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Self-Assembled Polymers Based on *bis*-Tetra-Urea Calix[4]arenes Connected via the Wide Rim

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Dedicated to Prof. David N. Reinhoudt

Six double calixarenes were synthesised in which two tetra-urea calix[4]arenes are linked by a rigid spacer between the urea functions at their wide rim. The dimerisation of their tetra-urea parts leads to hydrogen-bonded polymeric assemblies in apolar solvents. The addition of the stoichiometric amount of a tetra-tosylurea calix[4]arene disrupts the polymeric structures due to the preferred formation of heterodimeric capsules between tetra-aryl and tetra-tosylurea calix[4]arenes. The existence of polymeric assemblies was further established by AFM studies on spin-coated samples.

Keywords: *Bis*-tetra-urea calix[4]arene; Self-assembly; Hydrogen bonds; NMR spectroscopy; Atomic force microscopy

INTRODUCTION

The self-organisation of macromolecules [1,2] (e.g. the folding of peptides) or the self-assembly of smaller molecules into well-ordered structures [3–5] is one of the central topics in supramolecular chemistry. Various structural motifs based on reversible hydrogen bonding were utilised for those purposes [6–10]. Among them, the dimerisation of tetra-urea calix[4]-arene derivatives in apolar solvents has been studied in detail [11–16]. These dimers are based on a belt of intermolecular hydrogen bonds, involving alternatingly the urea residues attached to the wide rims of the calixarene counterparts. The cavity of the capsule-like dimers contains usually a solvent molecule as guest. Due to its high electron density, it is especially attractive for positively charged species and the solvent molecule can be exchanged against cations of appropriate size, such as tetraethylammonium [17] or cobaltocenium [18]. The formation of the dimers and their inclusion phenomena in solution were studied by ^{1}H NMR and ESI mass spectrometry [19]. Several dimeric structures were also confirmed by X-ray analysis in the crystalline state [15,20]. The preorganisation of functional groups achieved in (hetero)-dimers has recently been used for the synthesis of *bis*-[21] and tetra-loop derivatives [22], which are building blocks for novel multi-catenanes [22,23] and rotaxanes [22,23], for the construction of dendritic assemblies [24] and the preparation of self-assembled monolayers [25].

Derivatives, in which two calix[4]arenes, each bearing four arylurea groups at its wide rim, are covalently connected via their narrow rims, form polymeric assemblies in apolar solvents due to the intermolecular dimerisation of their tetra-urea counterparts [26–30].

The only example in which the two calixarenes are connected via their wide rim was (also) described by Rebek *et al.* [31]. It was synthesised by linking two molecules of trinitro monoamino calix[4]arene tetrapropylether with 1,6-diisocyanatohexane followed by reduction of the six nitro groups and subsequent

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acylation with (*n*-heptyl)phenylisocyanate. This *bis*-calixarene formed a discrete assembly (a so-called 'unimolecular capsule') by intramolecular dimerisation in apolar solvents as shown by complexation studies, ^{1}H NMR and ESI mass spectra. The exclusive formation of *bis*-heterodimers was found for this kind of *bis*-calixarene in the presence of the double amount of tetra-tosylurea calix[4]arene, the preference of which to form heterodimers with tetra-arylurea calix[4]arenes is known [27]. This observation proves that not only an intramolecular but also an intermolecular dimerisation of the tetra-urea parts is possible with these compounds.

We describe in the following the synthesis and the dimerisation abilities of *bis*-tetra-urea calix[4]arenes connected via their wide rims by rigid spacer groups which entirely prevents their intramolecular dimerisation.

RESULTS AND DISCUSSION

General Considerations

If two tetra-urea calix[4]arenes are connected by a rigid spacer X between their urea groups, which allows their dimerisation, their self-assembly in apolar solvents can still result in supramolecular polymers. However, in contrast to the polymers designed by Rebek *et al*. [26–30], the conformational freedom of our target self-assembled polymers is more restricted. In a dimeric assembly of two *bis*-calixarene molecules, the hydrogen-bonded tetra-urea counterparts are turned by an angle of 45° around their common axis with respect to each other. The other two dimerisation sites are thus arranged under an angle of 45° (proximal) or 135° (distal), as illustrated schematically in Fig. 1b. From these possibilities, the distal arrangement should be strongly favoured, since it is sterically less hindered than the proximal one. If by additional reversible intramolecular interactions one direction for this 135° kink could be favoured, the formation of helical segments/polymers could occur in an ideal case.

Syntheses

In contrast to the synthetic sequence used by Rebek *et al*., we have chosen the easily available [32] tetrapentoxy tetraamino calix[4]arene **1** as a starting compound. The protection of three amino groups by Boc-anhydride was already described [33] and successfully applied to the synthesis of tri-tolylurea monoacetamides [34]. The coupling of two tri-Boc-protected calixarenes **2** with activated *bis*-urethanes

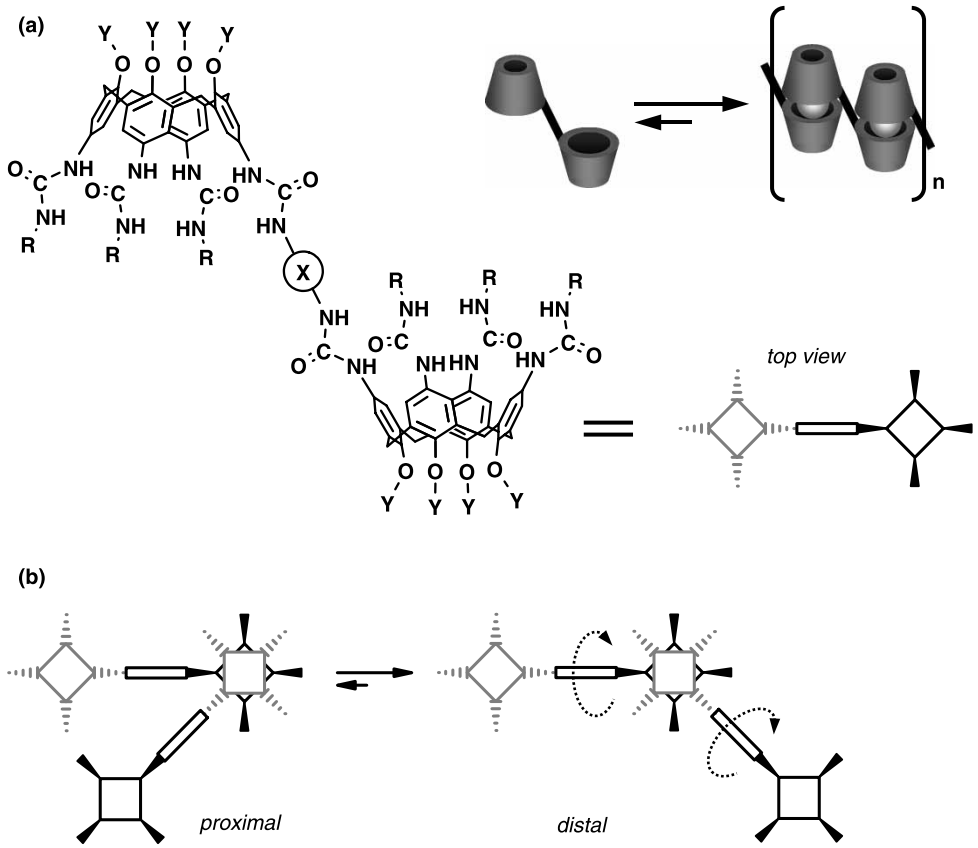
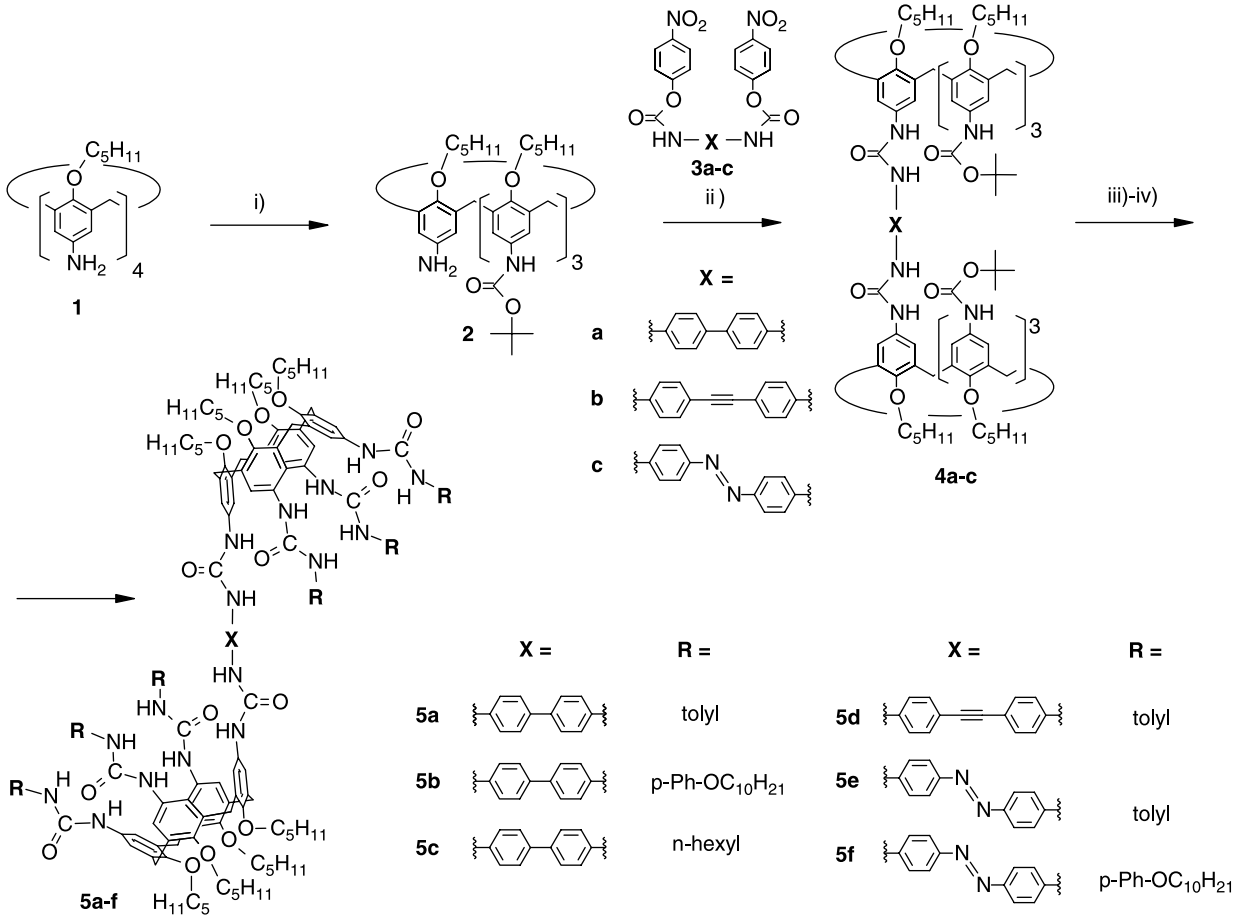


FIGURE 1 (a) General formula of the wide rim linked *bis*-tetra-urea calix[4]arenes and their schematic representation (b) Possible arrangement of the two *bis*-tetra-urea molecules in a dimeric segment.



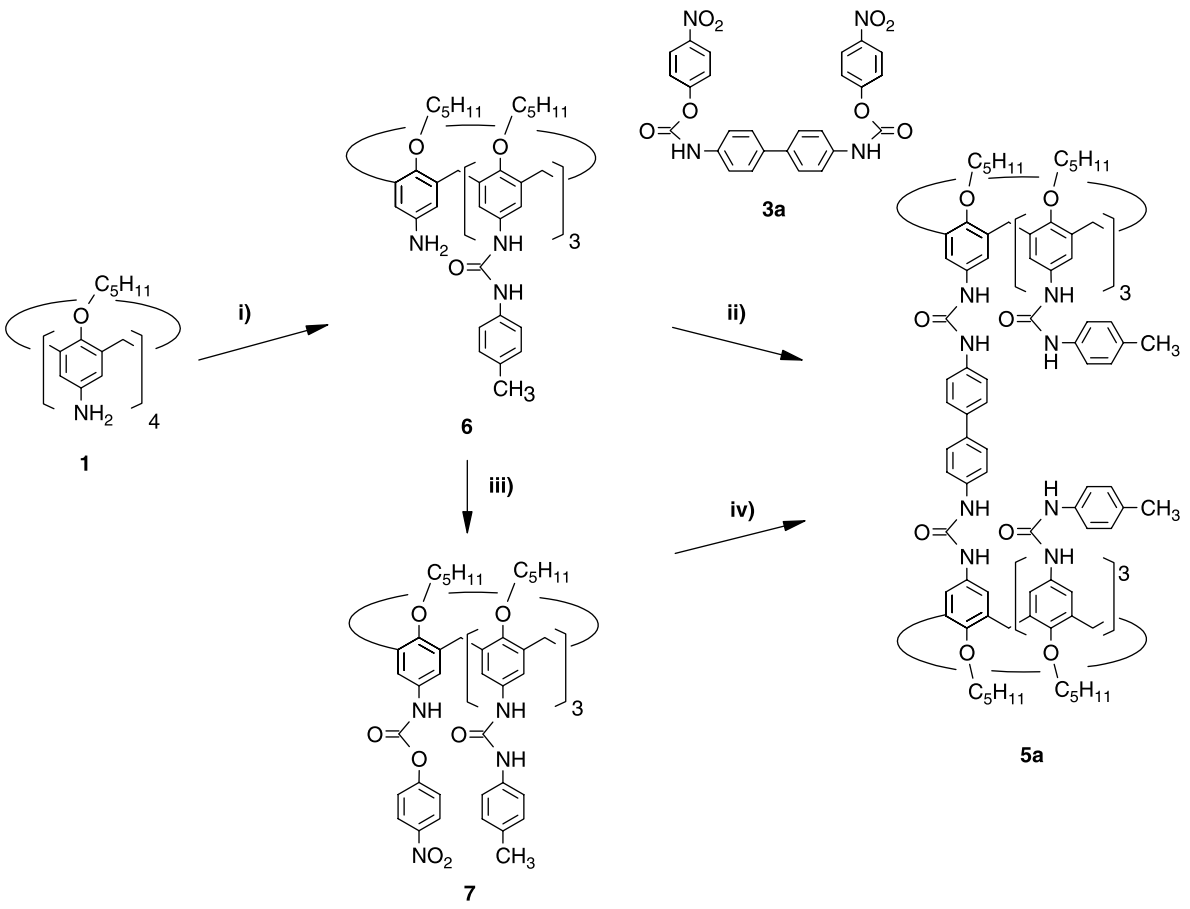
SCHEME 1 Pathways to *bis*-tetra-urea calix[4]arenes. (i) Boc_2O, CH_2Cl_2; (ii) *i*-Pr_2EtN, DMF or THF; (iii) CF_3COOH, CH_2Cl_2; (iv) *i*-Pr_2EtN, R-NCO or R-NH(CO)–*p*–O–C_6H_4–NO_2, THF.

3a–c in the presence of a base produced the corresponding *bis*-calixarenes **4a–c** in 67–86% yield (Scheme 1). The necessary *bis*-urethanes **3a–c** were easily prepared in 70–85% yield by acylation of appropriate *bis*-anilines with an excess of *p*-nitrophenyl chloroformate. Deprotection by trifluoroacetic acid and subsequent reaction with an excess of the respective isocyanate or *p*-nitrophenylcarbamate produced the target *bis*-(tetra-urea) derivatives **5a–f** in 69–87% yield.

The tri-Boc-protected calix[4]arene **2** is formed from tetraamine **1** by acylation with Boc-anhydride on a more or less statistical basis. As an alternative approach, we therefore attempted the direct statistical tri-acylation of the tetraamine **1** by tolylisocyanate (Scheme 2). Luckily, it was possible to isolate the tri-urea calix[4]arene **6** without chromatographic separation. Pure tri-tolylurea **6** was extracted from the crude product by dichloromethane/methanol (1:4) in 51% yield. Reaction of the *bis*-urethane **3a** with the tri-urea **6** in DMF in the presence of *i*-Pr_2EtN resulted in double calixarene **5a**. However, due to the low solubility of both starting compounds and of the product, the purification of **5a** was difficult in this case. Several subsequent recrystallisations of the crude product from THF/methanol finally yielded the target compound with 33% yield in acceptable purity. Similar problems appeared when the activated tri-urea monourethane **7** (prepared in 75% yield by the reaction of the tri-tolylurea **6** with *p*-nitrophenyl chloroformate) was coupled with benzidine under the same conditions (DMF, *i*-Pr_2EtN). Now, the double calixarene **5a** was obtained in 40% yield.

In summary, the strategy involving tri-Boc-protection was more efficient for the preparation of the target compounds **5** than the approach using the statistical formation of tri-urea derivatives (as shown by the example of tri-tolylurea). The ease of the purification of *bis*-calixarenes **4a–c** and of the introduction of various residues **R** makes the protection/deprotection strategy favourable. Moreover, the purity of the *bis*-calixarenes **5a–f** obtained by this procedure and the overall yield were considerably higher.

The structure and the purity of all compounds were confirmed by their ^1H NMR and FD or ESI mass spectra. In all cases, signals related to the complete



SCHEME 2 An alternative approach to *bis*-tetra-urea calix[4]arenes attempted for **5a**. (i) *p*-Tolylisocyanate, CH_2Cl_2; (ii) Et_3N, DMF; (iii) *p*-nitrophenyl chloroformate, $CHCl_3$; (iv) benzidine, *i*-Pr_2EtN, DMF.

molecules (M^+, M + Na^+, M + 2Na^+) were found with high abundance for compounds **4** and **5**. It must be emphasised that this information is entirely sufficient for a complete characterisation since we are dealing with a stepwise synthesis, starting with compounds described before and using well-known reagents and reactions. High-resolution mass spectrometry would be necessary only for the characterisation of entirely unknown compounds.

Self-assembly

^{1}H NMR Spectroscopy

Assuming free rotation around the connector X, two positions with the highest symmetry can be expected for compounds **5**, an 'S-shaped' conformation with C_{2h} symmetry, as suggested in Fig. 1, and, after a rotation by 180°, a C-shaped conformation with C_{2v} symmetry, where the wide rims of the calixarenes are face-to-face oriented. In both cases, the two C_S-symmetrical calixarene parts are bisected by a symmetry plane and related to each other by a twofold axis or a symmetry plane perpendicular to it. The ^{1}H NMR spectra of compounds **5a–f** recorded in polar solvents such as DMSO-d_6 reflect these symmetry properties (see an example in Fig. 2a). However, the picture observed for these *bis*-calixarenes changes dramatically in apolar solvents such as $CDCl_3$ or C_6D_6, which are frequently used for the dimerisation of tetra-urea calix[4]arenes (Fig. 2b). Now, the signals for the protons of *bis*-calixarenes are similar to those described for the formation of a single tetra-urea dimer. Typical observations are the downfield shift for the NH protons of the urea groups (appearing at about 9.3 ppm) and the splitting of the signals for the aromatic protons of the calixarene skeleton, one of which appears at about 6 ppm. These characteristic changes together with the general broadening of the signals in the ^{1}H NMR spectra indicate the formation of oligo- or polymer-like structures by the intermolecular dimerisation of the tetra-urea moieties.

As shown for the selected compounds **5a,b** and **5e**, the polymeric assemblies are degraded by the addition of tetra-tosylurea calix[4]arene **8** during the formation of the corresponding *bis*-heterodimers with two molecules of **8**. The downfield shift of the signals for the tosyl NH protons (10.4–10.8 ppm) and the sharpness of the signals in the ^{1}H NMR spectrum in $CDCl_3$ provide clear evidence for the formation of *bis*-heterodimers (as shown for **5a** in Fig. 2c).

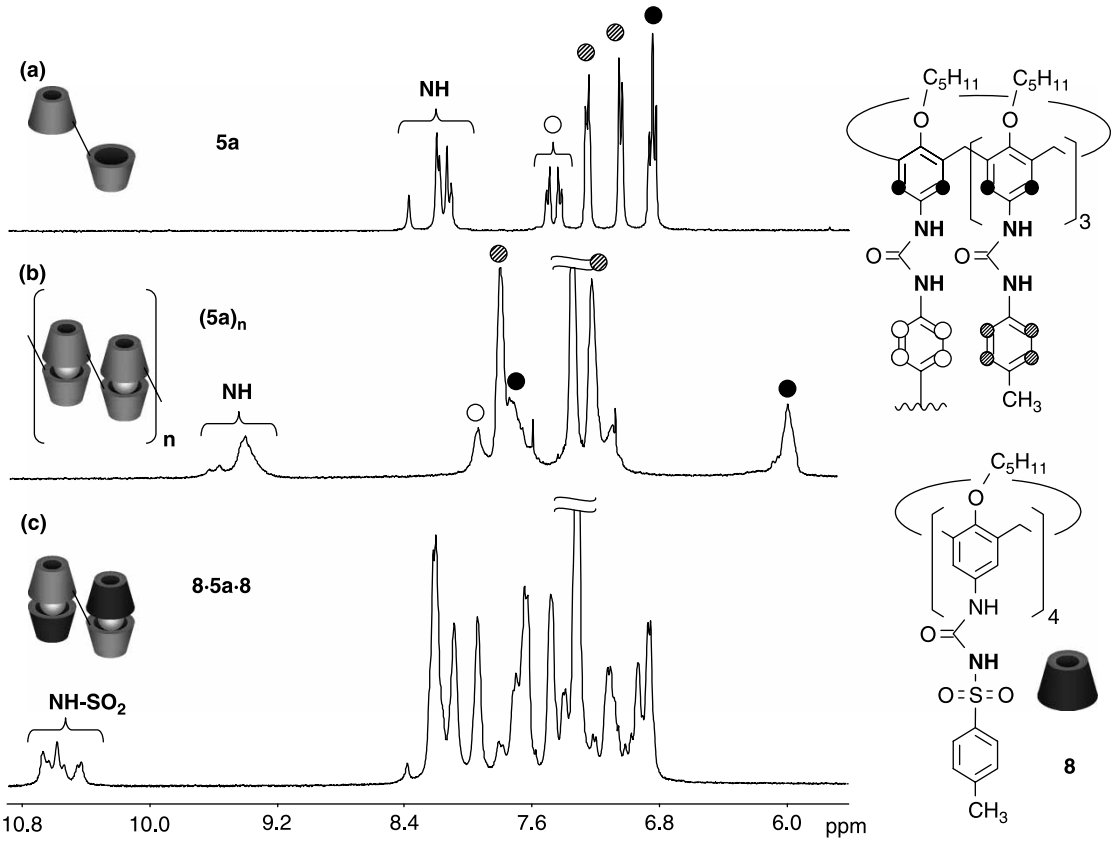


FIGURE 2 ^{1}H NMR spectra of *bis*-calixarene **5a**. (a) **5a** in DMSO-d_6, 50°C; (b) **5a** in $CDCl_3$, RT; (c) **5a** and tetra-tosylurea calix[4]arene **8** in the ratio of 1:2; $CDCl_3$, RT (*bis*-heterodimer **8·5a·8**).

Table I gives a survey of the self-assembly of **5a–f** according to the ^{1}H NMR studies.

Like single tetra-urea dimers, the polymers formed from *bis*-calixarenes **5a–f** are able to include appropriate molecules or cations. The inclusion of neutral guests was proved by the exchange of chloroform against *p*-difluorobenzene (F-Ph-F), which is known to be a 'better' guest for tetra-urea dimers than chloroform. Upon addition of 5% volume of F-Ph-F to the solution of **5b** (this compound was chosen due to its good solubility) in $CDCl_3$, the signal of *p*-difluorobenzene included in the dimeric capsules appeared at 2.78 ppm. Slight shifts of the signals for the urea protons, the aryl protons and the protons of the methylene bridges of the calixarene skeleton were also observed.

The inclusion of the tetraethylammonium cation in the capsules of polymeric **5b** is evident from the ^{1}H NMR spectrum in $CDCl_3$, where the signals for protons of the cation's methyl groups are splitted, caused by a specific orientation of the cationic ethyl groups in the tetra-urea dimer [17] and shifted to -0.14 and −3.29 ppm due to the aromatic walls of the host cavity.

TABLE I The self-assembling properties of *bis*-tetra-urea calix[4]arenes **5a–f** monitored by ^{1}H NMR spectroscopy.

Component 1	Component 2	Solvent	Temperature	Observations
5a	–	$CDCl_3$	RT	Polymerisation
5a	–	C_6D_6	75°C	Polymerisation
5a	**8**	$CDCl_3$	RT	*Bis*-heterodimer
5b	–	$CDCl_3$, C_6D_6	RT	Polymerisation
5b	**8**	$CDCl_3$	RT	*Bis*-heterodimer
5c	–	$CDCl_3$, TCE, C_6D_6	RT, 55°C	Insoluble
5c	–	TCE	75°C	Insoluble
5d	–	$CDCl_3$	RT	Polymerisation
5e	–	$CDCl_3$	RT, 55°C	Polymerisation
5e	**8**	$CDCl_3$	RT	*Bis*-heterodimer
5e	–	TCE	75°C	Polymerisation
5f	–	$CDCl_3$	RT	Polymerisation

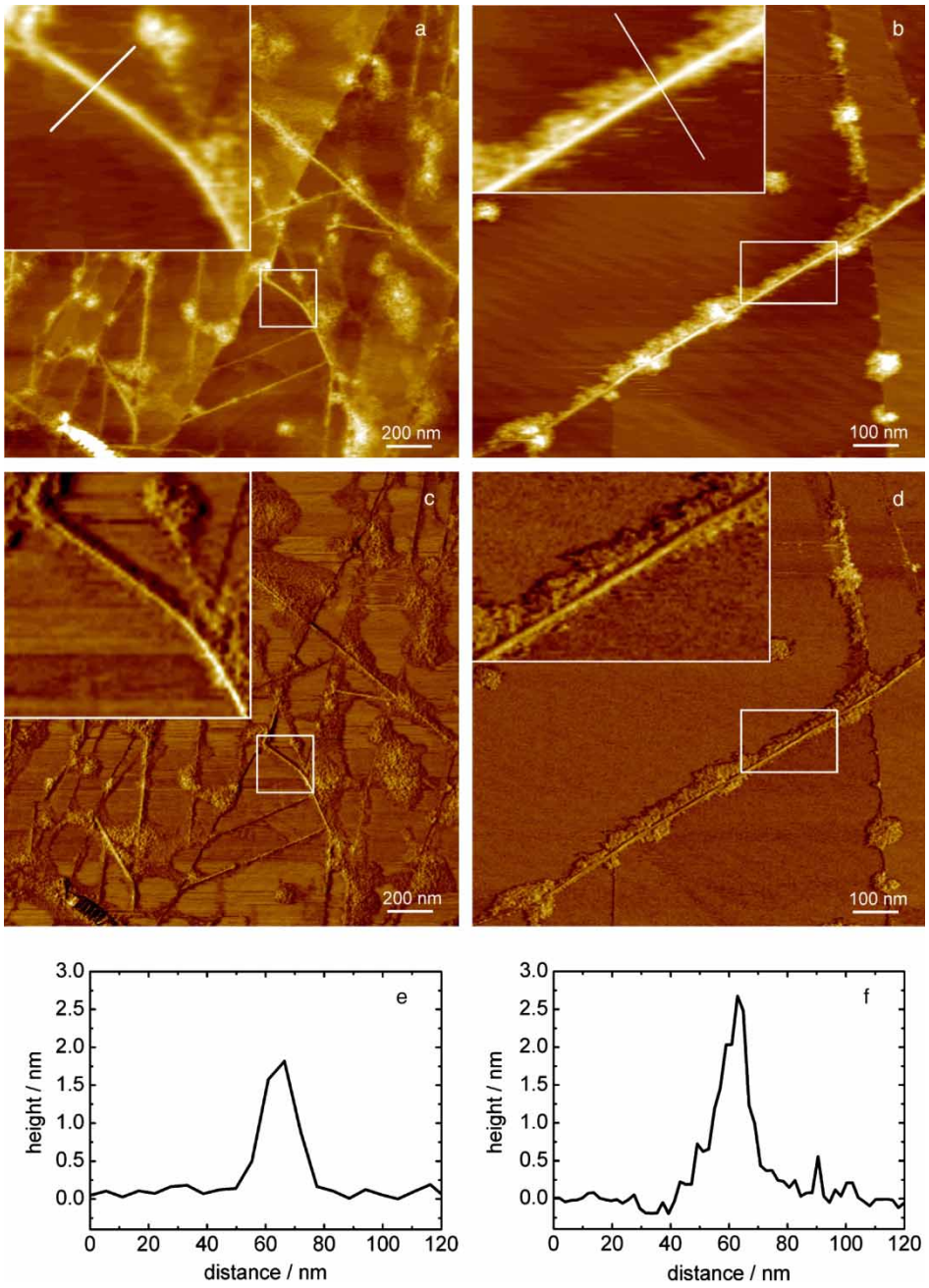


FIGURE 3 (a, b) AFM height and (c, d) phase images of the *bis*-calixarene **4b** on HOPG prepared by spin-coating of solutions C = 0.01 mg/ml. (a) $CHCl_3$; (b) $CHCl_3$ +5% *p*-difluorobenzene; (c) $CHCl_3$; (d) $CHCl_3$ +5% *p*-difluorobenzene; (e) cross section along the line shown in (a); (f) cross section along the line shown in (b).

Atomic Force Microscopy

Additional evidence for the formation of polymeric assemblies is provided by AFM imaging of spin-coated samples. Measurements of compound **5b** reveal a coexistence of rod-like and amorphous structures, probably representing highly as well as less-ordered *bis*-calixarene polymers (Fig. 3). The images display coiled structures as well as outstretched assemblies, which might be aligned according to the underlying graphite lattice.

According to average cross sections of AFM height images, the fibres exhibit a width of 16 ± 2 nm and a height of 1.8 ± 0.2 nm for the pure chloroform solution and a width of 13 ± 2 nm and a height of 2.5 ± 0.2 nm for chloroform solution containing 5% *p*-difluorobenzene as an additive. This finding is particularly interesting since it is known that difluorobenzene is a preferred guest molecule. Hence, we conclude that the inclusion complex modulates either the structure or the elastic properties of the calixarene polymers.

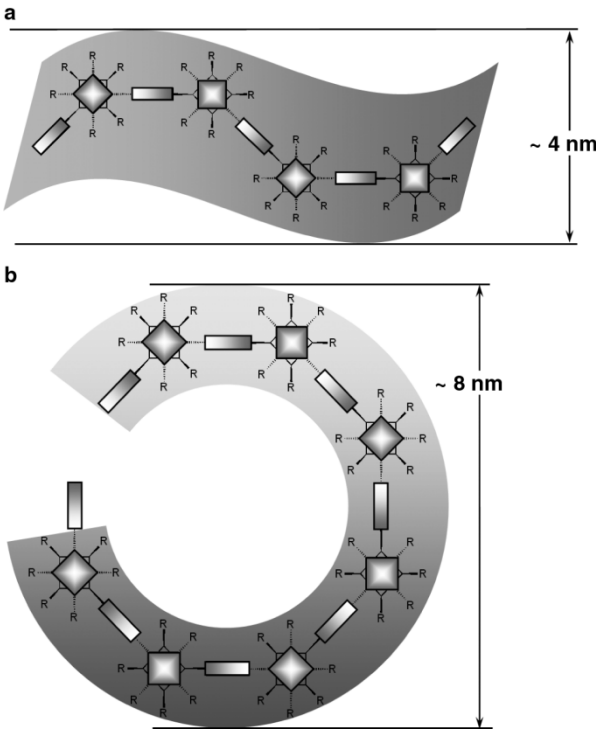


FIGURE 4 Idealised representation of a polymeric assembly in a (a) 'stretched' or (b) 'helical' arrangement.

From the images, we infer that the highly ordered polymers adopt a rather stiff conformation displaying straight structures over 0.1–1 μm. The reasons for this lie in either the polymeric structure or the underlying graphite lattice directing the adsorption of the polymer. The latter one is supported by the 60 and 120° angles sometimes observed for the adsorbed straight polymers.

The analysis of the AFM images led us to the conclusion that the band structure is the preferred superstructure (Fig. 4). This statement can be reasoned as follows: from the height analysis we conclude that the superstructure adopts a rather flat conformation exhibiting a height of 1.8–2.5 nm, depending on the guest molecule. The minimal width of the polymer strands as extracted from high-resolution phase imaging, however, was found to be between merely 7 and 8 nm. This value is an upper limit due to the finite size of the tip. Assuming preservation of the volume, which would imply either a greater height (approximately 8 nm) or, in the case of severe flattening of the structure on the surface, a substantially greater width, we can safely rule out the occurrence of a helical superstructure on the surface, which would require a height and width of about 8 nm.

CONCLUSIONS AND OUTLOOK

Bis-calixarenes **5** in which two tetra-urea calix[4]arenes are connected by a rigid spacer between the urea functions at their wide rim can be easily synthesised in three steps, starting with tetraamino tetrapentoxy calix[4]arene. In apolar solvents, they form polymeric assemblies via 'homodimerisation' of the tetra-urea units. The capsules thus formed keep their ability to host small molecules, e.g. difluorobenzene, or organic cations, e.g. tetraethylammonium. The addition of tetra-tosylurea **8**, which forms exclusively heterodimers with tetra-arylurea calix[4]arenes, leads to the degradation of the polymers. These results show that the usual dimerisation of tetra-urea calix[4]arenes is not hindered by the spacer. A distal arrangement within the dimeric capsules seems likely, and may be further favoured by bulky substituents at the two adjacent urea functions. Interactions between additional functional groups could be used in the future to favour, for instance, a helical over a stretched arrangement of adjacent dimeric capsules along the polymeric chain.

EXPERIMENTAL

Solvents and all other chemicals were purchased from Acros, Aldrich and Lancaster and used without further purification. ^{1}H NMR spectra were recorded on a Bruker DRX400 Avance instrument (at 400 MHz). FD and ESI mass spectra were measured on a Finnigan MAT 8230 spectrometer and a Micromass Q-TOF Ultima3 instrument, respectively. Melting points are uncorrected. *p*-Tetraamino calix[4]arene tetrapentylether **1** [32] and tri-*N*-Boc monoamine **2** [33] were prepared according to published procedures.

Synthesis of di-*p*-Nitrophenylurethane of Benzidine (3a)

4-Nitrophenyl chloroformate (1.64 g, 8.14 mmol) was added to a solution of benzidine (0.50 g, 2.71 mmol) in THF (15 ml). The reaction mixture was refluxed for 2 h. The solid product was filtered off, washed with ethylacetate and dried to give a grey powder. Yield: 1.19 g (85%); m.p. >270°C (decomp.); ^{1}H NMR (DMSO-d_6) 10.57 (s, N–*H*, 2H), 8.29 (d, Ar–*H*, 4H, $^3J_{HH} = 9.2$ Hz), 7.72–7.50 (m, Ar–*H*, 12H). MS (FD): *m/e* calcd for $C_{26}H_{18}N_4O_8$ $(M)^+$514, found 514.

Synthesis of di-*p*-Nitrophenylurethane of 4,4′-Diaminodiphenylacetylene (3b)

4-Nitrophenyl chloroformate (0.21 g, 1.03 mmol) was added to a solution of 4,4′-diaminodiphenylacetylene [35] (0.10 g, 0.49 mmol) in THF (25 ml). The reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was triturated with acetonitrile (25 ml). The solid product was filtered off, washed with acetonitrile

and dried to give a beige powder. Yield: 0.19 g (70%); m.p. >240°C (decomp.); ^{1}H NMR (DMSO-d_6, 35°C) 10.75 (s, N–*H*, 2H), 8.31 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.59 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.56 (d, Ar–*H*, 4H, $^3J_{HH} = 9.2$ Hz), 7.52 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz). MS (FD): *m/e* calcd for $C_{28}H_{18}N_4O_8$ $(M)^+$538, found 538.

Synthesis of di-p-Nitrophenylurethane of 4,4′-azodianiline (3c)

4-Nitrophenyl chloroformate (1.04 g, 5.13 mmol) was added to a solution of 4,4′-azodianiline (0.50 g, 2.36 mmol) in THF (30 ml). The reaction mixture was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was triturated with acetonitrile (50 ml). The solid product was filtered off, washed with acetonitrile and dried to give an orange powder. Yield: 1.08 g (84%); m.p. >220°C (decomp.); ^{1}H NMR (DMSO-d_6) 10.83 (s, N–*H*, 2H), 8.33 (d, Ar–*H*, 4H, $^3J_{HH} = 8.9$ Hz), 7.89 (d, Ar–*H*, 4H, $^3J_{HH} = 8.5$ Hz), 7.74 (d, Ar–*H*, 4H, $^3J_{HH} = 8.9$ Hz), 7.58 (d, Ar–*H*, 4H, $^3J_{HH} = 8.9$ Hz). MS (FD): *m/e* calcd for $C_{26}H_{18}N_6O_8$ $(M)^+$542, found 542.

Synthesis of 4a

Di-*p*-nitrophenylurethane **3a** (0.076 g, 0.148 mmol) and a solution of *N*,*N*-diisopropylethylamine (0.040 g, 0.310 mmol) in THF (5 ml) were added to a solution of tri-*N*-Boc monoamine **2** (0.30 g, 0.28 mmol) in THF (5 ml) and the reaction mixture was stirred at RT for 24 h. The solvent was removed under reduced pressure and the oily residue was triturated with methanol. The solid product was filtered off and washed with methanol to give the pure double calixarene as a white powder. Yield: 0.23 g (69%); m.p. >260°C (decomp.); ^{1}H NMR (DMSO-d_6) 8.90 (s, N–*H*, 4H), 8.60 (s, N–*H*, 2H), 8.27 (s, N–*H*, 2H), 8.08 (s, N–*H*, 2H), 7.49 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.40 (d, Ar–*H*, 4H, $^3J_{HH} = 8.3$ Hz), 6.96 (s, Ar–*H*, 8H), 6.72–6.49 (m, Ar–*H*, 8H), 4.31 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 12.2$ Hz), 4.30 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 12.2$ Hz), 3.87 (t, –O–CH_2–, 8H, $^3J_{HH} = 7.6$ Hz), 3.78–3.64 (m, –O–CH_2–, 8H), 3.05 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 13.2$ Hz), 3.01 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 13.2$ Hz), 1.98–1.78 (m, –O–CH$_2$–CH_2–, 16H), 1.50–1.26 (m, –CH_2–, –CH_3, 86H), 0.97–0.87 (m, –CH_3, 24H). MS (ESI): *m/e* calcd for $C_{140}H_{192}N_{10}O_{22}$ $(M + Na)^+$2390, $(M + 2Na)^{2+}$ 1206, found 2390 (74%), 1206 (100%).

Synthesis of 4b

Tri-*N*-Boc monoamine **2** (0.30 g, 0.28 mmol) and a solution of *N*,*N*-diisopropylethylamine (0.06 g, 0.48 mmol) in THF (4 ml) were added to a solution of di-*p*-nitrophenylurethane **3b** (0.08 g, 0.15 mmol) in THF (2.5 ml). The reaction mixture was stirred at RT for 24 h. Acetonitrile (20 ml) was added, the precipitate was filtered off and washed with acetonitrile to give the pure double calixarene as a white powder. Yield: 0.23 g (67%); m.p. >270°C (decomp.); ^{1}H NMR (DMSO-d_6) 8.88 (s, N–*H*, 4H), 8.68 (s, N–*H*, 2H), 8.60 (s, N–*H*, 2H), 8.30 (s, N–*H*, 2H), 7.40 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.37 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.07–6.80 (m, Ar–*H*, 8H), 6.76–6.47 (m, Ar–*H*, 8H), 4.42–4.20 (m, Ar–CH_2–Ar, 8H), 3.85 (br t, –O–CH_2–, 8H), 3.79–3.59 (m, –O–CH_2–, 8H), 3.12–2.91 (m, Ar–CH_2–Ar, 8H), 2.00–1.76 (m, –O–CH$_2$–CH_2–, 16H), 1.56–1.18 (m, –CH_2–, –CH_3, 86H), 0.92 (t, –CH_3, 24H, $^3J_{HH} =$ 6.6 Hz). MS (ESI): *m/e* calcd for $C_{142}H_{192}N_{10}O_{22}$ $(M + Na)^+$2414, $(M + 2Na)^{2+}$1218, found 2414 (100%), 1218 (46%).

Synthesis of 4c

Tri-*N*-Boc monoamine **2** (0.32 g, 0.30 mmol) and a solution of *N*,*N*-diisopropylethylamine (0.062 g, 0.479 mmol) in THF (5 ml) were added to a suspension of di-*p*-nitrophenylurethane **3c** (0.09 g, 0.16 mmol) in THF (5 ml) and the reaction mixture was stirred at RT for 24 h. Then, acetonitrile (30 ml) was added to the reaction mixture. The precipitate was filtered off and washed with acetonitrile to give analytically pure double calixarene as a white powder. Yield: 0.31 g (86%); m.p. >290°C (decomp.); ^{1}H NMR (DMSO–d_6, 75°C) 8.55 (s, N–*H*, 4H), 8.44 (s, N–*H*, 2H), 8.18 (s, N–*H*, 2H), 8.01 (s, N–*H*, 2H), 7.75 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.55 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.00–6.89 (m, Ar–*H*, 8H), 6.64–6.55 (m, Ar–*H*, 8H), 4.42–4.29 (m, Ar–CH_2–Ar, 8H), 3.91 (t, –O–CH_2–, 8H, $^3J_{HH} = 7.6$ Hz), 3.84–3.72 (m, –O–CH_2–, 8H), 3.12–2.97 (m under water peak, Ar–CH_2–Ar, 8H), 1.95–1.80 (m, –O–CH$_2$–CH_2–, 16H), 1.52–1.28 (m, –CH_2–, –CH_3, 86H), 1.00–0.87 (m, –CH_3, 24H). MS (ESI): *m/e* calcd for $C_{140}H_{192}N_{12}O_{22}$ $(M + Na)^+$2418, $(M + 2Na)^{2+}$1220, found 2418 (100%), 1220 (10%).

Synthesis of 6

A solution of *p*-tolylisocyanate (0.54 g, 4.05 mmol) in dichloromethane (100 ml) was added dropwise to a vigorously stirred solution of tetraamino calix[4]arene **1** (1.00 g, 1.31 mmol) in dichloromethane (100 ml). After 24 h of stirring at RT, the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane and the tetra-urea product was precipitated by methanol. It was filtered off and isolated as a white powder (0.52 g, 30%). The filtrate was evaporated and the residue was reprecipitated from dichloromethane/hexane to give the desired product **6** as a white powder. Yield: 0.78 g (51%); m.p. >250°C (decomp.); ^{1}H NMR (DMSO–d_6)

8.34–8.06 (m, N–*H*, 6H), 7.32–7.14 (m, Ar–*H*, 6H), 7.10–6.94 (m, Ar–*H*, 6H), 6.87–6.67 (m, Ar–*H*, 6H), 6.03 (s, Ar–*H*, 2H), 5.16–4.42 (br s, NH_2, 2H), 4.33 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.5$ Hz), 4.25 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.5$ Hz), 3.90–3.63 (m, –O–CH_2–, 8H), 3.09 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.8$ Hz), 2.97 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.8$ Hz), 2.22 (s, –CH_3, 9H), 1.98–1.76 (m, –O–CH$_2$–CH_2–, 8H), 1.49–1.25 (m, –CH_2–, 16H), 0.93 (br t, –CH_3, 12H).

Synthesis of 7

Tri-urea monoamine **6** (2.00 g, 1.91 mmol) was added to a stirred solution of 4-nitrophenyl chloroformate (2.55 g, 12.6 mmol) in $CHCl_3$ (22 ml). The reaction mixture was refluxed for 4 h, the solvent was evaporated and the residue was triturated with acetonitrile and stored in a refrigerator for 4–8 h. The solid product was filtered off, washed with acetonitrile and dried to give a light yellow powder. Yield: 2.65 g (75%); m.p. >200°C; ^{1}H NMR (DMSO-d_6) 9.95 (s, N–*H*, 1H), 8.25 (s, N–*H*, 3H), 7.21 (d, Ar–*H*, 2H, $^3J_{HH} = 8.8$ Hz), 8.15 (s, N–*H*, 3H), 7.37 (d, Ar–*H*, 2H, $^3J_{HH} = 8.8$ Hz), 7.30–7.18 (m, Ar–*H*, 6H), 7.16–6.97 (m, Ar–*H*, 6H), 6.94 (s, Ar–*H*, 2H), 6.81 (s, Ar–*H*, 4H), 6.75 (s, Ar–*H*, 2H), 4.35 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.3$ Hz), 4.33 (d, Ar–CH_2–Ar, 2H, $^2J_{HH} = 12.6$ Hz), 3.82–3.67 (m, –O–CH_2–, 8H), 3.11 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 12.9$ Hz), 2.21 (s, –CH_3, 6H), 2.20 (s, –CH_3, 3H), 2.00–1.84 (m, –O–CH$_2$–CH_2–, 8H), 1.49–1.30 (m, –CH_2–, 16H), 0.93 (t, –CH_3, 12H, $^3J_{HH} = 6.8$ Hz).

Synthesis of 5a

Procedure A

Trifluoroacetic acid (2 ml) was added to a solution of hexa-*N*-Boc-protected *bis*-calix[4]arene **4a** (97 mg, 0.041 mmol) in dichloromethane (10 ml) and the mixture was stirred at RT for 2 h. The solvent was evaporated, the residue was dissolved in THF (5 ml) and treated with *N*,*N*-diisopropylethylamine (0.034 g, 0.265 mmol). After 15 min a precipitate appeared, which slowly dissolved again after a solution of *p*-tolylisocyanate (0.049 g, 0.367 mmol) in THF (5 ml) was added. The solution was stirred at RT for 10–12 h under nitrogen. Half of the solvent was evaporated under reduced pressure and methanol (15 ml) was added to the residue to precipitate the product. The solid product was filtered off, washed with methanol and dried to give a light-beige powder. Yield: 85 mg (81%).

Procedure B

Benzidine (8.0 mg, 0.0435 mmol) and *N*,*N*-diisopropylethylamine (17 mg, 0.131 mmol) were added to a solution of monourethane **7** (0.116 g, 0.087 mmol) in DMF (5 ml). The mixture was stirred at 50°C for 72 h under nitrogen and poured into cooled water (15 ml). The precipitate formed was filtered off and washed with water and methanol. Repeated reprecipitation from THF/methanol gave the desired product as a beige powder. Yield: 60 mg (40%).

Procedure C

Di-*p*-nitrophenylurethane **3a** (23 mg, 0.045 mmol) and a solution of triethylamine (43 mg, 0.429 mmol) in DMF (5 ml) were added to a solution of tri-urea monoamine **6** (100 mg, 0.0859 mmol) in DMF (5 ml). The reaction mixture was stirred at RT for 24 h. Water (20 ml) was added, the formed precipitate was filtered off and washed with water and methanol. Repeated reprecipitation from THF/methanol gave the desired product as a beige powder. Yield: 36 mg (33%); m.p. >255°C (decomp.); ^{1}H NMR (DMSO-d_6, 50°C) 8.33 (s, N–*H*, 2H), 8.21–8.01 (m, N–*H*, 14H), 7.46 (d, Ar–*H*, 4H, $^3J_{HH} = 8.3$ Hz), 7.39 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.22 (d, Ar–*H*, 12H, $^3J_{HH} = 8.3$ Hz), 7.01 (d, Ar–*H*, 12H, $^3J_{HH} = 7.8$ Hz), 6.84 (s, Ar–*H*, 4H), 6.82 (s, Ar–*H*, 8H), 6.80 (s, Ar–*H*, 4H), 4.36 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 12.7$ Hz), 3.85 (m, –O–CH_2–, 16H), 3.11 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 11.2$ Hz), 2.21 (s, –CH_3, 18H), 1.92 (m, –O–CH$_2$–CH_2–, 16H), 1.41 (m, –CH_2–, 32H), 0.95 (br t, –CH_3, 24H). MS (ESI): *m*/*e* calcd for $C_{158}H_{186}N_{16}O_{16}$ $(M + 2Na)^{2+}$ 1305, found 1305 (100%).

Synthesis of 5b

Prepared from *bis*-calix[4]arene **4a** (80 mg, 0.0338 mmol), trifluoroacetic acid (2 ml) and dichloromethane (10 ml), as described for **5a** (procedure A). After deprotection, an excess of *N*,*N*-diisopropylethylamine (63 mg, 0.487 mmol) in THF (10 ml) and of the *p*-nitrophenylurethane of *p*-decyloxyaniline (140 mg, 0.338 mmol) were added. The product was purified by reprecipitation from THF/methanol. Yield: 80 mg (69%); m.p. >210°C (decomp.); ^{1}H NMR (DMSO-d_6, 65°C) 8.28 (s, N–*H*, 2H), 8.07 (s, N–*H*, 2H), 8.00 (s, N–*H*, 6H), 7.97 (s, N–*H*, 6H), 7.46 (d, Ar–*H*, 4H, $^3J_{HH} = 8.5$ Hz), 7.39 (d, Ar–*H*, 4H, $^3J_{HH} = 8.2$ Hz), 7.22 (d, Ar–*H*, 12H, $^3J_{HH} = 8.5$ Hz), 6.90–6.68 (m, Ar–*H*, 28H), 4.37 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 12.0$ Hz), 4.98–3.75 (m, –O–CH_2–, 28H), 3.20 (d under the water peak, Ar–CH_2–Ar, 8H), 1.92 (m, –O–CH$_2$–CH_2–, 16H), 1.66 (m, –O–CH$_2$–CH_2–, 12H), 1.50–1.14 (m, –CH_2–, 116H), 0.95 (br t, –CH_3, 24H), 0.85 (br t, –CH_3, 18H). MS (ESI): *m*/*e* calcd for $C_{212}H_{294}N_{16}O_{22}$ $(M + 2Na)^{2+}$ 1732, found 1732 (100%).

Synthesis of 5c

Prepared from *bis*-calix[4]arene **4a** (100 mg, 0.0417 mmol), trifluoroacetic acid (2 ml) and dichloromethane (10 ml), as described for **5a** (procedure A). After deprotection, *N*,*N*-diisopropylethylamine (63 mg, 0.487 mmol) and *n*-hexylisocyanate (54 mg, 0.422 mmol) in THF (20 ml) were added; the product was purified by reprecipitation from THF/methanol. Yield: 85 mg (79%); m.p. >230°C (decomp.); ^{1}H NMR (DMSO-d_6) 8.40 (s, N–*H*, 2H), 8.11 (s, N–*H*, 2H), 7.97 (s, N–*H*, 4H), 7.82 (s, N–*H*, 2H), 7.48 (d, Ar–*H*, 4H, $^3J_{HH} = 8.4$ Hz), 7.42 (d, Ar–*H*, 4H, $^3J_{HH} = 8.4$ Hz), 6.82 (s, Ar–*H*, 4H), 6.79 (s, Ar–*H*, 4H), 6.70 (s, Ar–*H*, 4H), 6.61 (s, Ar–*H*, 4H), 5.82 (br t, N–*H*, 4H, $^3J_{HH} = 4.8$ Hz), 5.69 (br t, N–*H*, 2H, $^3J_{HH} = 5.3$ Hz), 4.44 (m, Ar–CH_2–Ar, 8H), 3.98–3.61 (m, –O–CH_2–, –NH–CH_2–, 28H), 3.17–2.86 (m, Ar–CH_2–Ar, –NH–CH$_2$–CH_2–, 12H), 2.05–1.70 (m, –O–CH$_2$–CH_2–, 16H), 1.60–1.05 (m, –CH_2–, 68H), 1.01–0.73 (m, –CH_3, 42H). MS (ESI): *m*/*e* calcd for $C_{152}H_{222}N_{16}O_{16}$ $(M + Na)^+$2552, $(M + 2Na)^{2+}$ 1287, found 2552 (46%), 1287 (100%).

Synthesis of 5d

Prepared from *bis*-calix[4]arene **4b** (100 mg, 0.0417 mmol), trifluoroacetic acid (2 ml) and dichloromethane (10 ml), as described for **5a** (procedure A). After deprotection, the salt was dissolved in THF (10 ml) and treated with *N*,*N*-diisopropylethylamine (108 mg, 0.836 mmol) and *p*-tolylisocyanate (56 mg, 0.418 mmol). Trituration with acetonitrile (15 ml) gave the product as a light-beige powder. Yield: 72 mg (66%); m.p. >250°C (decomp.); ^{1}H NMR (DMSO-d_6, 50°C) 8.54 (s, N–*H*, 2H), 8.28–8.02 (m, N–*H*, 14H), 7.36 (s, Ar–*H*, 4H), 7.28–7.12 (m, Ar–*H*, 16H), 7.07–6.93 (m, Ar–*H*, 12H), 6.88–6.68 (m, Ar–*H*, 20H), 4.33 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 11.7$ Hz), 3.97–3.67 (m, –O–CH_2–, 16H), 3.10 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 11.4$ Hz), 2.29–2.07 (m, –CH_3, 18H), 2.01–1.76 (m, –O–CH$_2$–CH_2–, 16H), 1.50–1.28 (m, –CH_2–, 32H), 0.94 (br t, –CH_3, 24H). MS (ESI): *m*/*e* calcd for $C_{160}H_{186}N_{16}O_{16}$ $(M + 2Na)^{2+}$1317, found 1317 (100%).

Synthesis of 5e

Prepared from *bis*-calix[4]arene **4c** (100 mg, 0.0417 mmol), trifluoroacetic acid (2 ml) and dichloromethane (10 ml), as described for **5a** (procedure A). After deprotection, *N*,*N*-diisopropylethylamine (108 mg, 0.834 mmol) and *p*-tolylisocyanate (49 mg, 0.367 mmol) in THF (7 ml) were added. Trituration with acetonitrile (20 ml) gave the product as a yellow powder. Yield: 95 mg (87%); m.p. >290°C (decomp.); ^{1}H NMR (DMSO-d_6, 75°C) 8.54 (s, N–*H*, 2H), 8.12 (s, N–*H*, 2H), 8.08 (s, N–*H*, 4H), 8.05 (s, N–*H*, 2H), 8.02 (s, N–*H*, 4H), 7.94 (s, N–*H*, 2H), 7.73 (d, Ar–*H*, 4H, $^3J_{HH} = 8.3$ Hz), 7.51 (d, Ar–*H*, 4H, $^3J_{HH} = 8.8$ Hz), 7.28–7.15 (m, Ar–*H*, 12H), 7.06–6.95 (m, Ar–*H*, 12H), 6.87 (s, Ar–*H*, 4H), 6.85 (s, Ar–*H*, 4H), 6.80 (s, Ar–*H*, 4H), 6.77 (s, Ar–*H*, 4H), 4.40 (d, Ar–CH_2–Ar, 8H, $^2J_{HH} = 12.2$ Hz), 3.96–3.79 (m, –O–CH_2–, 16H), 3.19–3.08 (m, Ar–CH_2–Ar, 8H), 2.22 (s, –CH_3, 18H), 1.92 (br s, –O–CH$_2$–CH_2–, 16H), 1.42 (br s, –CH_2–, 32H), 0.95 (br s, –CH_3, 24H). MS (ESI): *m*/*e* calcd for $C_{158}H_{186}N_{18}O_{16}$ $(M + 2Na)^{2+}$1320, found 1320 (100%).

Synthesis of 5f

Prepared from *bis*-calix[4]arene **4c** (50 mg, 0.021 mmol), trifluoroacetic acid (2 ml) and dichloromethane (10 ml), as described for **5a** (procedure A). After deprotection, *N*,*N*-diisopropylethylamine (108 mg, 0.834 mmol) and *p*-nitrophenylurethane of *p*-decyloxyaniline (87 mg, 0.209 mmol) in THF (10 ml) were added; reprecipitation from THF/acetonitrile gave the product as a yellow powder. Yield: 63 mg (87%); m.p. >200°C (decomp.); ^{1}H NMR (DMSO-d_6, 75°C) 8.55 (s, N–*H*, 2H), 8.11 (s, N–*H*, 2H), 7.99 (s, N–*H*, 4H), 7.96 (s, N–*H*, 6H), 7.90 (s, N–*H*, 2H), 7.73 (d, Ar–*H*, 4H, $^3J_{HH} = 8.7$ Hz), 7.51 (d, Ar–*H*, 4H, $^3J_{HH} = 9.1$ Hz), 7.29–7.10 (m, Ar–*H*, 12H), 6.94–6.63 (m, Ar–*H*, 28H), 4.40 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 12.8$ Hz), 4.38 (d, Ar–CH_2–Ar, 4H, $^2J_{HH} = 12.8$ Hz), 4.00–3.73 (m, –O–CH_2–, 28H), 3.19–3.08 (m, Ar–CH_2–Ar, 8H), 2.00–1.83 (m, –O–CH$_2$–CH_2–, 16H), 1.73–1.59 (m, –O–CH$_2$–CH_2–, 12H), 1.52–1.14 (m, –CH_2–, 118H), 0.95 (t, –CH_3, 24H, $^3J_{HH} = 6.4$ Hz), 0.85 (t, –CH_3, 18H, $^3J_{HH} = 6.8$ Hz). MS (ESI): *m*/*e* calcd for $C_{212}H_{294}N_{18}O_{22}$ $(M + 2Na)^{2+}$1746, found 1746 (100%).

Atomic Force Microscopy

Submonolayers of *bis*-calix[4]arene derivatives were prepared by spin coating. The *bis*-calix[4]arenes were dissolved in either pure chloroform or a mixture of 95/5 vol% chloroform/*p*-difluorobenzene resulting in a concentration of 10^{-2} to 10^{-4} mg ml^{-1}. A droplet of 30 μl was deposited on a freshly cleaved highly oriented pyrolytic graphite (HOPG; purchased from Plano GmbH, Wetzlar, Germany) surface and the sample was spun at 1000 rpm for 30 s. Samples were imaged at room temperature with a commercial AFM (Multimode equiped with Nanoscope IIIa controller, Veeco Digital Instruments, Santa Barbara, California) in tapping mode at 1–2 lines per second using rectangular silicon cantilevers (Nanoworld NCH). To control and enhance the range of the attractive interaction regime, the instrument was equipped with a special active feedback circuit, called Q-control (Nanoanalytics, Germany), as described previously [36]. The quality factor Q of this oscillating

system is increased by one order of magnitude. As a consequence, the sensitivity and lateral resolution are enhanced, allowing us to prevent the onset of intermittent repulsive contact and thereby to operate the SFM constantly in the attractive interaction regime.

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