LETTER

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# Fibriform one-dimensional hydrogen-bonded network composed of 1,2-*alt* calix[4]arene tetra acetic acid†

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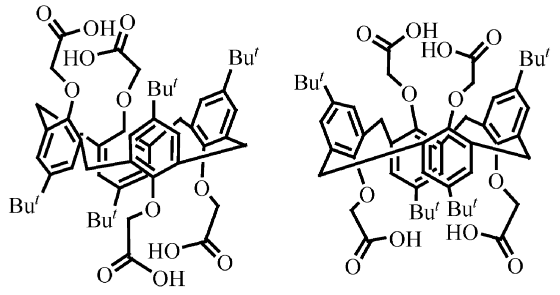
**1,2-*alt* *p*-*tert*-Butylcalix[4]arene tetraacid can self-assemble *via* hydrogen-bonds into a one dimensional network with channel of diameter *ca.* 0.5 nm, and ethanol molecules were incorporated into the network playing roles of hydrogen bond donors and acceptors simultaneously.**

One-dimensional nano structures have become the focus of intensive research owing to their unique applications in mesoscopic physics and for the fabrication of nanoscale devices.[1] Bottom-up chemical construction was used to generate nanostructures.[2] Nano tubes have been made from cyclic peptides,[3] hydrogen-bonded rosettes[4] and coordination complexes.[5] Thus supramolecular tubes, organized by suitable building blocks *via* reversible bonds, have been paid much attention on.[6,7] Calixarenes have attracted consideration as molecular platforms to construct supramolecular synthons.[8] Rebek and coworkers have shown some self-complementary cone conformation calixarenes.[9] Davis also reported a 1,3-alternate calix[4]arene self-assembled into nanotubes in the presence of $Na^+$.[10] Reinhoudt's calixarene rosette architecture formed the template-assisted assembly of a hydrogen-bonded trimer.[4]

By observation with Atom Force Microscopy (AFM), we found that a fibriform assembly was formed by a one dimensional network composed of 1,2-alternate *p*-*tert*-butylcalix[4]arene tetraacetic acid. X-Ray diffraction analysis indicated that the assembly contained channels of *ca.* 0.5 nm diameter assisted by solvent ethanol molecules. No similar assembling phenomena could be observed with the 1,3-alternate conformer with an analogous structure under similar conditions. Here we present the results.

1,2-*alt*-Tetrakis((ethoxycarbonyl)methoxy)-*p*-*tert*-butylcalix[4]arene **1** and 1,3-*alt*-tetrakis((ethoxycarbonyl)methoxy)-*p*-*tert*-butylcalix[4]arene **2** were synthesized as reported in the literature.[11] These two calixarene conformers were derived with difficulty from *p*-*tert*-butylcalix[4]arene directly and were seldom studied. The 1,2-*alt* *p*-*tert*-butylcalix[4]arene tetraacid **3** or 1,3-*alt* *p*-*tert*-butylcalix[4]arene tetraacid **4** (Fig. 1) could be obtained in quantitative yields by reacting corresponding *p*-*tert*-butylcalix[4]arene tetraethyl acetate with NaOH in a solution of ethanol and water. The solubility of compounds **3** and **4** was quite different. Compound **3** was sparingly soluble in $CHCl_3$. When **3** was added to pure $CDCl_3$ only the signals of ethanol were observed in the $^1H$ NMR spectrum.[12] After a little $CF_3COOH$ was added, the obvious signals of **3** appeared (Fig. 2) besides the signals of ethanol. The singlet at 1.29 ppm is due to all the *tert*-butyl groups. A pair of doublets at 3.30 ppm and 4.60 ppm, and a singlet at 4.01 ppm could be assigned as four methylene protons of $ArCH_2Ar$ each. These signals of $ArCH_2Ar$ proved **3** to exist as the 1,2-alternate structure. The doublets at 4.19 ppm and 4.40 ppm are the $OCH_2CO$ protons in different chemical environments. Two doublets at 7.08 ppm and 7.34 ppm showed two different ArH groups in the molecule of **3**. The 1,3-*alt* *p*-*tert*-butylcalix[4]arene tetraacid **4** is very soluble in $CHCl_3$: all proton resonance signals of **4** were clear and sharp peaks in the $^1H$ NMR spectrum in pure $CDCl_3$.[12]

The $10^{-6}$ mol $L^{-1}$ ethanol solutions of compound **3** and **4** were deposited on a mica substrate, and observed by AFM.[13] Fig. 3 showed that ordered fibres appeared on the mica substrate for compound **3**. The width of the nano fibres was about 50–100 nm, while the length of the fibres was above 1000 nm or more. The width and height confirmed that the nano



**3** **4**

**Fig. 1** Structures of compound **3** and **4**.

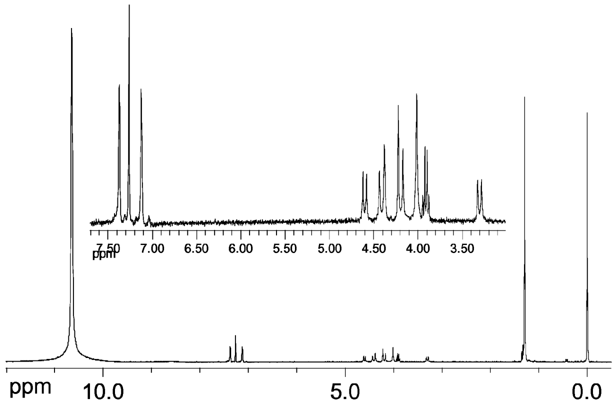


**Fig. 2** $^1H$ NMR spectrum of compound **3** in $CDCl_3$ adding a little $CF_3COOH$.

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† Electronic supplementary information (ESI) available: NMR spectra of compounds **3** and **4**, and colour versions of Fig. 3–7. See http://dx.doi.org/10.1039/b509092j

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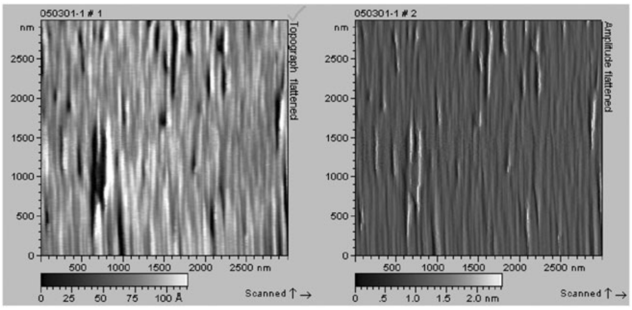

**Fig. 3** AFM micrographs and image of **3**, concentration = $10^{-6}$ mol $L^{-1}$, fibre width *ca.* 50–100 nm.

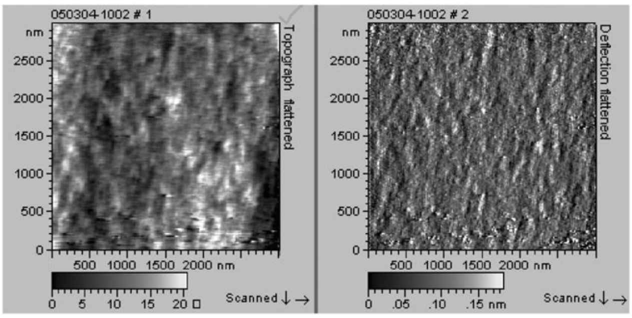

**Fig. 4** AFM micrographs and image of **4**, concentration = $10^{-6}$ mol $L^{-1}$, no fibre observed.

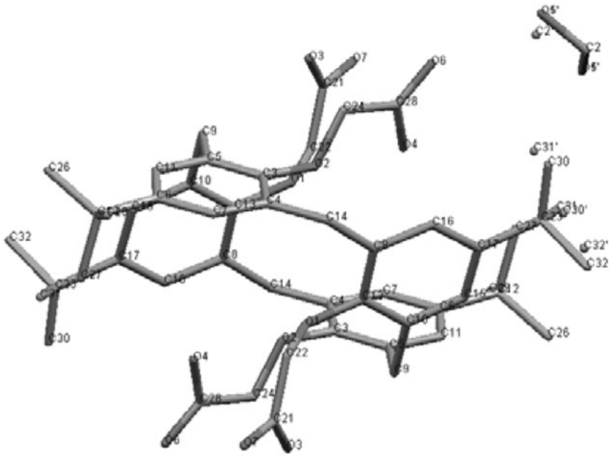

**Fig. 5** The molecular structure (Mercury1.21 Drawing) of **3** with hydrogen atoms omitted for clarity.

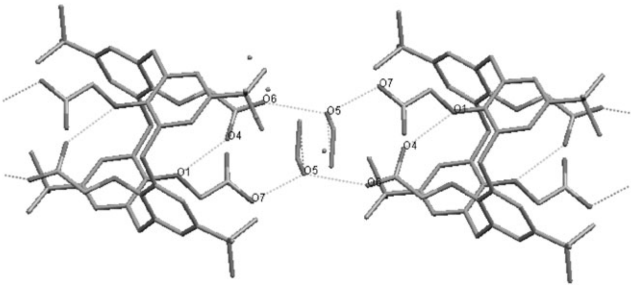

**Fig. 6** Projection showing the hydrogen-bonded network in the presence of ethanol. Hydrogen bonded interactions are shown as broken lines.

fibres consisted of bundles of single calixarene molecule chains. The fibre length reveals that one dimension is preferentially extended. Only an amorphous image was showed by AFM for compound **4** (Fig. 4). From the AFM experiment, the different self-assembling behavior of two *p-tert*-butylcalix[4]arene tetra acid conformers was evidenced. 1,2-*alt* *p-tert*-Butylcalix[4]arene tetraacid **3** could self-assemble in ethanol solution, but **4** could not under the same conditions.

Crystals of the colorless molecular complex, $\mathbf{3}\cdot 2EtOH$,[14] suitable for X-ray diffraction analysis were obtained easily from 1,2-*alt* *p-tert*-butylcalix[4]arene tetraacid ethanol solution by slow evaporation. The molecular structure of **3** is shown in Fig. 5. C30′-C32′ are the disordered methyls of the *tert*-butyl group. C1′, C2′ and O5′ are another disordered ethanol molecule. As shown in Fig. 6, neighboring molecules of **3** are associated with each other *via* two hydrogen bonds by contacting with ethanol. The hydrogen bond network is formed by two linear hydrogen bonds, O5···O6 ($d_{O\cdots O}$ = 2.780 Å) and O5···O7 ($d_{O\cdots O}$ = 2.603 Å). The ethanol acts simultaneously as hydrogen bond donor and acceptor. The distance between O1 and O4 is equal to 2.963 Å. The carboxyl chains of **3** are fixed weakly by an intramolecular hydrogen bond between O1 and O4. This was also supported by the $^1$H NMR spectra. The $OCH_2$ splits into two pairs of doublets, which proves that the two $OCH_2$ hydrogen atoms are situated in different chemical environments. Because each carboxylic side chain was fixed cooperatively by two hydrogen bonds, this one-dimensional network was much stable resulting in insolubility in the aprotic solvent $CHCl_3$. As shown in Fig. 7, this network was parallel to the *a* axis, which was consistent with the results of AFM observations. The structure from single crystal X-ray diffraction confirmed channels of diameter *ca.* 0.5 nm through the self-assembling of calixarene molecular frame.

Furukawa reported that a one-dimensional hydrogen-bonded network was formed by self assembly of calix[4]resorcinarene tetracarboxylic acid which is an aromatic carboxylic acid,[15] but no example concerning a one dimensional network composed of aliphatic carboxylic acids has been reported up to now to the best of our knowledge. The ultimate challenge in crystal design engineering of supramolecular chemistry is to be able to predict the crystal packing based on the molecular attributes.[16] These results help us to understand self-assembly and molecular structure by the study concerning the self-assembly of calixarene aliphatic carboxylic acid.

As mentioned above, the poor solubility of **3** in $CHCl_3$ is attributed to the formation of a one-dimensional network caused by the strong intermolecular interaction between **3** and ethanol. The intramolecular hydrogen bonding between

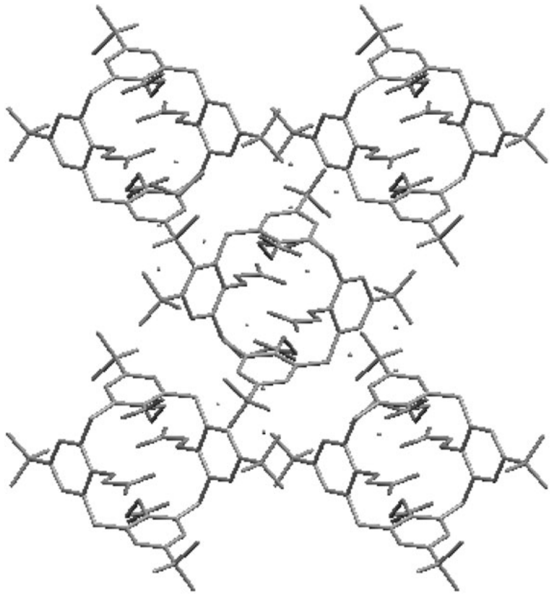

**Fig. 7** Packing diagram of **3** in front view parallel to *a* axis.

O1 and O4 in the 1,2-alternate conformer is auxiliary for the pseudo-rigid structure.

In conclusion, the assembly of 1,2-alternate *p*-*tert*-butylcalix[4]arene tetraacetic acid was studied by X-ray diffraction and AFM. Nano fibres of 50–100 nm diameter can form on the surface of a mica substrate. Both intramolecular and intermolecular hydrogen bonds are necessary for its assembly.

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12 Compound **3**: $^1$H NMR (300 MHz, $CDCl_3$, 295 K), $\delta$: 1.27 (t, $J$ = 6.6 Hz, 3H, $CH_3CH_2OH$ with $\mathit{H_3}$ italic: C*H*$_3$CH$_2$OH), 1.30 (br, 1H, CH$_3$CH$_2$O*H*), 3.74 (q, $J$ = 6.6 Hz, 2H, CH$_3$C*H*$_2$OH); $^1$H NMR (300 MHz, CDCl$_3$ + a little CF$_3$COOH, 295 K), $\delta$: 1.29 (s, C(CH$_3$)$_3$, 36H), 1.27 (t, $J$ = 6.6 Hz, C*H*$_3$CH$_2$OH), 1.30 (overlapped, CH$_3$CH$_2$O*H*), 3.30 (d, $J$ = 12.9 Hz, ArCH$_2$Ar, 2H), 3.74 (q, $J$ = 6.6 Hz, CH$_3$C*H*$_2$OH), 4.01 (s, ArCH$_2$Ar, 4H), 4.19 (d, $J$ = 16.5 Hz, OCH$_2$CO, 4H), 4.40 (d, $J$ = 16.5 Hz, OCH$_2$CO, 4H), 4.60 (d, $J$ = 12.9 Hz, ArCH$_2$Ar, 2H), 7.08 (d, $J$ = 2.4 Hz, ArH, 4H), 7.34 (d, $J$ = 2.1 Hz, ArH, 4H), 10.64 (s, COOH); FAB-MS: 903 [M + Na]$^+$. Compound **4**: $^1$H NMR (300 MHz, CDCl$_3$, 295 K), $\delta$: 1.25 (s, C(CH$_3$)$_3$, 36H), 3.95 (s, ArCH$_2$Ar, 8H), 4.14 (s, OCH$_2$CO, 8H), 7.09 (s, ArH, 8H), 10.26 (s, COOH, 4H); FAB-MS: 903 [M + Na]$^+$.

13 AFM imaging: Samples were analyzed using a Picoscan atomic force microscope (Molecular Imaging, Tempe, AZ, USA) in MAC mode with commercial MAClever II tips (Molecular Imaging, USA), with a spring constant of 0.95 N m$^{-1}$. The scan speed was 2.8 lines s$^{-1}$. 5 µL of the sample was dropped on mica (1.5 × 1.5 cm$^2$), dried in air for AFM imaging.

14 Crystal data for **3**: $C_{56}H_{76}O_{14}$; $M$ = 973.17, Monoclinic, space group $P2(1)/n$, $a$ = 14.5678(19) Å, $b$ = 12.3123(16) Å, $c$ = 16.266(2) Å, $\alpha$ = 90.00°, $\beta$ = 110.806(2)°, $\gamma$ = 90.00°, $V$ = 2727.2(6) Å$^3$, $Z$ = 2, 5913 unique, 4096 observed with $I > 2\sigma(I)$; final $R$ = 0.0657 (observed), 0.0822 (all), $wR(F^2)$ 0.197 (observed), 0.215 (all), final GoF = 1.056. All calculations were performed using the SHELX-TL software suite. All non-hydrogen atoms were refined anisotropically and, with the exception of the hydroxy group hydrogen atoms which are disordered, hydrogens were placed in calculated positions. The *tert*-butyl group was disordered over two orientations and was modeled accordingly. The final model also included ethanol and disordered ethanol solvent molecules. CCDC 254298. See http://dx.doi.org/10.1039/b509092j for crystallographic data in CIF or other electronic format.

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