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Molecular tectonics: design, synthesis and structural analysis of a molecular network based on inclusion processes using a doubly fused *p*-isopropylcalix[4]arene

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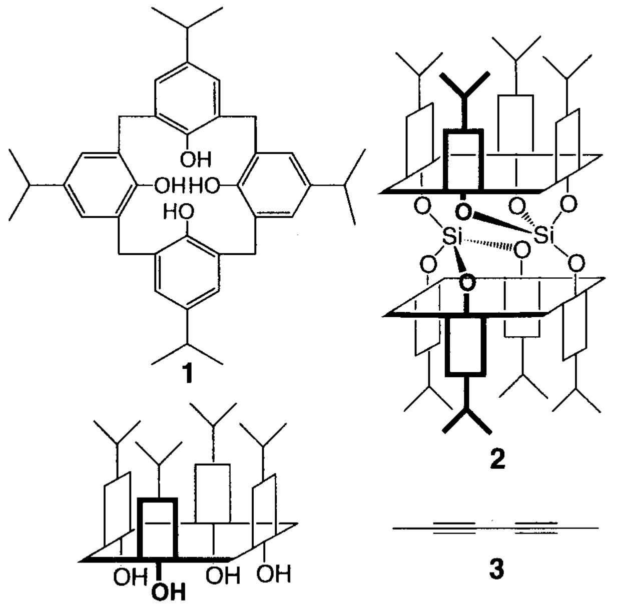
The synthesis of a hollow molecular module (koiland) possessing two divergent cavities was achieved by double fusion of two *p*-isopropylcalix[4]arenes in cone conformation by two silicon atoms. The formation of either a discrete binuclear inclusion complex in the presence of CH_2Cl_2 acting as stopper or of an infinite 1-D inclusion network (koilate) in the presence of hexadiyne acting as connector was demonstrated in the solid state by single-crystal diffraction studies. The inclusion network was based on the interconnection of consecutive koilands by connector molecules.

Over the last ten years much attention has been focused on molecular crystal engineering and the design of molecular networks in the solid state is still a subject of current interest.[1] The majority of reported molecular networks are either based on hydrogen bonding[2,3] or on coordination bonds.[4,5] However, we have proposed that one may use inclusion processes based on van der Waals interactions as a construction principle to design molecular networks in the solid state.[6] Thus, we demonstrated that 1-D molecular networks (koilates)[7] may be generated under self-assembly conditions using hollow molecular receptors (koilands)[8] possessing at least two divergent cavities and connector molecules capable of bridging by double inclusion consecutive koilands (Fig. 1).

Here we describe the synthesis of a new koiland as well as its use in the formation of either a discrete exobinuclear inclusion complex or an infinite 1-D molecular network in the solid state.



Scheme 1 Structures of *p*-isopropylcalix[4]arene **1** and of hexadiyne **3** as welle as schematic representations of **1** in cone conformation and of the koiland **2** obtained upon fusion of two units **1** by two silicon atoms.

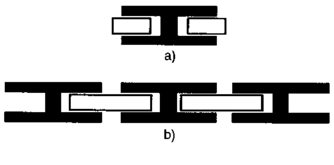


Fig. 1 Schematic representation of a discrete exobinuclear inclusion complex (a) and of an infinite inclusion network (b) formed between an hollow molecular module and a stopper or connector units respectively.

The design of the koiland **2** is based on the double fusion by two silicon atoms of two *p*-isopropylcalix[4]arenes **1** (Scheme 1). The latter appeared to be an interesting backbone since it has been shown that in the presence of *p*-xylene it forms (1 : 1) and (2 : 1) inclusion complexes in the solid state.[9] Although the preparation of **1** based on Ni catalysed direct isopropylation of calix[4]arene using propene was recently reported,[10] for the sake of experimental simplicity, we modified the reported Zinke–Conforth procedure[11] by heating at 110 °C for 2 h a 50 : 75 : 10 mixture of *p*-isopropylphenol, formaldehyde and sodium hydroxide. The pure compound **1** was obtained in 9% yield by crystallisation from a 1 : 9 mixture of CH_2Cl_2–hexane.

The synthesis of **2** (Scheme 1) was achieved in 39% yield upon treatment of **1** in dry THF by NaH followed by addition of $SiCl_4$.[7] Compound **2** was obtained as colourless crystalline material after crystallisation from a CH_2Cl_2–MeOH mixture. In addition to ^1H and ^{13}C NMR spectroscopy, mass spectrometry and elemental analysis, compound **2** was also characterised by ^{29}Si NMR in $CDCl_3$ which revealed, as expected, a signal at −112.48 ppm.†

In order to study the inclusion ability of **2**, the latter was crystallised from solvents capable of acting as stoppers. Thus, in the presence of CH_2Cl_2, **2**, possessing two divergent cavities, formed indeed a discrete exobinuclear inclusion complex in the solid state. Single crystals (air stable rod-type morphology) were obtained upon slow diffusion of MeOH into a CH_2Cl_2 solution of **2**. The X-ray analysis‡ (Fig. 2) revealed the following features: (i) **2** possessing a centre of symmetry was indeed composed of two *p*-isopropylcalix[4]arene units in cone conformation fused by two Si atoms adopting a tetrahedral coordination geometry with an average Si–C distance of *ca.* 1.61 Å and OSiO angle of *ca.* 109.4°; (ii) a discrete binuclear inclusion complex was formed between **2** and two CH_2Cl_2 molecules; (iii) each cavity of the koiland was occupied by

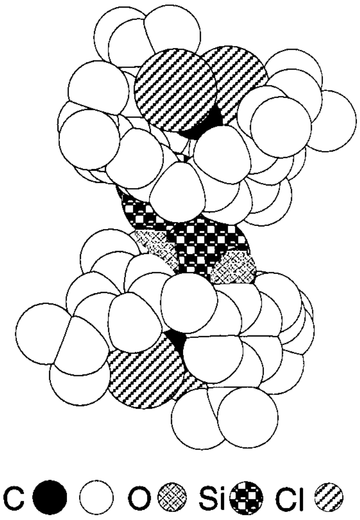


Fig. 2 Crystal structure of the exobinuclear inclusion complex formed between **2** and CH_2Cl_2 molecules acting as stoppers. For sake of clarity, H atoms are not presented.

one solvent molecule with the shortest distance of *ca.* 3.68 Å between the carbon atom of the solvent and one of the carbon atoms of the koiland; (iv) whereas hydrogen atoms of the solvent were oriented towards the interior, the chlorine atoms were facing the exterior of the cavity.

The ability of **2** to form linear molecular networks based on inclusion processes was studied using as connector **3** possessing a cylindrical shape. Upon slow diffusion at 21 °C of MeOH into a $CHCl_3$ solution of **2** and **3** in large excess (200-fold), suitable colourless single crystals (rhombic morphology) were obained after 8 h. The crystals, unstable outside the solution, thus obtained were studied by X-ray diffraction§ which revealed the following features: (i) the crystals (monoclinic, $P2_1/a$ space group) were compared of **2**, **3** and $CHCl_3$ molecules; (ii) as predicted, a 1-D network was formed between **2** and **3** (Fig. 3), the solvent molecules were not participating directly in the formation of the network; (iii) the observed network resulted from the interconnection, through inclusion processes, of **2** by **3**; (iv) the assembling core leading to the formation of the 1-D network by translational symmetry could be identified as the inclusion of one of the methyl groups of **3** within a cavity of **2**; (v) both the connector and the koiland were centrosymmetric; (vi) the coordination geometry around the silicon atoms was tetrahedral with an average Si–O distance of 1.60 Å and an average OSiO angle of 109.4°; (vii) the shortest C–C distance of 3.56 Å between the CH_3 group of connector and one of the carbon atoms bearing the phenolic group at the bottom of the cavity indicated a high degree of inclusion.

In conclusion, a molecular module possessing two divergent cavities was shown to form in the crystalline phase either a discrete exobinuclear inclusion complex in the presence of solvent molecules acting as stoppers, or an infinite inclusion molecular network in the presence of connector molecules. Thus, one may use as a construction principle inclusion processes between hollow molecular modules and full connector units to design molecular networks in the solid state. Further research dealing with the formation of inclusion networks using chiral hollow molecular modules is currently under investigation.

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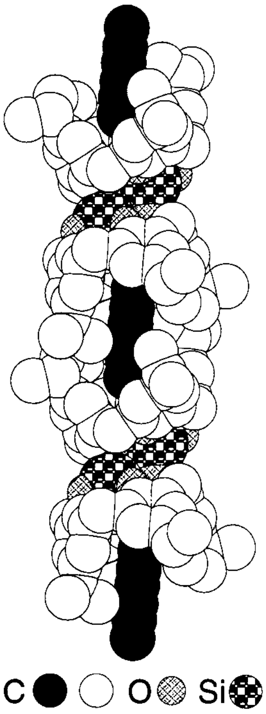

Fig. 3 A portion of the crystal structure showing the formation of an infinite inclusion network between koilands **2** and connectors **3**. For sake of clarity, $CHCl_3$ molecules present in the lattice and H atoms are not presented.

Notes and references

† ^1H NMR: ($CDCl_3$, 300 MHz; 25 °C): δ 1.07 (d, CH_3, 12H, 6.8 Hz), 1.13 (d, CH_3, 12H, 6.8 Hz), 1.22 (d, CH_3, 24H, 6.8 Hz), 2.74 (m, isopr., 8H); 3.31 (d, CH_2, 4H, 13.4 Hz), 3.39 (d, CH_2, 4H, 13.9 Hz), 4.48 (d, CH_2, 4H, 13.6 Hz), 4.58 (d, CH_2, 4H, 13.4 Hz), 6.79 (s, arom., 4H), 6.89 (s, arom., 4H), 6.91 (s, arom., 8H), ^{13}C NMR: ($CDCl_3$, 50.32 MHz, 25 °C): δ 23.67, 23.83, 24.12, 32.73, 33.15, 33.54, 34.44, 126.04, 126.12, 127.19, 127.29, 129.14, 130.13, 132.66, 142.36, 145.02, 148.44; ^{29}Si NMR: ($CDCl_3$, 59.63 MHz, 25 °C): δ −112.48; FAB$^+$ (*meta*-nitrobenzyl alcohol matrix) *m*/*z* 1232.7 ($M^{\cdot+}$, 100%), 1217.6 ($M^{\cdot+}$ $-CH_3$, 25%); Found: C 73.35, H 6.70; Calc. for $C_{80}H_{88}O_8Si_2{\cdot}CH_2Cl_2$ (1232.60) C 73.78, H 6.88%.

‡ *Crystal data* for **2**·$2CH_2Cl_2$: (colorless, 173 K): $C_{80}H_{88}O_8Si_2{\cdot}2CH_2Cl_2$, $M=1403.63$, triclinic, $a=11.6667(4)$, $b=13.0829(5)$, $c=13.8915(5)$ Å, $\alpha=108.628(9)$, $\beta=110.871(9)$, $\gamma=91.648(9)°$, $U=1852.9(5)$ Å^3, space group $P\bar{1}$, $Z=1$, $D_c=1.26$ g cm^{-3}, Nonius CCD, Mo-Kα, $\mu=0.244$ mm^{-1}, 4741 data with $I>3\sigma(I)$, $R=0.066$, $Rw=0.081$.

§ *Crystal data* for (**2**,**3**)*n* network (colorless, 173 K): $C_{80}H_{88}O_8Si_2{\cdot}C_6H_6{\cdot}2CHCl_3$, $M=1550.63$, monoclinic, $a=13.6981(3)$, $b=19.7336(6)$, $c=15.3589(4)$ Å, $\beta=95.721(9)$, $U=4131.0(4)$ Å^3, space group $P2_1/a$, $Z=2$, $D_c=1.25$ g cm^{-3}, Nonius CCD, Mo-Kα, $\mu=0.289$ mm^{-1}, 4567 data with $I>3\sigma(I)$, $R=0.065$, $Rw=0.081$. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/116.

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