Perfluorocarbon-Hydrocarbon Self-Assembly: Part X[+]

Interactions at the Outside Faces of Calix[4]arenes: Two-Dimensional Infinite Network Formation with Perfluoroarenes

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Abstract: Attractive π–π interactions between two of the four outside cavity faces of 1,3-bis-pyridylmethylcalix[4]arene (**1**) and both faces of 1,4-diiodotetrafluorobenzene (**2a**) form infinite one-dimensional non-covalent ribbons where the two modules alternate. These ribbons are cross-linked by electron donor–acceptor interactions between picolyl nitrogen atoms of calixarene **1** in one chain and iodine atoms of perfluoroarene **2a** in another chain and the two-dimensional supramolecular network **3a** is formed. A similar behaviour is also shown by 1,4-dibromotetrafluorobenzene (**2b**). The halogen bonding and the attractive π–π interactions occur in directions which are nearly orthogonal each other. Diiodotetrafluorobenzene, being involved in both these interactions, appears to be a particularly interesting tecton. The ability of electron-poor arenes to elicit the *exo*-receptor potential of calixarene module by connecting their outside faces through π–π interactions may be developed as a new and general binding protocol in calixarene self-assembly processes.

Keywords: calixarenes · donor–acceptor systems · host–guest chemistry · supramolecular chemistry

Introduction

Recent developments in the host–guest chemistry and in the supramolecular chemistry of calix[*n*]arenes have definitely shown the great potential of these compounds both in recognition processes and in the construction of highly organised and complex architectures.[1]

Calixarenes have frequently been used as versatile platforms for the covalent insertion of appendages which drive self-assembly processes by using weak forces such as hydrogen bonds,[2] co-ordination bonds,[3] and van der Waals interactions.[4] However, in most cases, calixarenes have been used as *endo*-receptors[5] (concave molecules), a role they are perfectly tailored to by the cone conformation they frequently adopt. A wide variety of metal cations (alkaline, alkaline earth, transition metal, lanthanide cations) have been complexed in the solid state and in solution and the ion has invariably been included in the calixarene cavity region.[6] Neutral molecules, as diverse as toluene, acetonitrile, acetone and water, have also been included in the solid state within the calixarene cavity.[1c,d, 7] By connecting two or more calixarene units into larger assemblies such as carcerands and holands, cavities of nanosize dimensions have been formed hosting even molecular clusters[8] and molecules as large as the fullerene.[9] The π-basic character of the cavity significantly contributes to the ability of calixarenes to work as effective host molecules in inclusion and recognition processes. The attractive cation···π,[10] C-H···π,[11] and O-H···π[12] interactions which determine, or at least favour, the binding of the guest involve the calixarene aromatic ring faces directed inside the cavity. To the best of our knowledge, the outside faces of calixarene rings have worked as π-basic motifs (*exo*-receptors)[5] only towards transition metal derivatives and very few cases of this behaviour have been reported.[13]

Here we describe the first case where calixarenes work as *exo*-receptors (convex molecules) of neutral molecules. Specifically, calixarene **1** forms infinite chains with perfluoroarene **2a** (Scheme 1) as the calixarene phenol ring faces directed

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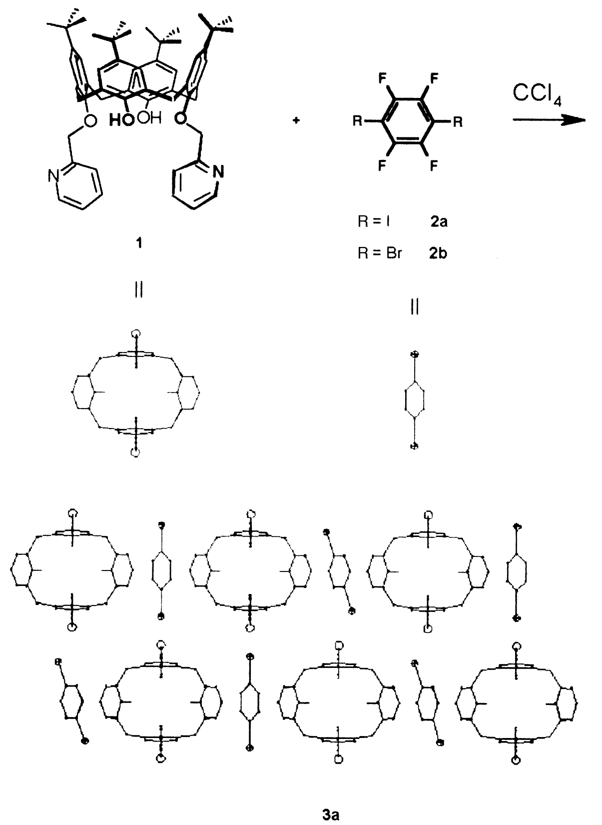

Scheme 1. Ortep views[33a] of the molecules **1** and **2** and of the two-dimensional network **3a**. Calixarene **1** has been symmetrized by using the program SYMMOL.[33b] Fluorine and hydrogen atoms and methyl groups are omitted for clarity.

outside the cavity are involved in attractive $\pi-\pi$ interactions with the perfluoroarene **2a** faces (Figure 1). These chains are cross-linked by electron donor–acceptor interactions between picolyl nitrogen atoms of calixarene **1** in one chain and iodine atoms of perfluoroarene **2a** in another chain (Figure 2) so that the two-dimensional infinite network **3a** is formed. A similar behaviour is also shown by 1,4-dibromotetrafluorobenzene (**2b**).

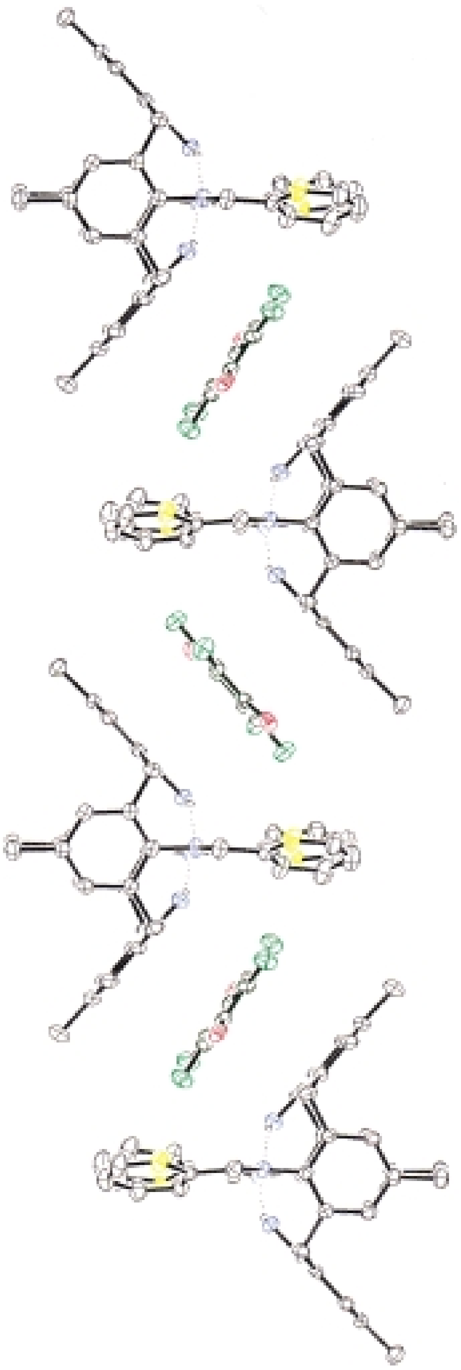

Figure 1. Crystal packing of the two-dimensional network **3a**. Colours are as follows: black, carbon; blue, oxygen; yellow, nitrogen; red, iodine; green, fluorine. Hydrogen atoms and methyl groups of calixarene module are omitted for clarity.

Results and Discussion

Crystallisation of equimolar amounts of bis-pyridylmethyl-tetra-*tert*-butylcalix[4]arene (**1**)[14] and 1,4-diiodotetrafluorobenzene (**2a**) or its 1,4-dibromo analogue **2b** by slow solvent diffusion (carbon tetrachloride/vaseline oil system) affords white crystalline solid, **3a** and **3b**, respectively, which are stable to air and moisture at room temperature. Microanalyses (C, H, N, I, Br) and ^{1}H/^{19}F-NMR spectra in the presence of 2,2,2-trifluoroethyl ether as internal standard (see Experimental Section) reveal that the calixarene (CA) and perfluorocarbon (PFC) components **1** and **2** are present in a 1:1 ratio in co-crystal **3**. IR spectra of these co-crystals (KBr, pellets) are not the exact sum of the spectra of pure components. Single absorption bands of the CA and PFC modules are present in the spectra of the co-crystals, but some interesting shifts in the absorption maxima also occur. For instance, the C–H and C–I stretching modes of the pure CA and PFC modules are shifted to higher and lower frequencies, respectively, in co-crystal **3a** (the absorptions at 3056 and 761 cm^{-1} of **1** and **2a** appear at 3068 and 754 cm^{-1} in **3a**). Similar spectral changes are typical for the electron donor–acceptor interaction between nitrogen and iodine atoms of hydrocarbon and PFC derivatives, respectively.[15, 16] For instance, when dihaloperfluoroarenes **2a**,**b** form co-crystals with various pyridine derivatives, such as 2,2′-, 4,4′-bypiridine, and 2,2′:6′,2″-terpyridine, a very similar trend is shown by the

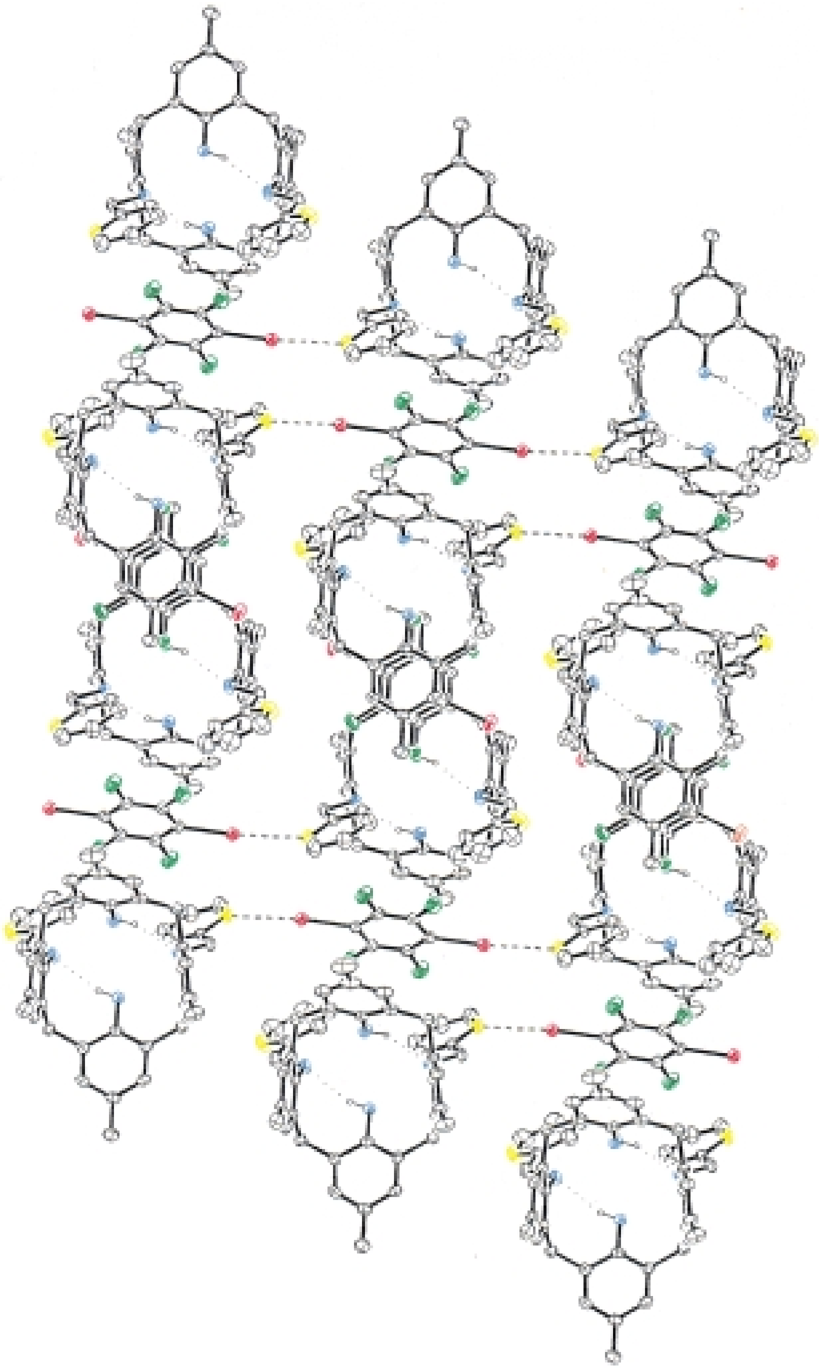

Figure 2. Crystal packing of the two-dimensional network **3a**. Colours are as follows: black, carbon; blue, oxygen; yellow, nitrogen; red, iodine; green, fluorine. Hydrogen atoms and methyl groups of calixarene module are omitted for clarity. Dotted lines represent the intramolecular hydrogen bonds; dashed lines represent the intermolecular N ··· I halogen bonds.

absorption bands of the hydrocarbon and PFC modules in the 3050 and 760 cm^{-1} region.[17]

^{1}H-NMR spectra show that the attractive interaction between the picolyl nitrogen atoms and the fluoroaryl iodine, or bromine, atoms exists also in solution[18] and gives rise to an association equilibrium which is rapid on the NMR time scale. On adding increasing amounts of **2a** to a chloroform solution of **1**, the picolyl residue signals are increasingly shifted downfield while the other signals show minor shifts, if any. Dibromotetrafluorobenzene (**2b**) behaves similarly and gives, as expected,[19] smaller shifts than the diiodo analogue **2a**. Similar low-field shifts have been observed also as a result of the interaction between pyridine derivatives and several iodo- and bromoperfluoroalkanes. In these complexes the electron donation from nitrogen to iodine, or bromine, atoms has been characterised by IR, Raman, and X-ray analyses in the solid and by ^{19}F- and ^{14}N-NMR spectroscopy in solution.[16c,d;17]

Single crystal X-ray analysis (Table 1) of the noncovalent assembly **3a** revealed the structural features of the supramolecular architecture. The CA and PFC modules, **1** and **2a**, respectively, alternate and form linear and infinite ribbons where molecules of **2a** (electron-poor motif) are in a sandwich arrangement between the phenol rings of two distinct molecules of **1** (electron-rich motif) (Figure 1). Two adjacent calixarenes are always oriented up–down in the ribbon in such a way that their more sterically demanding *tert*-butyl substituted rims are directed on opposite sides, thus forming linear and infinite arrangements.[21]

The CA and PFC modules are bound through attractive π–π interactions involving both faces of the electron poor perfluoroarene rings and the outside face of the electron rich phenol rings. Benzene and hexafluorobenzene have large molecular quadrupolar moments that are similar in magnitude, yet opposite in sign,[22] and numerous examples are reported in the literature of aryl/perfluoroaryl complexes in which the electrostatic potentials normal to the plane of the partner molecules interact attractively. Interplanar distances between hexafluorobenzene and various aromatic hydrocarbons span from 3.4 to 3.8 Å. Phenol/diiodotetrafluorobenzene interplanar distances in co-crystal **3a** are 3.51 and 3.53 Å (values refer to the two crystallographically independent molecules of **2a** in **3a**, see below), thus proving unequivocally the occurrence of attractive π–π interactions in co-crystal **3a**. This is the first time that 1,4-diiodotetrafluorobenzene **2a** gives intermolecular π–π

Table 1. Selected crystallographic and data collection parameters for co-crystal **3a**.

molecular formula	$(C_{56}H_{66}N_2O_4)\cdot(C_6F_4I_2)\cdot(CCl_4)$
M	1386.8
crystal colour	colourless
dimension [mm^3]	$0.48 \times 0.36 \times 0.20$
crystal system	triclinic
space group	$P1$
a [Å]	10.9306(7)
b [Å]	15.9053(10)
c [Å]	19.2587(14)
α [°]	89.080(6)
β [°]	83.319(6)
γ [°]	83.401(6)
U [Å^3]	3323.9(4)
Z	2
T [K]	291(1)
ρ_{calcd} [g cm^{-1}]	1.388
$2\theta_{max}$ [°]	50
data collected	12360
unique data (R_{int})	11690 (0.0162)
observed data	7713 [$I > 2\sigma(I)$]
transmission factors	0.595–0.737
No. parameters (No. restraints)	865 (670)
R_{all}, R_{obs}	0.0923, 0.0560
wR_{all}, wR_{obs}	0.1566, 0.1356
weighting scheme,[a] a, b	0.0771, 3.5631
goodness-of-fit (restrained)	1.004 (1.045)
$\Delta\rho_{min,max}$ [e Å^{-3}]	-0.626, 1.163

[a] $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ where $P = (F_o^2 + 2_c^2)/3$.

interactions and its π-electron acceptor ability seems similar to that of hexafluorobenzene. As far as π–π interaction is concerned, calixarene **1** behaves as a bidentate electron donor (the two phenol rings are stacked face-to-face with two distinct perfluorobenzene modules) and perhalobenzene **2a** behaves as a bidentate electron acceptor (the attractive π–π interactions occur on both faces of the electron-poor ring).

The two phenol ether rings of **1** are not involved in attractive π–π interactions with **2a**. The high cohesion of the co-crystal **3a** probably also derives from the attractive N···I interaction between the nitrogen atoms of the picolyl residues of the CA module **1** and the iodine atoms of the PFC module **2a** (Figure 2). This interaction, whose features in solution have been discussed above, has been named "halogen bonding"[23] and its ability to drive the self-assembly of hydrocarbon and perfluorocarbon modules has already been proven in various systems.[16, 17] In the crystallographic cell of **3a** two independent units of diiodotetrafluorobenzene (**2a**) alternate. For one of these independent molecules no N···I interaction is observed while for the other the distance between the iodine atoms and the nitrogen atoms of two distinct picolyl residues (belonging to two adjacent infinite chains) is 2.90 Å, significantly shorter than the sum of the nitrogen and iodine van der Waals radii (1.55 and 1.98 Å). These halogen bondings secure the cross linking of the one-dimensional infinite ribbons, assembled via attractive π–π interactions, into a two-dimensional network. Similar to other cases,[16, 17] the N···I interaction in **3a** is highly directional and occurs nearly on the extension of the C–I bond (the N···I-C angle is 169°). As far as halogen bonding is concerned, perfluoroarene **2a** behaves, on average, as a monodentate electron acceptor (one molecule forms two bonds, the other is not bonded) and calixarene **1** also works as a monodentate donor (only one out of the two picolyl residues of any calixarene is halogen bonded).

Conclusion

When involved in intermolecular interaction processes, CAs typically work as *endo*-receptors[5] and give in most cases dimeric aggregates.[1, 6, 7] Polymeric structures (infinite one-dimensional networks) have been obtained only when CAs undergo self-inclusion processes,[24] when metal ions bridge calix[4]arenes in the 1,3-alternate conformation,[25] or when neutral molecules connect calixarene dimers through a double inclusion process.[26] Here, we have reported a new approach to the formation of infinite networks where calixarene **1** acts as an *exo*-receptor in relation to both π–π interactions, which form linear ribbons, and halogen bondings, which cross-link the ribbons.

CA **1** prefers in this case to work as an *exo*- rather than an *endo*-receptor probably in order to maximise π–π interactions. If perfluoroarene **2a** entered the cavity of **1** parallel to the phenol ether rings, the size and shape of the cavity would prevent the perfluoroarene ring from diving into the cavity deeply enough to face the two phenol ether rings and create effective π–π stabilisation. If perfluoroarenes **2a** entered the cavity of **1** normal to the phenol ether rings, the two phenol rings could not lay stacked and parallel on its two faces being nearly orthogonal to each other. In contrast, a perfectly aligned face-to-face disposition occurs in the sandwich arrangement allowed by the *exo*-receptor behaviour of calixarene **1** in co-crystal **3a**.

Iodine atoms of PFC **2a** already have formed halogen bondings with iodide, bromide, and chloride anions[27] giving trimeric and oligomeric assembles. Here iodine atoms of PFC **2a** form halogen bondings with neutral electron donors (the picolyl nitrogen atoms) and the electron poor fluorobenzene rings form attractive π–π interactions with the electron rich calixarene phenol rings so that two-dimensional infinite networks result. From the geometric point of view, the halogen bondings and the π–π interactions occur in directions which are roughly orthogonal each other and **2a** is shown to be a particularly interesting tecton.[28]

Attractive π–π interactions similar to those given by hexafluorobenzene[22] have been observed between electron-rich arenes and various benzene derivatives bearing electron withdrawing residues, for example picric acid, trimethyl 1,3,5-benzenetricarboxylate, and fluoroanil.[29] The ability of electron-poor arenes to elicit the *exo*-receptor potential of CA modules by connecting their outside faces through π–π interactions may be developed into a general heuristic principle in calixarene self-assembly. Studies are presently in process in our laboratory to test how general this ability is.

Experimental Section

General methods: All materials were obtained from commercial suppliers and were used without further purification. Reagent grade solvents were used without further purification. ^{19}F-NMR spectra were recorded with a Bruker AV 500 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker ARX 400 spectrometer. The IR spectra were recorded with a Perkin–Elmer 2000 FT-IR spectrophotometer. Selected IR and NMR spectral properties of starting materials **2** are reported to show the changes occurring on adduct **3** formation.

25,27-Dihydroxy-26,28-bis(2-pyridylmethyl)oxy-5,11,17,23-tetra-*tert*-butyl-calix[4]arene (1): An anhydrous DMF solution of *p-tert*-butylcalix[4]arene was stirred at 60 °C with 2-(chloromethyl)pyridinehydrochloride (4 equiv) in the presence of NaH for 3 h. A mixture of proximal bis[(2-pyridylmethyl)oxy]calix[4]arene (m.p. 204–206 °C, major product) and of mono[(2-pyridylmethyl)oxy]calix[4]arene (m.p. 275–277 °C), distal[(2-pyridylmethyl)oxy]calix[4]arene (**1**), and tris[(2-pyridylmethyl)oxy]calix[4]arene (m.p. 219–222 °C) was formed. Product ratio was depending on reaction time and temperature, the last three compounds being formed in minor amounts. Chromatography (SiO_2, column) with AcOEt/cyclohexane 1:2 as the eluent gave pure **1** as a white solid. M.p. 250–252 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 8.61$ (d, $J = 4$ Hz, 2 H, H_α), 8.29 (d, $J = 7$ Hz, 2 H, H_δ), 7.60 (t, $J = 7$ Hz, 2 H, H_γ), 7.25 (t, $J = 7$ Hz, 2 H, H_β), 7.20 (s, 2 H; OH), 7.08 (s, 4 H; ArH), 6.80 (s, 4 H; ArH), 5.20 (s, 4 H; OCH_2Py), 4.31 (q, $J = 13.1$ Hz, 4 H; $ArCH_2Ar$), 3.35 (q, $J = 13.1$ Hz, 4 H; $ArCH_2Ar$), 1.30 (s, 18 H, CH_3), 0.94 (s, 18 H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta =$ 157.7, 150.6, 149.5, 148.9, 147.3, 141.7, 137.2, 132.3, 127.6, 125.6, 125.1, 122.5, 121.3, 78.1, 33.9, 33.8, 31.7, 31.5, 30.9; IR (KBr pellets): $\tilde{\nu} = 3056, 2953, 1487, 761$ cm^{-1}; elemental analysis calcd (%) for $C_{56}H_{66}N_2O_4$ (831.1): C 80.93, H 8.00, N 3.37; found C 80.57, H 8.01, N 3.64.

1,4-Diiodotetrafluorobenzene (2a): ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): $\delta = -119.3$; IR (KBr pellets): $\tilde{\nu} = 1468$ (C=C), 944 (C–F), 761 (C–I) cm^{-1}.

1,4-Dibromotetrafluorobenzene (2b): ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): $\delta = -132.7$; IR (KBr pellets): $\tilde{\nu} = 1497$ (C=C), 956 (C–F), 789 (C–Br) cm^{-1}.

Synthesis of infinite chain 3a: Compounds **1** (0.05 g, 0.06 mmol) and **2a** (0.025 g, 0.06 mmol) were dissolved in carbon tetrachloride (2.0 mL) at room temperature in a clear borosilicate glass 5 mL vial. The open vial was placed in a closed cylindrical wide-mouth bottle (50 mL) containing vaseline oil (10 mL). Volatiles were allowed to diffuse slowly at room temperature. After five days, colourless crystals of **3a** (0.04 g) were filtered, washed with cold carbon tetrachloride, and analysed. ^{1}H NMR (400 MHz, $CDCl_3$ 0.06 M, 25 °C): $\delta = 8.61$ (d, $J = 4$ Hz, 2 H, H_α), 8.29 (d, $J = 7$ Hz, 2 H, H_δ), 7.61 (t, $J = 7$ Hz, 2 H, H_γ), 7.25 (t, $J = 7$ Hz, 2 H, H_β), 7.20 (s, 2 H; OH), 7.08 (s, 4 H; ArH), 6.80 (s, 4 H; ArH), 5.20 (s, 4 H; OCH_2Py), 4.31 (q, $J =$ 13.1 Hz, 4 H; $ArCH_2Ar$), 3.35 (q, $J = 13.1$ Hz, 4 H; $ArCH_2Ar$), 1.30 (s, 18 H, CH_3), 0.94 (s, 18 H, CH_3); ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): $\delta = -119.3$; IR (KBr pellets): $\tilde{\nu} = 3068, 2961, 1464, 943, 754$ cm^{-1}; elemental analysis calcd (%) for $C_{56}H_{66}N_2O_4 \cdot C_6F_4I_2 \cdot CCl_4$ (1386.8): C 54.56, Cl 10.23, H 4.80, I 18.30, N 2.02; found C 54.17, Cl 10.51, H 4.86, I 18.67, N 2.29.

Synthesis of infinite chain 3b: Compounds **1** (0.05 g, 0.06 mmol) and **2b** (0.018 g, 0.06 mmol) were dissolved in carbon tetrachloride (1.5 mL) at room temperature in a 5 mL clear borosilicate glass vial. The open vial was placed in a closed cylindrical wide-mouth bottle (50 mL) containing vaseline oil (10 mL). Volatiles were allowed to diffuse slowly at room temperature. The evaporation to dryness of the solvent gave colourless crystals of **3b** (0.065 g) which were filtered, washed with cold carbon tetrachloride, and analysed. ^{19}F NMR (470 MHz, $CDCl_3$, 25 °C): $\delta = -132.7$; ^{1}H NMR (400 MHz, $CDCl_3$ 0.06 M, 25 °C): $\delta = 8.61$ (d, $J = 4$ Hz, 2 H, H_α), 8.29 (d, $J = 7$ Hz, 2 H, H_δ), 7.60 (t, $J = 7$ Hz, 2 H, H_γ), 7.25 (t, $J =$ 7 Hz, 2 H, H_β), 7.20 (s, 2 H; OH), 7.08 (s, 4 H; ArH), 6.80 (s, 4 H; ArH), 5.20 (s, 4 H; OCH_2Py), 4.31 (q, $J = 13.1$ Hz, 4 H; $ArCH_2Ar$), 3.35 (q, $J = 13.1$ Hz, 4 H; $ArCH_2Ar$), 1.30 (s, 18 H, CH_3), 0.94 (s, 18 H, CH_3); IR (KBr pellets): $\tilde{\nu} = 3067, 2960, 955$ cm^{-1}; elemental analysis calcd (%) for $C_{56}H_{66}N_2O_4 \cdot C_6F_4Br_2 \cdot CCl_4$ (1283.7): Br 12.45, C 58.94, Cl 11.05, H 5.18, N 2.18; found Br 12.76, C 58.59, Cl 11.30, H 5.12, N 2.45.

Single crystal X-ray analyses: The crystal used for data collection was completely coated with a glue to prevent loss of tetrachloromethane. Data were collected with a Siemens P4 diffractometer, $Mo_{K\alpha}$ radiation, $\lambda =$ 0.71069 [Å], graphite monochromator, $\omega/2\theta$ scans; data were corrected for absorption on the basis of ψ scan.[30] The structure was solved by *SIR*92,[31] and refined on all 11 690 independent reflections F^2 by full-matrix least-squares by using by *SHELX*97.[32] Heavy atoms were anisotropic, H atoms isotropic; disordered *tert*-butyl groups and carbon tetrachloride were refined with constraints (see text). The highest peaks on the final Fourier map (<1.2 e Å^{-3}) were located near the two independent iodine atoms; they are probably due to an insufficient absorption correction.

Crystallographic data (excluding structure factors) for the structure **3a** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-138256. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

The crystal packing of **3a** has cavities in the region where the *tert*-butyl residues of different calixarene molecules are facing. In these lypophylic cavities crystallisation solvent molecules are hosted (one carbon tetrachloride molecule per calixarene molecule). These solvent molecules show disorder which was modelled by splitting carbon and chlorine atoms over two locations 0.57 Å apart each other with occupancy factor 0.5 and then refined with restraints to make the two models about tetrahedral. Both in Scheme 1 and in Figures 1 and 2 the solvent molecules have been omitted to allow a better comprehension of the overall packing structure but the related data can be found in the Cambridge Crystallographic Data Centre publication no. CCDC-138256. Also *tert*-butyl pendants on calixarenes **1** show rotational disorder which has been modelled by splitting each methyl group over two locations with occupancy factor 0.5. In this case the restraints that the C–CH_3 bond distances and the CH_3-C-CH_3 dihedral angles of the two locations are about the same have been added. The disorder of carbon tetrachloride and of the *tert*-butyl residues has been modelled by using the SADI and SIMU subroutines of *SHELX97*.[32]

NMR experiments: To establish the **1**:**2** ratio in co-crystals **3a,b**, their ^{1}H- and ^{19}F-NMR spectra were registered in the presence of 2,2,2-trifluoroethyl ether as an internal standard. On calibrating integration parameters so that in the ^{1}H-NMR spectrum the CH_2O quartet of 2,2,2-trifluoroethyl ether was corresponding to four and in the ^{19}F-NMR spectrum the CF_3 triplet of 2,2,2-trifluoroethyl ether was corresponding to six, the ratio of the OCH_2Py singlet area (deriving from **1**) and the CF singlet area (deriving from **2**) is one thus revealing that also the **1**:**2** ratio in **3a,b** is one.

Experiments proving the N···I and N···Br halogen bonding in solution: A 0.06 M deuterochloroform solution of **3a** showed: $\Delta\delta_{H}$ (ppm) $= \delta_{\text{adduct }\mathbf{3a}} - \delta_{\text{pure calix }\mathbf{1}}$; $\Delta\delta_{\text{N-C-C}H} = 0.0031$, $\Delta\delta_{\text{N-CH-CH-C}H} = 0.0061$, $\Delta\delta_{\text{O-C}H_2} = 0.0031$. On changing the **1**:**2a** molar ratio of this solution from 1:1 to 1:10 (by addition of **2a**), the same shifts became: $\Delta\delta_{\text{N-C-C}H} = 0.0263$, $\Delta\delta_{\text{N-CH-CH-C}H} = 0.0324$, $\Delta\delta_{\text{O-C}H_2} = 0.0231$. A deuterochloroform solution 0.06 M in **1** and 0.6 M in **2b** showed the following shifts: $\Delta\delta_{\text{N-C-C}H} = 0.0197$, $\Delta\delta_{\text{N-CH-CH-C}H} = 0.0240$, $\Delta\delta_{\text{O-C}H_2} = 0.0092$.

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[1] a) C. D. Gutsche, *Calixarene Revisited*, Royal Society of Chemistry, Cambridge, **1998**; b) A. Arduini, A. Casnati, E. Dalcanale, A. Pochini, F. Ugozzoli, R. Ungaro in *Supramolecular Science*: *Where It Is and Where It Is Going* (Eds.: R. Ungaro, E. Dalcanale), Kluwer, **1998**, 67–94; c) C. D. Gutsche, *Aldrichimica Acta* **1995**, *28*, 3–9; d) V. Böhmer, *Angew. Chem.* **1995**, *107*, 785–817; *Angew. Chem. Int. Ed.* **1995**, *34*, 713–745.

[2] a) D. N. Reinhoudt, P. Timmerman, F. Fardullo, M. Greco-Calama in *Supramolecular Science*: *Where It Is and Where It Is Going* (Eds.: R. Ungaro, E. Dalcanale), Kluwer, **1998**, 181–196; b) L. J. Prins, J. Huskens, F. de Jong, P. Timmerman, D. N. Reinhoudt, *Nature* **1999**, *398*, 498–502; c) J. J. Gonzalez, P. Prados, J. de Mendoza, *Angew. Chem.* **1999**, *111*, 546–549; *Angew. Chem. Int. Ed.* **1999**, *38*, 525–528.

[3] A. Ikeda, S. Shinkai, *Chem. Rev.* **1997**, *97*, 1713–1734;

[4] Y. Tanaka, M. Miyachi, Y. Kobuke, *Angew. Chem.* **1999**, *111*, 565–567; *Angew. Chem. Int. Ed.* **1999**, *38*, 504–506.

[5] O. Félix, M. W. Hosseini, A. De Cian, J. Fischer, *Tetrahedron Lett.* **1997**, *38*, 1755–1758.

[6] R. Ungaro, A. Pochini in *Frontiers in Supramolecular Organic Chemistry and Photochemistry* (Eds.: H. Dürr, H.-J. Schneider), VCH, **1991**.

[7] a) S. Blanchard, B. Chansou, A. F. Duprat, L. Le Clainche, Y. Le Mest, M.-N. Rager, O. Reinaud, J.-P. Tuchagues, *Angew. Chem.* **1998**, *110*, 2861 – 2864; *Angew. Chem. Int. Ed.* **1999**, *37*, 2732 – 2735; b) A. Arduini, M. Cantoni, E. Graviani, A. Pochini, A. Secchi, A. R. Sicuri, R. Ungaro, M. Vincenti, *Tetrahedron* **1995**, *51*, 599 – 606.

[8] a) A. Jasat, J. C. Sherman, *Chem. Rev.* **1999**, *99*, 931 – 967; b) N. Chopra, J. C. Sherman, *Angew. Chem.* **1999**, *111*, 2109 – 2111; *Angew. Chem. Int. Ed.* **1999**, *38*, 1955 – 1957; c) C. A. Schalley, R. K. Castellano, M. S. Brody, D. M. Rudkevich, G. Siuzdak, J. Rebek, Jr., *J. Am. Chem. Soc.* **1999**, *121*, 4568 – 4579; d) M. S. Brody, C. A. Schalley, D. M. Rudkevich, J. Rebek, Jr., *Angew. Chem.* **1999**, *111*, 1738 – 1742; *Angew. Chem. Int. Ed.* **1999**, *38*, 1640 – 1644; e) I. Higler, P. Timmerman, W. Verboom, D. N. Reinhoudt, *Eur. J. Org. Chem.* **1998**, 2689 – 2702.

[9] a) T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem.* **1997**, *109*, 288 – 290; *Angew. Chem. Int. Ed.* **1997**, *36*, 259 – 260; b) C. Fukuhara, A. Ikeda, M. Yoshimura, S. Shinkai, H. Udzu, *J. Am. Chem. Soc.* **1999**, *121*, 4296 – 4297; c) A. Ikeda, Y. Suzuki, M. Yoshimura, S. Shinkai, *Tetrahedron* **1998**, *54*, 2497 – 2508.

[10] a) H. Otsuka, Y. Suzuki, A. Ikeda, K. Araki, S. Shinkai, *Tetrahedron* **1998**, *54*, 423 – 446; b) A. Ikeda, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1994**, 2375 – 2376; c) A. Ikeda, S. Shinkai, *J. Am. Chem. Soc.* **1994**, *116*, 3102 – 3110.

[11] a) M. Nishio, M. Hirota, Y. Umezawa, *The CH – π Interaction, Evidence, Nature, and Consequences*, Wiley-VCH, **1998**; b) K. Kobayashi, Y. Asakawa, J. Kikuchi, H. Toi, Y. Aoyama, *J. Am. Chem. Soc.* **1993**, *115*, 2648 – 2654.

[12] J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr, R. L. Vincent, *Nature* **1991**, *349*, 683 – 684.

[13] a) H. Iki, T. Kikuchi, S. Shinkai, *J. Chem. Soc. Perkin Trans. 1* **1992**, 669 – 671; b) M. Staffilani, K. S. B. Hancock, J. W. Steed, K. Travis Holman, J. L. Atwood, R. K. Juneja, R. S. Burkhalter *J. Am. Chem. Soc.* **1997**, *119*, 6324 – 6335.

[14] F. Bottino, L. Giunta, S. Pappalardo, *J. Org. Chem.* **1989**, *54*, 5409 – 5411.

[15] N. F. Cheetham, I. J. Mc Naught, A. D. E. Pullin, *Aust. J. Chem.* **1974**, *27*, 973.

[16] a) A. Lunghi, P. Cardillo, T. Messina, P. Metrangolo, W. Panzeri, G. Resnati, *J. Fluorine Chem.* **1998**, *91*, 191 – 194; b) M. T. Messina, P. Metrangolo, W. Navarrini, S. Radice, G. Resnati, G. Zerbi, *J. Mol. Struct. 524*, 87 – 94; c) M. T. Messina, P. Metrangolo, W. Panzeri, E. Ragg, G. Resnati, *Tetrahedron Lett.* **1998**, *39*, 9069 – 9072; d) E. Corradi, S. V. Meille, M. T. Messina, P. Metrangolo, G. Resnati, *Tetrahedron Lett.* **1999**, *40*, 7519 – 7523; e) V. Amico, S. V. Meille, E. Corradi, M. T. Messina, G. Resnati, *J. Am. Chem. Soc.* **1998**, *120*, 8261 – 8262; f) M. T. Messina, P. Metrangolo, G. Resnati, *Asymmetric Fluoro-Organic Chemistry*: *Synthesis*, *Applications*, *and Future Directions*, *ACS Symposium Series No. 746* (Ed.: P. V. Ramachandran), American Chemical Society, Washington, DC, **1999**.

[17] a) E. Corradi, S. V. Meille, M. T. Messina, P. Metrangolo, G. Resnati, *Angew. Chem.* **2000**, *39*, 1782 – 1786; *Angew. Chem. Int. Ed.* **2000**, *112*, 1852 – 1856; b) A. Manfredi, M. T. Messina, P. Metrangolo, T. Pilati, S. Quici, G. Resnati, *Supramolecular Chem.*, in press.

[18] S. Ma, U. Obst, J. Rebek, P. L. Wash, *J. Am. Chem. Soc.* **1999**, *121*, 7973 – 7974.

[19] Numerous analytical techniques[15, 16c, 18] and theoretical calculations[20] consistently show that the strength of the attractive nitrogen$\cdots$halogen interaction parallels the ranking of halogen polarisation and/or charge-transfer energies (I > Br > Cl).

[20] F. H. Allen, J. P. M. Lommerse, A. J. Stone, R. Taylor, *J. Am. Chem. Soc.* **1996**, *118*, 3108 – 3116; G. Valerio, G. Raos, S. V. Meille, P. Metrangolo, G. Resnati, *J. Phys. Chem. A 104*, 1617 – 1620.

[21] In co-crystal **3a** calixarene molecules adopt a distorted cone conformation with a nearly C_{2v} symmetry where the two phenol rings and the two phenol ether rings are nearly perpendicular and parallel, respectively (the ring planes form angles of 88.4(2)° and 16.3(2)°). This conformation is locked by hydrogen bonds between the phenol hydrogen atoms and the phenol ether oxygen atoms (O-2$\cdots$O-1 distance 2.962(5) Å, O-2$\cdots$O-4 = 3.042(5) Å, O-4$\cdots$O-1 = 2.955(5) Å, O-4$\cdots$O-3 = 2.816(5) Å). Cone-shaped calixarene modules **1** assembling with the larger upper rim regularly oriented on the same side, circular aggregates would probably result in which calixarene modules oligomerize in micelle-like structures.

[22] J. H. Williams, *Acc. Chem. Res.* **1993**, *26*, 593 – 598; G. W. Coates, D. A. Dougherty, A. R. Dunn, R. H. Grubbs, L. M. Henling, *Angew. Chem.* **1997**, *109*, 290 – 293; *Angew. Chem. Int. Ed.* **1997**, *36*, 248 – 251; F. Cozzi, F. Ponzini, R. Annunziata, M. Cinquini, Y. S. Siegel, *Angew. Chem.* **1995**, *107*, 1092 – 1093; Angew. *Chem. Int. Ed.* **1995**, *34*, 1019 – 1020.

[23] J.-M. Dumas, M. Gomel, M. Guerin, *The Chemistry of Functional Groups*, *Supplement D* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1983**; A. C. Legon, *Angew. Chem.* **1999**, *111*, 2850 – 2877; Angew. *Chem. Int. Ed.* **1999**, *38*, 2687 – 2714; A. C. Legon, *Chem. Eur. J.* **1998**, *4*, 1890 – 1897.

[24] V. Böhmer, G. Ferguson, J. F. Gallagher, D. Kraft, W. Vogt, *J. Chem. Soc. Perkin Trans. 1* **1994**, 1221 – 1230; A. Zanotti-Gerosa, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *Chem. Commun.* **1996**, 119 – 120.

[25] G. Mislin, E. Graf, M. W. Hosseini, A. De Cian, N. Kyritsakas, J. Fischer, *Chem. Commun.* **1998**, 2545 – 2546.

[26] F. Hajek, E. Graf, M. W. Hosseini, X. Delaigue, A. De Cian, J. Fischer, *Tetrahedron Lett.* **1996**, *37*, 1401 – 1404; F. Hajek, , M. W. Hosseini, E. Graf, A. De Cian, J. Fischer, *Angew. Chem.* **1997**, *109*, 1830 – 1832; *Angew. Chem. Int. Ed.* **1997**, *36*, 1760 – 1762; M. W. Hosseini, A. De Cian, *Chem. Commun.* **1998**, 727 – 733.

[27] K. Dehnicke, G. Geiseler, J. Grebe, K. Harms, B. Neumüller, *Angew. Chem.* **1999**, *111*, 183 – 186; *Angew. Chem. Int. Ed.* **1999**, *38*, 222 – 225; K. Dehnicke, G. Geiseler, J. Grebe, K. Harms, *Z. Naturforsch.* **1999**, *B54*, 77 – 86.

[28] M. Simard, D. Su, J. D. Wuest, *J. Am. Chem. Soc.* **1991**, *113*, 4696 – 4698.

[29] B. Colonna, S. Menzer, F. M. Raymo, J. F. Stoddart, D. J. Williams, *Tetrahedron Lett.* **1998**, *39*, 5155 – 5158; H. M. Colquhoun, S. M. Doughty, A. M. Z. Slawin, J. F. Stoddart, D. J. Williams, *J. Chem. Soc. Perkin Trans. 2* **1986**, 253 – 257; T. Dahl, *Acta Chem. Scand.* **1998**, *52*, 1006 – 1009.

[30] A. C. T. North, D. C. Phillips, F. S. Mathews *Acta Crystallogr.* **1968**, *A24*, 351 – 359.

[31] A. Altomare, C. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[32] G. M. Sheldrick, *SHELX97. Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

[33] a) M. N. Burnett, C. K. Johnson, ORTEPIII, Report ORNL-6895, Oak Ridge, National Laboratory, Tennessee, USA, **1996**; b) T. Pilati, A. Forni, *J. Appl. Crystallogr.* **1998**, *31*, 503 – 504.

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