M.p. 294–302 °C. – ¹H NMR (300 MHz, [D₆]DMSO, ppm): δ = 0.99 (d, J = 6.8 Hz, 24H,
Table 1. Crystallographic data for multicomponent complexes 3, 4, 5, and 6.

<table>
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<tr>
<th>Complex</th>
<th>3 ((\text{C}<em>{24n+6}\text{H}</em>{40}\text{O}<em>8)) - ((\text{C}</em>{2}n\text{H}_{16}\text{N}_4))</th>
<th>4 ((\text{C}<em>{24n+6}\text{H}</em>{40}\text{O}<em>8)) - ((\text{C}</em>{14n}\text{H}_{28}\text{N}_2)_2)</th>
<th>5 ((\text{C}<em>{28n}\text{H}</em>{42}\text{O}<em>8)) - ((\text{C}</em>{14n}\text{H}_{28}\text{N}_2))</th>
<th>6 ((\text{C}<em>{28n}\text{H}</em>{42}\text{O}<em>8)) - ((\text{C}</em>{14n}+2\text{H}_{2}n\text{O}_2))</th>
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<tr>
<td>Empirical formula</td>
<td>(\text{C}<em>{65n+1}\text{H}</em>{110}\text{N}<em>5\text{O}</em>{12.5})</td>
<td>(\text{C}<em>{66n+1}\text{H}</em>{106}\text{N}<em>5\text{O}</em>{10})</td>
<td>(\text{C}<em>{62n+1}\text{H}</em>{108}\text{N}_5\text{O}_8)</td>
<td>(\text{C}<em>{60n+1}\text{H}</em>{62}\text{N}<em>2\text{O}</em>{10.5})</td>
</tr>
<tr>
<td>Formula weight</td>
<td>1112.29</td>
<td>1092.26</td>
<td>994.08</td>
<td>971.12</td>
</tr>
<tr>
<td>Crystal size, (\text{mm}^3)</td>
<td>0.18 (\times) 0.18 (\times) 0.15</td>
<td>0.45 (\times) 0.40 (\times) 0.32</td>
<td>0.24 (\times) 0.20 (\times) 0.18</td>
<td>0.46 (\times) 0.40 (\times) 0.38</td>
</tr>
<tr>
<td>Space group</td>
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<td>(P2_n/n)</td>
<td>(P2_1/c)</td>
<td>(P1)</td>
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<tr>
<td>(a, ; \text{Å})</td>
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<td>17.4163(12)</td>
<td>11.5578(6)</td>
<td>13.2748(7)</td>
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<td>(b, ; \text{Å})</td>
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<td>9.2246(7)</td>
<td>7.3364(4)</td>
<td>14.0586(7)</td>
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<tr>
<td>(c, ; \text{Å})</td>
<td>24.854(11)</td>
<td>19.6092(14)</td>
<td>30.2748(17)</td>
<td>18.2857(9)</td>
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<td>(\alpha, ; \text{deg})</td>
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<td>(\beta, ; \text{deg})</td>
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<td>99.987(2)</td>
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<td>(T, ; \text{K})</td>
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<td>90</td>
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<td>3144.4(4)</td>
<td>2527.6(2)</td>
<td>2991.9(3)</td>
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<tr>
<td>(Z)</td>
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<td>2</td>
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<tr>
<td>(\mu(\text{MoK}_{\alpha}), ; \text{mm}^{-1})</td>
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<td>0.078</td>
<td>0.087</td>
<td>0.073</td>
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<tr>
<td>(D_d, ; \text{g} ; \text{cm}^{-3})</td>
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<td>1.154</td>
<td>1.31</td>
<td>1.08</td>
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<td>14661</td>
<td>24725</td>
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<tr>
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<td>5540 (0.031)</td>
<td>4460 (0.036)</td>
<td>10545 (0.030)</td>
</tr>
<tr>
<td>Final (R_1, ; wR_2) ([I \geq 2\sigma(I)])</td>
<td>0.078, 0.150</td>
<td>0.060, 0.118</td>
<td>0.057, 0.145</td>
<td>0.071, 0.156</td>
</tr>
<tr>
<td>Final (R_1, ; wR_2) ([\text{all data}])</td>
<td>0.114, 0.238</td>
<td>0.071, 0.151</td>
<td>0.097, 0.145</td>
<td>0.090, 0.206</td>
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<td>Goodness-of-fit on (F^2)</td>
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<td>1.03</td>
<td>1.02</td>
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<td>Residual (\rho, ; e ; \text{Å}^{-3})</td>
<td>+0.64/−0.33</td>
<td>+0.61/−0.46</td>
<td>+0.51/−0.44</td>
<td>+0.56/−0.22</td>
</tr>
</tbody>
</table>

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CH\(_2\), 1.52 (m, 4H, CH(\(\text{CH}_3\)_2), 1.61 (s, 3H, \(\text{CH}_3\)OH), 2.14 (t, \(J=7.4\;\text{Hz}\), 8H, \(\text{CH}_2\)), 4.54 (t, 4H, \(\text{Ar}_2\text{CH}\)), 7.12 (s, 4H, \(\text{ArH, ortho to OH}\)), 7.25 (s, 4H, \(\text{ArH, meta to OH}\)), 8.09 (dd, 4H, \(J=7.2\;\text{Hz}, \text{H in py}\)), 8.65 (bs, 8H, \(\text{ArOH}\)), 9.22 (dd, 4H, \(J=7.2\;\text{Hz}, \text{H in py}\)). Based on the NMR integrals, the ratio of the components in the bulk crystalline material was deduced to be 1:1:2 of 1: bpb: methanol. – Anal. for \((\text{C}_{24n+6}\text{H}_{40}\text{O}_8)\) \(\cdot\) \((\text{C}_{14n}\text{H}_{28}\text{N}_2)\) \(\cdot\) \((\text{C}_{2}n\text{H}_{16}\text{N}_4)\): calcd. C 74.1, H 6.38, N 2.88; found C 73.8, H 6.23, N 2.81.

X-Ray crystallography

X-Ray diffraction data were collected with the SMART program on a Bruker Apex 1000 CCD diffractometer installed at a rotating anode source (\(\text{MoK}_{\alpha}\) radiation \(\lambda=0.71073\;\text{Å}\)). To avoid loss of solvent of crystallization in an air atmosphere, the mounted single crystals were quickly glued onto the end of a thin glass fiber after being removed from their mother liquor. Unit cells were initially determined based on reflections harvested from a set of three scans measured in orthogonal wedges of reciprocal space. The raw data frames were integrated with the SAINT program using a narrow-frame integration algorithm. Corrections for Lorentz and polarization effects were also applied by means of SAINT [22]. An empirical absorption correction based on the multiple measurement of equivalent reflections was applied by using the program SADABS [23]. The structures were solved by Direct Methods and refined by full-matrix least-squares on \(F^2\) using the SHELXTL program package [24]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located in difference Fourier maps and refined without constraints. The water and ethanol solvents in 3 were described without hydrogen atoms due to the disordered atom positions. The carbon and oxygen atoms of the methanol solvent of 6 were refined isotropically without hydrogen atoms due to obvious disorder. The crystallographic and structure refinement data of 3, 4, 5, and 6 are summarized in Table 1.

CCDC 632239, 632240, 632241, 632242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Complex 3 obtained on self-assembly of the components resorcinarene 1 and bipy in warm 95 % ethanol solution crystallized as yellow blocks. The X-ray crystal structure shows that a carcerand-like capsule was indeed formed (Scheme 1).

Pairs of bowl-shaped resorcinarenes are held together in a capsule-like geometry by O–H···N hydrogen bonds to four bipy ligands, as shown in Fig. 1. It should be noted that MacGillivray and Coppens et al. previously reported that self-assembly of C-methyl-resorcinarene and bipy in both solution and solid state afforded a similar 0D carcerand-like capsule [4, 11]. Within each resorcinarene 1,
three of the phenol hydrogens form intramolecular O–H…O hydrogen bonds [O6···O7 = 2.772 Å, O6–H6···O7 = 163.5°; O4···O5 = 2.786 Å, O4–H4···O5 = 137.0°; O1···O8 = 2.787 Å, O1–H1···O8 = 135.8°]. Stacked bipy dimers connect two resorcinarene molecules in a head-to-head fashion through O–H···N hydrogen bonds [O3···N4 = 2.712 Å, O3–H3···N4 = 136.2°; O7a···N3 = 2.723 Å, O7–H7a···N3 = 172.6°; O8a···N2 = 2.716 Å, O8a–H8a···N2 = 173.1°, a: −x, −y + 1, −z]. Two other phenol hydrogens interact with the free water molecules through weak intermolecular O–H···O hydrogen bonds [O2···O1w = 2.956 Å, O2–H2···O1w = 142.9°; O5···O1w = 2.980 Å, O5–H5···O1w = 140.7°]. The bipy is essentially planar with typical bond lengths. It is noteworthy that the bipys are cofacially π-stacked in unsymmetric pairs with a centroid-centroid distance of adjacent pyridine rings of 3.95 Å. As judged by the intermolecular distances between the opposing oxygen atoms in a pair of two bowl-shaped resorcinarene molecules (av. 12.2 Å), the cavity size in 2 is ca. 64.6 Å³ which is the same as in the two structures with the carcerand capsule. The disordered water and ethanol molecules are encapsulated in the cavity.

Self-assembly of the same components, resorcinarene 1 and bipy, in acetonitrile yielded complex 4 as orange prisms. These crystals were indefinitely stable. 1H NMR spectral and elemental analyses indicated that the ratio of 1:bipy:CH₃CN:H₂O was 1:2:1:2 (Scheme 2).

Single-crystal X-ray diffraction analysis revealed that the structure comprised stacked resorcinarene bowls interlinked by water molecules and bridging bipys. The stacked bowls encapsulate acetonitrile molecules. Within each resorcinarene 1, four of the phenol hydrogens form intramolecular O–H···O hydrogen bonds [O1···O4a = 2.796 Å, O1–H1A···O4a = 178.2°; O2···O3 = 2.769 Å, O2–H2A···O3 = 176.6°; a: −x + 1/2, y, −z + 1/2]. Others interact with water and bipy by O–H···O [O3···O1W = 2.684 Å, O3–H3···O1W = 167.7°] and O–H···N [O4···N2a = 2.750 Å, O4–H4···N2a = 161.9°; a: −x + 1/2, y, −z + 1/2] hydrogen bonds, respectively. Adjacent stacks of the resorcinarene bowls face in opposite directions, and the con-
Fig. 2. View of the central $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen-bonded hexagon formed between four phenol moieties and two water molecules in complex 4.

(a)

(b)

Fig. 3. Two orthogonal views of the resorcinarene bowls in complex 4 that are linked by the hexagonal hydrogen-bonded ring containing two water molecules and four phenol groups: (a) top view and (b) side view.

Connections between stacks involve hydrogen-bonded water bridges and water/bipy hydrogen-bonded bridges. It is interesting to note that the hydrogen-bonded linkage between these resorcinarene bowls is essentially planar hexagonal ring (Fig. 2) containing twelve atoms of six OH groups from two water molecules and four phenol hydroxyl groups of two resorcinarene molecules. In the hexagonal ring, the hydrogen bonds have $\text{O} \cdots \text{O}$ hydrogen bond lengths in the range of $2.684 - 2.866 \text{ Å}$ along with an average $\text{O} \cdots \text{H} \cdots \text{O}$ bond angle of $169.9^\circ$. These water molecules are also hydrogen-bonded to a bipy ligand with an $\text{O} \cdots \text{N}$ hydrogen-bond length and an $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen-bond angle of $2.849 \text{ Å}$ and $158.6^\circ$, respectively. This hexagonal arrangement has also been observed in the self-assembly system of the components $\text{C}_m$-methyl-resorcinarene and 1,2-bis(5′-pyrimidyl)ethyne in acetonitrile and diphenylmethane as cosolvents [25]. The present structural mode of the hydrogen-bonded hexagonal ring thus is the second example in the multicomponent system involving resorcinarene and a bipyridine.

As shown in Figs. 3a and 3b (side view and top view), the hydrogen-bonded hexamer connects to opposite sides of each resorcinarene and thereby sets up 1D wave-like ribbons of water-bridged resorcinarenes. The two pyridines of each bipy form an angle of approximately $38.7^\circ$, which may be effectively adjusted to adapt to the electronic and geometric features of the constituent resorcinarene molecules. As a consequence of those forces, apart from formation of water/bipy hydrogen-bonded bridges, the pyridine units of bipy interact as hydrogen bond acceptors with a resorcinarene molecule of the 1D wave-like ribbon by an $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bond [$\text{N}2 \cdots \text{O}4 = 2.750 \text{ Å}, \text{N}2 \cdots \text{H}4 \cdots \text{O}4 = 161.9^\circ$]. Thus, the orientation of these hydrogen bonds $\text{O} \cdots \text{H} \cdots \text{N}$ generates a wave-like 1D ribbon connected to form a 2D wave-
like layered sheet, as shown in Fig. 4. A view of the extended structure of 4 in the xy plane is shown in Fig. 5. The resorcinarene molecules within each layer are held together by intermolecular hydrogen-bonded interactions with center-to-center distances of 9.225 Å, an indication of the absence of obvious π-π stacking interactions within interplanar layers. The channels formed from parallel networks with a dimension of $4.9 \times 4.9$ Å$^2$ are well separated by the host framework, which may be potentially used as a nanoscale organic supramolecular template.

Atwood and coworkers have demonstrated the ability of pyridine and exo-bidentate bis-pyridine to give a cavity by forming walls, which enable 2 to form inclusion complexes with guests previously unobserved for this macrocycle [8]. In particular in the case of 4,4'-bipyridine (4,4'-bipy), the assembly process has resulted in the formation of a 1D self-included hydrogen-bonded array owing to the ability of 4,4'-bipy to act as a linear bifunctional hydrogen bond acceptor [12]. In the present study we are exploring the same idea using 1,4-bis(4-pyridyl)butadiyne (bpb) as the hydrogen bond acceptor to form a deep, extended cavity as a molecular host. The bpb was normally used as a bridging ligand to bind transition metal ions to form coordination polymers [26]. Of special significance is the rigid carbon-carbon chain of the exo-bidentate bis-pyridine, which may result in the formation of a large caged cavity. To test this proposal, 2 was added to a warm solution of acetonitrile containing 2 equiv. of bpb, which immediately afforded a yellow precipitate of 5 (Scheme 3). The $^1$H NMR spectrum of 5 shows two singlets at $\delta = 6.26$ and 6.83 ppm for the aromatic protons. The protons of the hydroxyl groups were observed as a broad peak at 8.52 ppm. Two doublets at $\delta = 8.05$ and 9.13 ppm may be attributed to the protons in the pyridine units of bpb.

A perspective view of the crystal structure of complex 5 is shown in Fig. 6. The bowl-shaped resorcinarene molecule retains $C_2$ symmetry due to the symmetric orientation of the hydrogen bonding in the solid state. This distribution is not surprising since the intramolecular hydrogen bonds hold the resorcinarene in the bowl-like conformation [27]. Within resorcinarene 2, four of the phenol hydrogen atoms
form intramolecular hydrogen bonds with O⋯O distances in the O−H⋯O units of 2.831 and 2.832 Å.

The other four phenolic hydrogen atoms are hydrogen-bonded to two pairs of 2 with intermolecular O−H⋯N distances of 2.772 and 2.782 Å. One MeCN molecule is encapsulated as a guest in the cavity of resorcinarene 2, as shown in Fig. 7. The bpb acts as a nearly linear bifunctional hydrogen bond acceptor to interact with resorcinarene 1 in a head-to-tail arrangement. Two pyridine units of each bpb are slightly distorted at an angle of approximately 16.6°, which may be effectively adjusted to adapt to the electronic and geometric features of the constituent resorcinarene molecules. As a consequence of those forces, the components of 5 [2·2(bpb)·MeCN] assemble in a similar way as the molecular solid [2·2(4,4′-bipy)·MeCN] [12], to form a 1D hydrogen-bonded wave-like polymer held together by a combination of O−H⋯N and O−H⋯O forces (Fig. 8). Thus, like 2·2(4,4-bipyridine)·MeCN [12], 5 is a solvent- and self-inclusion molecular solid. The structural behavior of 5 may be attributed to controlling effects of the spacer and the flexibility of the hydrogen bonds which have provided access to a deepened cavity that permits the formation of self-organized multiple host-guest aggregates in a stacked fashion [28, 29].

Encouraged by the above results with using the long bpb as a spacer, we studied the self-assembly of bpb with 1 in methanol as the solvent. Our initial choice of 1 was guided by the retained $C_{4v}$ symmetric structure of the bowl-shaped crown conformer which may provide the highest ability to form supramolecular capsules [5]. Treatment of 1 with 2 equiv. of bpb in a warm solution of methanol gave a clear orange solution, from which yellowish-orange crystals deposited (Scheme 4). The formulation of 2·2(bpb)·2MeOH (6) was confirmed by single-crystal X-ray diffraction, $^1$H NMR spectroscopy and microanalyses. Results of elemental analyses indicated that there are probably two methanol solvent molecules in the crystalline solid; this conclusion is supported by the X-ray crystallographic analysis, although the methanol solvent molecules were found to be seriously disordered.

The asymmetric unit of the crystal structure of complex 6 contains one unique C-iso-butyl-resorcinarene, one unique bpb, and two disordered methanol molecules. The resorcinarene adopts the bowl-shaped conformation, and four hydroxyl groups
Fig. 9. Top view showing the pair of resorcinarene molecules in complex 6 forming a tape doubly bridged by bpb.

Fig. 10. Side view showing hydrogen bonds to the resorcinarene molecules in the adjacent tapes in complex 6. The pyridine groups of the bpb are nestled in the bowl of resorcinarene molecules.

Form four intramolecular hydrogen bonds [O···O separations (Å): O8···O1 2.823(4), O3···O2 2.845(4), O4···O5 2.710(4), O7···O6 2.843(4)] within each resorcinarene molecule. As shown in Fig. 9, in 6 each resorcinarene 2 is linked to adjacent resorcinarene molecules by four phenoxyl O–H···O hydrogen bonds to form a side-to-side wave-like chain [O8···O1a 2.749(4) Å, O6···O4a 2.713(4) Å, a: x, y−1, z] along the crystallographic [010] direction (also see Fig. 3 from side view). Each bpb links two resorcinarene molecules by N···H–O hydrogen bonds: the distances N2···O2 and N2···H2 are 2.694(4) and 1.920(3) Å, respectively, with a bond angle N2···H2–O2 of 157.1(2)°, and the distances N1···O5 and N1···H5 are 2.675(4) and 1.978(3) Å, respectively, with a bond angle N1···H5–O5 of 154.2(2)°. The two pyridine units of each bpb are almost perpendicular to each other with a dihedral angle of 91.9°. It is interesting to note that the pyridine groups of the bpb are nestled in the bowl of resorcinarene molecules, as shown in Fig. 10. Because the long bpb with two nearly perpendicular pyridine rings as bifunctional hydrogen bond acceptors interact with two resorcinarene molecules with the same directional arrangement [18], the orientation of these hydrogen bonds O–H···N makes wave-like 1D tapes connected to form a 2D sheet, as shown in Fig. 11. In the crystal structure diagram shown in Fig. 12, two wave-like 2D sheets are arranged in the xy plane formed by double layers in the same orientation, suggestive of supramolecular behavior in the present multicomponent complex 6.

In summary, the self-assembly of bifunctional 4,4′-bipyridine (bipy) with bowl-shaped C-iso-butyl-resorcinarene (1) under two different conditions was investigated. The 0D carcerand-like capsule complex 1·2(bipy)·0.5EtOH·4H2O (3) with four stacked bipys and the 2D wave-like layered sheet complex 1·2(bipy)·CH3CN·2H2O (4), constructed by bipy bridging of 1D wave-like ribbons via hydrogen-bonded planar hexagonal rings, were obtained in 95 % ethanol solution and in a wet acetonitrile solution, respectively. Two structural motifs 2·2(bpb)·MeCN (5) and 1·(bpb)·2MeOH (6) were identified for the self-assembly of the long 1,4-bis(4-pyridyl)butadiyne (bpb) with C-methyl-resorcinarene (2) in acetonitrile and 1 in methanol, respectively. In the structure of 5, the bpb acts as a nearly linear bifunctional hydrogen bond acceptor to interact with resorcinarene 1 with head-to-tail arrangement. The wave-like 1D hydrogen bonding polymer contains a deepened cavity due to the long bpb as a spacer. In the structure of 6, the bpb with two perpendicular pyridines makes wave-like 1D tapes, formed by resorcinarene 2 in a side-to-side hydrogen bonding, which are connected to form a 2D sheet. Both multicomponent complexes show layer structures in the crystal.
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