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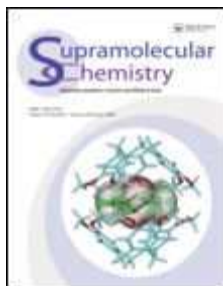
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Self-assembled polymers based on bis-tetra-urea calix[4]arenes connected via the wide rim

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5 **Self-assembled polymers based on *bis*-tetra-urea calix[4]arenes**
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8 **connected via the wide rim**
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10
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41 Dedicated to Prof. David N. Reinhoudt
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46
47 *Keywords:* *Bis*-tetra-urea calix[4]arene; Self-assembly; Hydrogen bonds; NMR-
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49 spectroscopy; Atomic force microscopy
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55 Six double calixarenes were synthesized in which two tetra-urea calix[4]arenes are
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57 linked by a rigid spacer between the urea functions at their wide rim. The dimerization
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59 of their tetra-urea parts leads to hydrogen bonded polymeric assemblies in apolar
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4 solvents. Addition of the stoichiometric amount of a tetra-tosylurea calix[4]arene
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6 disrupts the polymeric structures due to the preferred formation of heterodimeric
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8 capsules between tetra-aryl and tetra-tosylurea calix[4]arenes. The existence of
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10 polymeric assemblies was further established by AFM studies on spin coated samples.
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17 INTRODUCTION

20 The self-organization of macromolecules [1,2] (e.g. the folding of peptides) or the self-
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22 assembly of smaller molecules into well ordered structures [3-5] is one of the central
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24 topics in supramolecular chemistry. Various structural motifs based on reversible
25
26 hydrogen bonding were utilized for those purposes [6-10]. Among them the
27
28 dimerization of tetra-urea calix[4]arene derivatives in apolar solvents has been studied
29
30 in detail [11-16]. These dimers are based on a belt of intermolecular hydrogen bonds,
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32 involving alternately the urea residues attached to the wide rims of the calixarene
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34 counterparts. The cavity of the capsule-like dimers contains usually a solvent molecule
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36 as guest. Due to its high electron density, it is especially attractive for positively
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38 charged species and the solvent molecule can be exchanged against cations of
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40 appropriate size, such as tetraethylammonium [17] or cobaltocenium [18]. The
41
42 formation of the dimers and their inclusion phenomena in solution were studied by ¹H
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44 NMR and MS-ESI spectrometry [19]. Several dimeric structures were also confirmed
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46 by X-ray analysis in the crystalline state [15,20]. The preorganization of functional
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48 groups achieved in (hetero)dimers has recently been used for the synthesis of *bis*- [21]
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50 and tetra-loop derivatives [22] which are building blocks for novel multi-catenanes
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52 [22,23] and rotaxanes [22,23], for the construction of dendritic assemblies [24] and the
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54 preparation of self-assembled monolayers [25].
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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 dimerization 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 synthesized 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 acylation with (*n*-heptyl)phenylisocyanate. This *bis*-calixarene formed a discrete assembly (a so-called “unimolecular capsule”) by intramolecular dimerization in apolar solvents as shown by complexation studies, ¹H 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 dimerization of the tetra-urea parts is possible with these compounds.

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

RESULTS AND DISCUSSION

1 General Considerations

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If two tetra-urea calix[4]arenes are connected by a rigid spacer X between their urea groups, which allows their dimerization, their self-assembly in apolar solvents still can 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 45° around their common axis with respect to each other. The other two dimerization 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 favored, the formation of helical segments/polymers could occur in an ideal case.

[Insert figure 1 about here]

2 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 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]. Coupling of two tri-Boc-protected calixarenes **2** with activated *bis*-urethanes **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

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4 trifluoroacetic acid and subsequent reaction with an excess of the respective isocyanate
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6 or *p*-nitrophenylcarbamate produced the target *bis*-(tetra-urea) derivatives **5a-f** in 69-
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8
9 87% yield.

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11 [Insert scheme 1 about here]

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15 The tri-Boc protected calix[4]arene **2** is formed from tetraamine **1** by acylation
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17 with Boc-anhydride on a more or less statistical basis. As an alternative approach we
18
19 therefore attempted the direct statistical tri-acylation of the tetraamine **1** by
20
21 tolylisocyanate (Scheme 2). Luckily, it was possible to isolate the tri-urea calix[4]arene
22
23 **6** without chromatographic separation. Pure tri-tolylurea **6** was extracted from the crude
24
25 product by dichloromethane : methanol (1 : 4) in 51% yield. Reaction of the *bis*-
26
27 urethane **3a** with the tri-urea **6** in DMF in the presence of *i*-Pr₂EtN resulted in double
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29 calixarene **5a**. However, due to the low solubility of both starting compounds and of the
30
31 product, the purification of **5a** was difficult in this case. Several subsequent
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33 recrystallizations of the crude product from THF/methanol yielded finally the target
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35 compound with 33% yield in acceptable purity. Similar problems appeared when the
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37 activated tri-urea monourethane **7** (prepared in 75% yield by the reaction of the tri-
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39 tolylurea **6** with *p*-nitrophenyl chloroformate) was coupled with benzidine under the
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41 same conditions (DMF, *i*-Pr₂EtN). Now the double calixarene **5a** was obtained in 40%
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50 yield.

51 [Insert scheme 2 about here]

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54 In summary, the strategy involving tri-Boc-protection was more efficient for the
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56 preparation of the target compounds **5** than the approach using the statistical formation
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58 of tri-urea derivatives (as shown by the example of tri-tolylurea). The ease of the
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4 purification of *bis*-calixarenes **4a-c** and of the introduction of various residues **R** makes
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6 the protection/deprotection strategy favourable. Moreover, the purity of the *bis*-
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8 calixarenes **5a-f** obtained by this procedure and the overall yield were considerably
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10 higher.
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14 The structure and the purity of all compounds were confirmed by their ^1H NMR
15
16 and FD or ESI mass spectra. In all cases signals related to the complete molecules (M^+ ,
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18 $\text{M}+\text{Na}^+$, $\text{M}+2\text{Na}^+$) were found with high abundance for compounds **4** and **5**. It must be
19
20 emphasized that this information is entirely sufficient for a complete characterisation
21
22 since we are dealing with a stepwise synthesis, starting with compounds described
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24 before and using well known reagents and reactions. High resolution mass spectrometry
25
26 would be necessary only for the characterization of entirely unknown compounds.
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34 **3 Self-assembly**

35 **3.1 ^1H NMR spectroscopy**

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37 Assuming free rotation around the connector X two positions with highest symmetry
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39 can be expected for compounds **5**, a “S-shaped” conformation with $\text{C}_{2\text{h}}$ -symmetry, as
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41 suggested in Fig. 1 and, after rotation by 180° , a C-shaped conformation with $\text{C}_{2\text{v}}$ -
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43 symmetry, where the wide rims of the calixarenes are face to face oriented. In both
44
45 cases the two C_s -symmetrical calixarene parts are bisected by a symmetry plane and
46
47 related to each other by a twofold axis or a symmetry plane perpendicular to it. The ^1H
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49 NMR spectra of compounds **5a-f** recorded in polar solvents such as DMSO-d_6 reflect
50
51 these symmetry properties (see an example in Fig. 2a). However, the picture observed
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53 for these *bis*-calixarenes changes dramatically in apolar solvents such as CDCl_3 or C_6D_6
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4 which are frequently used for the dimerization of tetra-urea calix[4]arenes (Fig. 2b).
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6 Now the signals for the protons of *bis*-calixarenes are similar to those described for the
7
8 formation of a single tetra-urea dimer. Typical observations are the downfield-shift for
9
10 the NH protons of the urea groups (appearing at about 9.3 ppm) and the splitting of the
11
12 signals for the aromatic protons of the calixarene skeleton one of which appears at about
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14 6 ppm. These characteristic changes together with the general broadening of the signals
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16 in the ^1H NMR spectra indicate the formation of oligo- or polymer-like structures by the
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18 intermolecular dimerization of the tetra-urea moieties.
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24 [Insert figure 2 about here]
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27 As shown for the selected compounds **5a,b** and **5e** the polymeric assemblies are
28
29 degraded by the addition of tetra-tosylurea calix[4]arene **8** under formation of the
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31 corresponding *bis*-heterodimers with two molecules of **8**. The downfield shift of the
32
33 signals for the tosyl NH protons (10.4 - 10.8 ppm) and the sharpness of the signals in ^1H
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35 NMR spectrum in CDCl_3 provide clear evidence for the formation of *bis*-heterodimers
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37 (as shown for **5a** in Fig. 2c).
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41 Table 1 gives a survey of the self-assembly of **5a-f** according to the ^1H NMR
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43 studies.
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47 [Insert table 1 about here]
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50 Like single tetra-urea dimers, the polymers formed from *bis*-calixarenes **5a-f** are
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52 able to include appropriate molecules or cations. The inclusion of neutral guests was
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54 proved by exchange of chloroform against *p*-difluorobenzene (F-Ph-F) which is known
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56 to be a “better” guest for tetra-urea dimers than chloroform. Upon addition of 5% vol. of
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58 F-Ph-F to the solution of **5b** (this compound was chosen due to its good solubility) in
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CDCl₃ 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 ¹H NMR spectrum in CDCl₃, 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 aromatic walls of the host cavity.

3.2 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.

[Insert figure 3 about here]

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 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

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4 inclusion complex either modulates the structure or the elastic properties of the
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6 calixarene polymers.
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10 From the images we infer that the highly ordered polymers adopt a rather stiff
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12 conformation displaying straight structures over 0.1 -1 μm . The reasons for this lie
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14 either in the polymeric structure or the underlying graphite lattice directing the
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16 adsorption of the polymer. The latter one is supported by the 60° and 120° angles
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18 sometimes observed for the adsorbed straight polymers.
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22 Analysis of the AFM images led us to the conclusion that the band structure is
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24 the preferred superstructure (see fig. 4). This statement can be reasoned as follows: from
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26 height analysis we conclude that the superstructure adopts a rather flat conformation
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28 exhibiting a height of 1.8 to 2.5 nm depending on the guest molecule. The minimal
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30 width of the polymer strands as extracted from high resolution phase imaging, however,
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32 was found to be between merely 7-8 nm. This value is an upper limit due to the finite
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34 size of the tip. Assuming preservation of the volume, which would imply either a
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36 greater height (approximately 8 nm) or in case of severe flattening of the structure on
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38 the surface a substantially greater width, we can safely rule out the occurrence of a
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40 helical superstructure on the surface which would require a height and width of about 8
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46 nm.
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49 [Insert figure 4 about here]
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54 CONCLUSIONS AND OUTLOOK

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

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36 Solvents and all other chemicals were purchased from Acros, Aldrich, and Lancaster
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38 and used without further purification. ¹H NMR spectra were recorded on a Bruker
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40 DRX400 Avance instrument (at 400 MHz). FD and ESI mass spectra were measured on
41
42 a Finnigan MAT 8230 spectrometer and a Micromass Q-TOF Ultima3 instrument,
43
44 respectively. Melting points are uncorrected. *p*-Tetraamino calix[4]arene
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46 tetrapentylether **1** [32] and tri-*N*-Boc monoamine **2** [33] were prepared according to
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48 published procedures.
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57 Synthesis of di-*p*-nitrophenylurethane of benzidine (3a)

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4 4-Nitrophenyl chloroformate (1.64 g, 8.14 mmol) was added to a solution of benzidine
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6 (0.50 g, 2.71 mmol) in THF (15 ml). The reaction mixture was refluxed for 2 hours. The
7
8 solid product was filtered off, washed with ethylacetate and dried to give a gray powder.
9
10 Yield: 1.19 g (85%). m.p. >270°C (decomp.); ¹H NMR (DMSO-d₆) 10.57 (s, N-H, 2 H),
11
12 8.29 (d, Ar-H, 4 H, ³J_{HH} 9.2 Hz), 7.72-7.50 (m, Ar-H, 12 H). MS (FD): m/e calcd for
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14 C₂₆H₁₈N₄O₈ (M)⁺ 514, found 514.
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22 **Synthesis of di-*p*-nitrophenylurethane of 4, 4'-aminodiphenylacetylene (3b)**

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24 4-Nitrophenyl chloroformate (0.21 g, 1.03 mmol) was added to a solution of 4,4'-
25
26 aminodiphenylacetylene [35] (0.10 g, 0.49 mmol) in THF (25 ml). The reaction mixture
27
28 was refluxed for 4 hours. The solvent was removed under reduced pressure and the
29
30 residue was triturated with acetonitrile (25 ml). The solid product was filtered off,
31
32 washed with acetonitrile and dried to give a beige powder. Yield: 0.19 g (70%). m.p.
33
34 >240°C (decomp.); ¹H NMR (DMSO-d₆, 35°C) 10.75 (s, N-H, 2 H), 8.31 (d, Ar-H, 4 H,
35
36 ³J_{HH} 8.8 Hz), 7.59 (d, Ar-H, 4 H, ³J_{HH} 8.8 Hz), 7.56 (d, Ar-H, 4 H, ³J_{HH} 9.2 Hz), 7.52 (d,
37
38 Ar-H, 4 H, ³J_{HH} 8.8 Hz). MS (FD): m/e calcd for C₂₈H₁₈N₄O₈ (M)⁺ 538, found 538.
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47 **Synthesis of di-*p*-nitrophenylurethane of 4, 4'-azodianiline (3c)**

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49 4-Nitrophenyl chloroformate (1.04 g, 5.13 mmol) was added to a solution of 4,4'-
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51 azodianiline (0.50 g, 2.36 mmol) in THF (30 ml). The reaction mixture was refluxed for
52
53 4 hours. The solvent was removed under reduced pressure and the residue was triturated
54
55 with acetonitrile (50 ml). The solid product was filtered off, washed with acetonitrile
56
57 and dried to give an orange powder. Yield: 1.08 g (84%). m.p. >220°C (decomp.); 581.3
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4 (M+K⁺); ¹H NMR (DMSO-d₆) 10.83 (s, N-H, 2 H), 8.33 (d, Ar-H, 4 H, ³J_{HH} 8.9 Hz),
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6 7.89 (d, Ar-H, 4 H, ³J_{HH} 8.5 Hz), 7.74 (d, Ar-H, 4 H, ³J_{HH} 8.9 Hz), 7.58 (d, Ar-H, 4 H,
7
8 ³J_{HH} 8.9 Hz). MS (FD): m/e calcd for C₂₆H₁₈N₆O₈ (M)⁺ 542, found 542.

15 Synthesis of 4a

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17 Di-*p*-nitrophenylurethane **3a** (0.076 g, 0.148 mmol) and a solution of N,N-
18 diisopropylethylamine (0.040 g, 0.310 mmol) in THF (5 ml) were added to a solution
19 tri-*N*-Boc monoamine **2** (0.30 g, 0.28 mmol) in THF (5 ml) and the reaction mixture
20 was stirred at rt for 24 hours. The solvent was removed under reduced pressure and the
21 oily residue was triturated with methanol. The solid product was filtered off and washed
22 with methanol to give the pure double calixarene as a white powder. Yield: 0.23 g
23 (69%). m.p. >260°C (decomp.); ¹H NMR (DMSO-d₆) 8.90 (s, N-H, 4 H), 8.60 (s, N-H,
24 2 H), 8.27 (s, N-H, 2 H), 8.08 (s, N-H, 2 H), 7.49 (d, Ar-H, 4 H, ³J_{HH} 8.8 Hz), 7.40 (d,
25 Ar-H, 4 H, ³J_{HH} 8.3 Hz), 6.96 (s, Ar-H, 8 H), 6.72-6.49 (m, Ar-H, 8 H), 4.31 (d, Ar-
26 CH₂-Ar, 4 H, ²J_{HH} 12.2 Hz), 4.30 (d, Ar-CH₂-Ar, 4 H, ²J_{HH} 12.2 Hz), 3.87 (t, -O-CH₂-, 8
27 H, ³J_{HH} 7.6 Hz), 3.78-3.64 (m, -O-CH₂-, 8 H), 3.05 (d, Ar-CH₂-Ar, 4 H, ²J_{HH} 13.2 Hz),
28 3.01 (d, Ar-CH₂-Ar, 4 H, ²J_{HH} 13.2 Hz), 1.98-1.78 (m, -O-CH₂-CH₂-, 16 H), 1.50-1.26
29 (m, -CH₂-, -CH₃, 86 H), 0.97-0.87 (m, -CH₃, 24 H). MS (ESI): m/e calcd for
30 C₁₄₀H₁₉₂N₁₀O₂₂ (M+Na)⁺ 2390, (M+2Na)²⁺ 1206, found 2390 74%; 1206 100%.

54 Synthesis of 4b

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56 Tri-*N*-Boc monoamine **2** (0.30 g, 0.28 mmol) and a solution of N,N-
57 diisopropylethylamine (0.06 g, 0.48 mmol) in THF (4 ml) were added to a solution of
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4 di-*p*-nitrophenylurethane **3b** (0.08 g, 0.15 mmol) in THF (2.5 ml). The reaction mixture
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6 was stirred at rt for 24 hours. Acetonitrile (20 ml) was added and the precipitate was
7
8 filtered off, washed with acetonitrile to give the pure double calixarene as a white
9
10 powder. Yield: 0.23 g (67%). m.p. >270°C (decomp.); ¹H NMR (DMSO-*d*₆) 8.88 (s, N-
11
12 *H*, 4 H), 8.68 (s, N-*H*, 2 H), 8.60 (s, N-*H*, 2 H), 8.30 (s, N-*H*, 2 H), 7.40 (d, Ar-*H*, 4 H,
13
14 ³*J*_{HH} 8.8 Hz), 7.37 (d, Ar-*H*, 4 H, ³*J*_{HH} 8.8 Hz), 7.07-6.80 (m, Ar-*H*, 8 H), 6.76-6.47 (m,
15
16 Ar-*H*, 8 H), 4.42-4.20 (m, Ar-*CH*₂-Ar, 8 H), 3.85 (br.t, -O-*CH*₂-, 8 H), 3.79-3.59 (m, -
17
18 O-*CH*₂-, 8 H), 3.12-2.91 (m, Ar-*CH*₂-Ar, 8 H), 2.00-1.76 (m, -O-*CH*₂-*CH*₂-, 16 H),
19
20 1.56-1.18 (m, -*CH*₂-, -*CH*₃, 86 H), 0.92 (t, -*CH*₃, 24 H, ³*J*_{HH} 6.6 Hz). MS (ESI): m/e
21
22 calcd for C₁₄₂H₁₉₂N₁₀O₂₂ (M+Na)⁺ 2414, (M+2Na)²⁺ 1218, found 2414 100%, 1218
23
24 46%.
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34 Synthesis of **4c**

35
36 Tri-*N*-Boc monoamine **2** (0.32 g, 0.30 mmol) and a solution of *N,N*-
37
38 diisopropylethylamine (0.062 g, 0.479 mmol) in THF (5 ml) were added to a suspension
39
40 of di-*p*-nitrophenylurethane **3c** (0.09 g, 0.16 mmol) in THF (5 ml) and the reaction
41
42 mixture was stirred at rt for 24 hours. Then acetonitrile (30 ml) was added to the
43
44 reaction mixture. The precipitate was filtered off, washed with acetonitrile to give
45
46 analytically pure double calixarene as a white powder. Yield: 0.31 g (86%). m.p.
47
48 >290°C (decomp.); ¹H NMR (DMSO-*d*₆, 75°C) 8.55 (s, N-*H*, 4 H), 8.44 (s, N-*H*, 2 H),
49
50 8.18 (s, N-*H*, 2 H), 8.01 (s, N-*H*, 2 H), 7.75 (d, Ar-*H*, 4 H, ³*J*_{HH} 8.8 Hz), 7.55 (d, Ar-*H*,
51
52 4 H, ³*J*_{HH} 8.8 Hz), 7.00-6.89 (m, Ar-*H*, 8 H), 6.64-6.55 (m, Ar-*H*, 8 H), 4.42-4.29 (m,
53
54 Ar-*CH*₂-Ar, 8 H), 3.91 (t, -O-*CH*₂-, 8 H, ³*J*_{HH} 7.6 Hz), 3.84-3.72 (m, -O-*CH*₂-, 8 H),
55
56 3.12-2.97 (m under water peak, Ar-*CH*₂-Ar, 8 H), 1.95-1.80 (m, -O-*CH*₂-*CH*₂-, 16 H),
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4 1.52-1.28 (m, $-CH_2-$, $-CH_3$, 86 H), 1.00-0.87 (m, $-CH_3$, 24 H). MS (ESI): m/e calcd for
5
6 $C_{140}H_{192}N_{12}O_{22} (M+Na)^+$ 2418, $(M+2Na)^{2+}$ 1220, found 2418 100%, 1220 10%.
7
8
9

10 11 12 13 **Synthesis of 6**

14
15 A solution of *p*-tolylisocyanate (0.54 g, 4.05 mmol) in dichloromethane (100 ml) was
16
17 added dropwise to a vigorously stirred solution of tetraamino calix[4]arene **1** (1.00 g,
18
19 1.31 mmol) in dichloromethane (100 ml). After 24 h of stirring at rt, the solvent was
20
21 evaporated under reduced pressure. The residue was dissolved in dichloromethane and
22
23 tetra-urea product was precipitated by methanol. It was filtered off and isolated as a
24
25 white powder (0.52 g, 30%). The filtrate was evaporated and the residue was
26
27 reprecipitated from dichloromethane/hexane to give the desired product **6** as a white
28
29 powder. Yield: 0.78 g (51%). **6**: m.p.: >250°C (decomp.); 1H NMR (DMSO- d_6) 8.34-
30
31 8.06 (m, N-H, 6 H), 7.32-7.14 (m, Ar-H, 6 H), 7.10-6.94 (m, Ar-H, 6 H), 6.87-6.67 (m,
32
33 Ar-H, 6 H), 6.03 (s, Ar-H, 2 H), 5.16-4.42 (br.s, N-H $_2$, 2 H), 4.33 (d, Ar-CH $_2$ -Ar, 2 H,
34
35 $^2J_{HH}$ 12.5 Hz), 4.25 (d, Ar-CH $_2$ -Ar, 2 H, $^2J_{HH}$ 12.5 Hz), 3.90-3.63 (m, -O-CH $_2-$, 8 H),
36
37 3.09 (d, Ar-CH $_2$ -Ar, 2 H, $^2J_{HH}$ 12.8 Hz), 2.97 (d, Ar-CH $_2$ -Ar, 2 H, $^2J_{HH}$ 12.8 Hz), 2.22
38
39 (s, $-CH_3$, 9 H), 1.98-1.76 (m, -O-CH $_2$ -CH $_2-$, 8 H), 1.49-1.25 (m, $-CH_2-$, 16 H), 0.93 (br.t,
40
41 $-CH_3$, 12 H).
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52 53 54 **Synthesis of 7**

55 Tri-urea monoamine **6** (2.00 g, 1.91 mmol) was added to a stirred solution of 4-
56
57 nitrophenyl chloroformate (2.55 g, 12.6 mmol) in $CHCl_3$ (22 ml). The reaction mixture
58
59 was refluxed for 4 hours, the solvent was evaporated, and the residue was triturated with
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4 acetonitrile and stored in a refrigerator for 4-8 hours. The solid product was filtered off,
5
6 washed with acetonitrile and dried to give a light-yellow powder. Yield: 2.65 g (75%).
7
8 m.p. >200°C; ¹H NMR (DMSO-d₆) 9.95 (s, N-H, 1 H), 8.25 (s, N-H, 3 H), 7.21 (d, Ar-
9
10 H, 2 H, ³J_{HH} 8.8 Hz), 8.15 (s, N-H, 3 H), 7.37 (d, Ar-H, 2 H, ³J_{HH} 8.8 Hz), 7.30-7.18 (m,
11
12 Ar-H, 6 H), 7.16-6.97 (m, Ar-H, 6 H), 6.94 (s, Ar-H, 2 H), 6.81 (s, Ar-H, 4 H), 6.75 (s,
13
14 Ar-H, 2 H), 4.35 (d, Ar-CH₂-Ar, 2 H, ²J_{HH} 12.3 Hz), 4.33 (d, Ar-CH₂-Ar, 2 H, ²J_{HH} 12.6
15
16 Hz), 3.82-3.67 (m, -O-CH₂-, 8 H), 3.11 (d, Ar-CH₂-Ar, 4 H, ²J_{HH} 12.9 Hz), 2.21 (s, -
17
18 CH₃, 6 H), 2.20 (s, -CH₃, 3 H), 2.00-1.84 (m, -O-CH₂-CH₂-, 8 H), 1.49-1.30 (m, -CH₂-,
19
20 16 H), 0.93 (t, -CH₃, 12 H, ³J_{HH} 6.8 Hz).
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29 Synthesis of 5a

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32 **Procedure A:** Trifluoroacetic acid (2 ml) was added to a solution of hexa-*N*-Boc-
33
34 protected *bis*-calix[4]arene **4a** (97 mg, 0.0410 mmol) in dichloromethane (10 ml) and
35
36 the mixture was stirred at rt for 2 h. The solvent was evaporated, the residue was
37
38 dissolved in THF (5 ml) and treated with N,N-diisopropylethylamine (0.034 g, 0.265
39
40 mmol). After 15 min a precipitate appeared which slowly dissolved again after a
41
42 solution of *p*-tolylisocyanate (0.049 g, 0.367 mmol) in THF (5 ml) was added. The
43
44 solution was stirred at rt for 10-12 h under nitrogen. Half of the solvent was evaporated
45
46 under reduced pressure, and methanol (15 ml) was added to the residue to precipitate
47
48 the product. The solid product was filtered off, washed with methanol and dried to give
49
50 a light-beige powder. Yield: 85 mg (81%).
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56 **Procedure B:** Benzidine (8.0 mg, 0.0435 mmol) and N,N-diisopropylethylamine (17
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58 mg, 0.131 mmol) were added to a solution of the monourethane **7** (0.116 g, 0.0870
59
60

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 hours. Water (20 ml) was added and the formed precipitate was filtered off, 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.); ¹H NMR (DMSO-d₆, 50°C) 8.33 (s, N-H, 2 H), 8.21-8.01 (m, N-H, 14 H), 7.46 (d, Ar-H, 4 H, ³J_{HH} 8.3 Hz), 7.39 (d, Ar-H, 4 H, ³J_{HH} 8.8 Hz), 7.22 (d, Ar-H, 12 H, ³J_{HH} 8.3 Hz), 7.01 (d, Ar-H, 12 H, ³J_{HH} 7.8 Hz), 6.84 (s, Ar-H, 4 H), 6.82 (s, Ar-H, 8 H), 6.80 (s, Ar-H, 4 H), 4.36 (d, Ar-CH₂-Ar, 8 H, ²J_{HH} 12.7 Hz), 3.85 (m, -O-CH₂-, 16 H), 3.11 (d, Ar-CH₂-Ar, 8 H, ²J_{HH} 11.2 Hz), 2.21 (s, -CH₃, 18 H), 1.92 (m, -O-CH₂-CH₂-, 16 H), 1.41 (m, -CH₂-, 32 H), 0.95 (br.t, -CH₃, 24 H). MS (ESI): m/e calcd for C₁₅₈H₁₈₆N₁₆O₁₆ (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), 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*-nitrophenyl urethane 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.); ¹H NMR (DMSO-d₆, 65°C) 8.28 (s, N-H, 2 H), 8.07 (s, N-H, 2 H), 8.00 (s, N-H, 6 H), 7.97 (s, N-H, 6 H), 7.46 (d, Ar-H, 4 H, ³J_{HH} 8.5 Hz), 7.39 (d, Ar-H, 4 H, ³J_{HH} 8.2 Hz), 7.22 (d, Ar-H, 12 H, ³J_{HH} 8.5 Hz), 6.90-6.68 (m, Ar-H, 28 H), 4.37 (d, Ar-CH₂-Ar, 8 H, ²J_{HH} 12.0 Hz), 4.98-3.75 (m, -O-CH₂-, 28 H), 3.20 (d under the water peak, Ar-CH₂-Ar, 8 H), 1.92 (m, -O-CH₂-CH₂-, 16 H), 1.66 (m, -O-CH₂-CH₂-, 12 H), 1.50-1.14 (m, -CH₂-, 116 H), 0.95 (br.t, -CH₃, 24 H), 0.85 (br.t, -CH₃, 18 H). MS (ESI): m/e calcd for C₂₁₂H₂₉₄N₁₆O₂₂ (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), 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.); ¹H NMR (DMSO-d₆) 8.40 (s, N-H, 2 H), 8.11 (s, N-H, 2 H), 7.97 (s, N-H, 4 H), 7.82 (s, N-H, 2 H), 7.48 (d, Ar-H, 4 H, ³J_{HH} 8.4 Hz), 7.42 (d, Ar-H, 4 H, ³J_{HH} 8.4 Hz), 6.82 (s, Ar-H, 4 H), 6.79 (s, Ar-H, 4 H), 6.70 (s, Ar-H, 4 H), 6.61 (s, Ar-H, 4 H), 5.82 (br.t, N-H, 4 H, ³J_{HH} 4.8 Hz), 5.69 (br.t, N-H, 2 H, ³J_{HH} 5.3 Hz), 4.44 (m, Ar-CH₂-Ar, 8 H), 3.98-3.61 (m, -O-CH₂-, -NH-CH₂-, 28 H), 3.17-2.86 (m, Ar-CH₂-Ar, -NH-CH₂-CH₂-, 12 H), 2.05-1.70 (m, -O-CH₂-CH₂-, 16 H), 1.60-1.05 (m, -CH₂-, 68 H), 1.01-0.73 (m, -CH₃, 42 H). MS (ESI): m/e calcd for C₁₅₂H₂₂₂N₁₆O₁₆ (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), dichloromethane (10 mL) as described for **5a** (procedure A). After deprotection the salt was dissolved in THF (10 mL), 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.); ¹H NMR (DMSO-d₆, 50°C) 8.54 (s, N-H, 2 H), 8.28-8.02 (m, N-H, 14 H), 7.36 (s, Ar-H, 4 H), 7.28-7.12 (m, Ar-H, 16 H), 7.07-6.93 (m, Ar-H, 12 H), 6.88-6.68 (m, Ar-H, 20 H), 4.33 (d, Ar-CH₂-Ar, 8 H, ²J_{HH} 11.7 Hz), 3.97-3.67 (m, -O-CH₂-, 16 H), 3.10 (d, Ar-CH₂-Ar, 8 H, ²J_{HH} 11.4 Hz), 2.29-2.07 (m, -CH₃, 18 H), 2.01-1.76 (m, -O-CH₂-CH₂-, 16 H), 1.50-1.28 (m, -CH₂-, 32 H), 0.94 (br.t, -CH₃, 24 H). MS (ESI): m/e calcd for C₁₆₀H₁₈₆N₁₆O₁₆ (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), 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.); ¹H NMR (DMSO-d₆, 75°C) 8.54 (s, N-H, 2 H), 8.12 (s, N-H, 2 H), 8.08 (s, N-H, 4 H), 8.05 (s, N-H, 2 H), 8.02 (s, N-H, 4 H), 7.94 (s, N-H, 2 H), 7.73 (d, Ar-H, 4 H, ³J_{HH} 8.3 Hz), 7.51 (d, Ar-H, 4 H, ³J_{HH} 8.8 Hz), 7.28-7.15 (m, Ar-H, 12 H), 7.06-6.95 (m, Ar-H, 12 H), 6.87 (s, Ar-H,

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4 H), 6.85 (s, Ar-*H*, 4 H), 6.80 (s, Ar-*H*, 4 H), 6.77 (s, Ar-*H*, 4 H), 4.40 (d, Ar-*CH*₂-Ar,
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6
7 8 H, ²*J*_{HH} 12.2 Hz), 3.96-3.79 (m, -O-*CH*₂-, 16 H), 3.19-3.08 (m, Ar-*CH*₂-Ar, 8 H), 2.22
8
9 (s, -*CH*₃, 18 H), 1.92 (br.s, -O-*CH*₂-*CH*₂-, 16 H), 1.42 (br.s, -*CH*₂-, 32 H), 0.95 (br.s, -
10
11
12 *CH*₃, 24 H). MS (ESI): *m/e* calcd for C₁₅₈H₁₈₆N₁₈O₁₆ (M+2Na)²⁺ 1320, found 1320
13
14 100%.

15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60

Synthesis of 5f

Prepared from *bis*-calix[4]arene **4c** (50 mg, 0.021 mmol), trifluoroacetic acid (2 mL),
dichloromethane (10 mL) as described for **5a** (procedure A). After deprotection N,N-
diisopropylethylamine (108 mg, 0.834 mmol) and *p*-nitrophenyl urethane 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.); ¹H NMR (DMSO-*d*₆, 75°C) 8.55 (s, N-*H*, 2 H), 8.11 (s, N-*H*, 2 H),
7.99 (s, N-*H*, 4 H), 7.96 (s, N-*H*, 6 H), 7.90 (s, N-*H*, 2 H), 7.73 (d, Ar-*H*, 4 H, ³*J*_{HH} 8.7
Hz), 7.51 (d, Ar-*H*, 4 H, ³*J*_{HH} 9.1 Hz), 7.29-7.10 (m, Ar-*H*, 12 H), 6.94-6.63 (m, Ar-*H*,
28 H), 4.40 (d, Ar-*CH*₂-Ar, 4 H, ²*J*_{HH} 12.8 Hz), 4.38 (d, Ar-*CH*₂-Ar, 4 H, ²*J*_{HH} 12.8 Hz),
4.00-3.73 (m, -O-*CH*₂-, 28 H), 3.19-3.08 (m, Ar-*CH*₂-Ar, 8 H), 2.00-1.83 (m, -O-*CH*₂-
*CH*₂-, 16 H), 1.73-1.59 (m, -O-*CH*₂-*CH*₂-, 12 H), 1.52-1.14 (m, -*CH*₂-, 118 H), 0.95 (t, -
*CH*₃, 24 H, ³*J*_{HH} 6.4 Hz), 0.85 (t, -*CH*₃, 18 H, ³*J*_{HH} 6.8 Hz). MS (ESI): *m/e* calcd for
C₂₁₂H₂₉₄N₁₈O₂₂ (M+2Na)²⁺ 1746, found 1746 100%.

Atomic Force Microscopy

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4 Submonolayers of *bis*-calix[4]arene derivatives were prepared by spin coating. The *bis*-
5 calix[4]arenes were dissolved in either pure chloroform or a mixture of 95/5 vol%
6 chloroform/*p*-difluorobenzene resulting in a concentration between 10^{-2} ~ 10^{-4} mg ml⁻¹. A
7 droplet of 30 μ l was deposited on a freshly cleaved HOPG (highly oriented pyrolytic
8 graphite, purchased from Plano GmbH, Wetzlar, Germany) surface and the sample was
9 spun at 1000 rpm for 30 s. Samples were imaged at room temperature with a
10 commercial AFM (Nanoscope IIIa, Veeco Digital Instruments, Santa Barbara,
11 California) in tapping mode at 1 to 2 lines per second using rectangular silicon
12 cantilevers (Nanoworld NCH). To control and enhance the range of the attractive
13 interaction regime the instrument was equipped with a special active feedback circuit,
14 called Q-control (Nanoanalytics, Germany) as described previously [36]. The quality
15 factor Q of this oscillating system is increased by one order of magnitude. As a
16 consequence, the sensitivity and lateral resolution are enhanced, allowing us to prevent
17 the onset of intermittent repulsive contact and thereby to operate the SFM constantly in
18 the attractive interaction regime.
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46 acknowledged.
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53 *References*

- 54
55 [1] Hill, D.J.; Mio, M.J.; Prince, R.B.; Hughes, T.S.; Moore, J.S. *Chem. Rev.* **2001**, *101*,
56 3893.
57
58 [2] Licini, G.; Prins, L.J.; Scrimin, P. *Eur. J. Org. Chem.* **2005**, 969.
59
60

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2
3
4 [3] McKinlay, R.M.; Atwood, J.L. *Angew. Chem. Int. Ed.* **2007**, *46*, 2394.
5
6
7 [4] Cañas-Ventura, M.E.; Xiao, W.; Wasserfallen, D.; Müllen, K.; Brune, H.; Barth,
8
9 J.V.; Fasel, R. *Angew. Chem. Int. Ed.* **2007**, *46*, 1814.
10
11 [5] Zaworotko, M.J. *Cryst. Growth Des.* **2007**, *7*, 4.
12
13 [6] MacGillivray, L.R.; Atwood, J.L. *Nature* **1997**, *389*, 469.
14
15 [7] Shivanyuk, A.; Rebek, J., Jr. *Chem. Commun.* **2001**, 2374.
16
17 [8] Mateos-Timoneda, M.A.; Kerckhoffs, J.M.C.A.; Reinhoudt, D.N.; Crego-Calama,
18
19 M. *Org. Biomol. Chem.* **2007**, *5*, 447.
20
21 [9] Davis, J.T.; Spada, G.P. *Chem. Soc. Rev.* **2007**, *36*, 296.
22
23 [10] Vickers, M.S.; Beer, P.D. *Chem. Soc. Rev.* **2007**, *36*, 211.
24
25 [11] Shimizu, K.D.; Rebek, J., Jr. *Proc. Natl. Acad. Sci. U. S. A.* **1995**, *92*, 12403.
26
27 [12] Hamann, B.C.; Shimizu, K.D.; Rebek, J., Jr. *Angew. Chem. Int. Ed.* **1996**, *35*, 1326.
28
29 [13] Castellano, R.K.; Kim, B.H.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1997**, *119*, 12671.
30
31 [14] Mogck, O.; Böhmer, V.; Vogt, W. *Tetrahedron* **1996**, *52*, 8489.
32
33 [15] Mogck, O.; Paulus, E. F.; Böhmer, V.; Thondorf, I.; Vogt, W. *Chem. Commun.*
34
35 **1996**, 2533.
36
37 [16] Mogck, O.; Pons, M.; Böhmer, V.; Vogt, W. *J. Am. Chem. Soc.* **1997**, *119*, 5706.
38
39 [17] Vysotsky, M.O.; Pop, A.; Broda, F.; Thondorf, I.; Böhmer, V. *Chem. Eur. J.* **2001**,
40
41 7, 4403.
42
43 [18] Frish, L.; Vysotsky, M.O.; Böhmer, V.; Cohen, Y. *Org. Biomol. Chem.* **2003**, *1*,
44
45 2011.
46
47 [19] Schalley, C.A.; Castellano, R.K.; Brody, M.S.; Rudkevich, D.M.; Siuzdak, G.;
48
49 Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 4568.
50
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52
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54
55
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57
58
59
60

- 1
2
3
4 [20] Thondorf, I.; Broda, F.; Rissanen, K.; Vysotsky, M.O.; Böhmer, V. *J. Chem. Soc.,*
5
6 *Perkin Trans. 2* **2002**, 1796.
7
8
9 [21] Molokanova, O.; Bogdan, A.; Vysotsky, M.O.; Bolte, M.; Ikai, T.; Okamoto, Y.;
10
11 Böhmer, V. *Chem. Eur. J.* **2007**, *13*, 6157.
12
13
14 [22] Wang, L.; Vysotsky, M.O.; Bogdan, A.; Bolte, M.; Böhmer, V. *Science* **2004**, *304*,
15
16 1312.
17
18 [23] Bogdan, A.; Rudzevich, Y.; Vysotsky, M. O.; Böhmer, V. *Chem. Commun.* **2006**,
19
20 2941.
21
22
23 [24] Rudzevich, Y.; Rudzevich, V.; Moon, C.; Schnell, I.; Fischer, K.; Böhmer, V. *J.*
24
25 *Am. Chem. Soc.* **2005**, *127*, 14168.
26
27
28 [25] Xu, S.; Podoprygorina, G.; Böhmer, V.; Ding, Z.; Rooney, D.; Rangan, C.; Mittler,
29
30 *S. Org. Biomol. Chem.* **2007**, *5*, 558.
31
32
33 [26] Castellano, R.K.; Rudkevich, D.M.; Rebek, J., Jr. *Proc. Nat. Acad. Sci. U. S. A.*
34
35 **1997**, *94*, 7132.
36
37 [27] Castellano, R.K.; Rebek, J., Jr., *J. Am. Chem. Soc.* **1998**, *120*, 3657.
38
39 [28] Castellano, R.K.; Clark, R.; Craig, S.L.; Nuckolls, C.; Rebek, J., Jr. *Proc. Nat.*
40
41 *Acad. Sci. U. S. A.* **2000**, *97*, 12418.
42
43
44 [29] Xu, H.; Stampf, S.P.; Rudkevich, D.M. *Org. Lett.* **2003**, *5*, 4583.
45
46 [30] Xu, H.; Hampe, E.M.; Rudkevich, D.M. *Chem. Commun.* **2003**, 2828.
47
48 [31] Brody, M.S.; Schalley, C.A.; Rudkevich, D.M.; Rebek, J., Jr. *Angew. Chem., Int.*
49
50 *Ed. Engl.* **1999**, *38*, 1640.
51
52
53 [32] Jakobi, R. A.; Böhmer, V.; Grüttner, C.; Kraft, D.; Vogt, W. *New J. Chem.* **1996**,
54
55 *20*, 493.
56
57 [33] Saadioui, M.; Shivanyuk, A.; Böhmer, V.; Vogt, W. *J. Org. Chem.* **1999**, *64*, 3774.
58
59
60

[34] Shivanyuk, A.; Saadioui, M.; Broda, F.; Thondorf, I.; Vysotsky, M.O.; Rissanen, K.; Kolehmainen, E.; Böhmer, V. *Chem. Eur. J.* **2004**, *10*, 2138.

[35] Deeming, A.J.; Hogarth, G.; Lee, M.; Saha, M.; Redmond, S.P.; Phetmung, H.; Orpen, A.G. *Inorg. Chim. Acta* **2000**, *309*, 109.

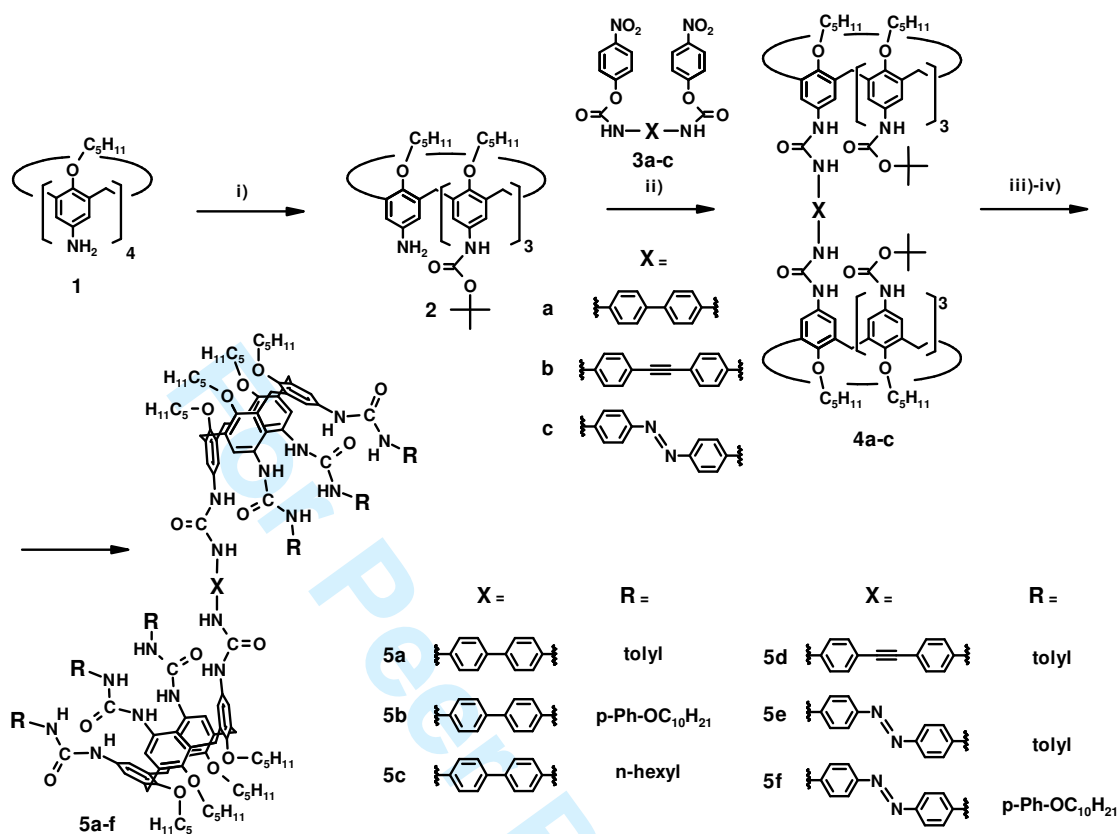
[36] Anczykowski, B.; Cleveland, J.P.; Krüger, D.; Elings, V.; Fuchs, H. *Appl. Phys. A*, **1998**, *66*, S885.

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

Component 1	Component 2	Solvent	Temperature	Observations
5a	-	CDCl ₃	rt	polymerization
5a	-	C ₆ D ₆	75°C	polymerization
5a	8	CDCl ₃	rt	<i>bis</i> -heterodimer
5b	-	CDCl ₃ C ₆ D ₆	rt	polymerization
5b	8	CDCl ₃	rt	<i>bis</i> -heterodimer
5c	-	CDCl ₃ TCE, C ₆ D ₆	rt, 55°C	insoluble
5c	-	TCE	75°C	insoluble
5d	-	CDCl ₃	rt	polymerization

5e	-	CDCl ₃	rt, 55°C	polymerization
5e	8	CDCl ₃	rt	<i>bis</i> -heterodimer
5e	-	TCE	75°C	polymerization
5f	-	CDCl ₃	rt	polymerization

SCHEME 1



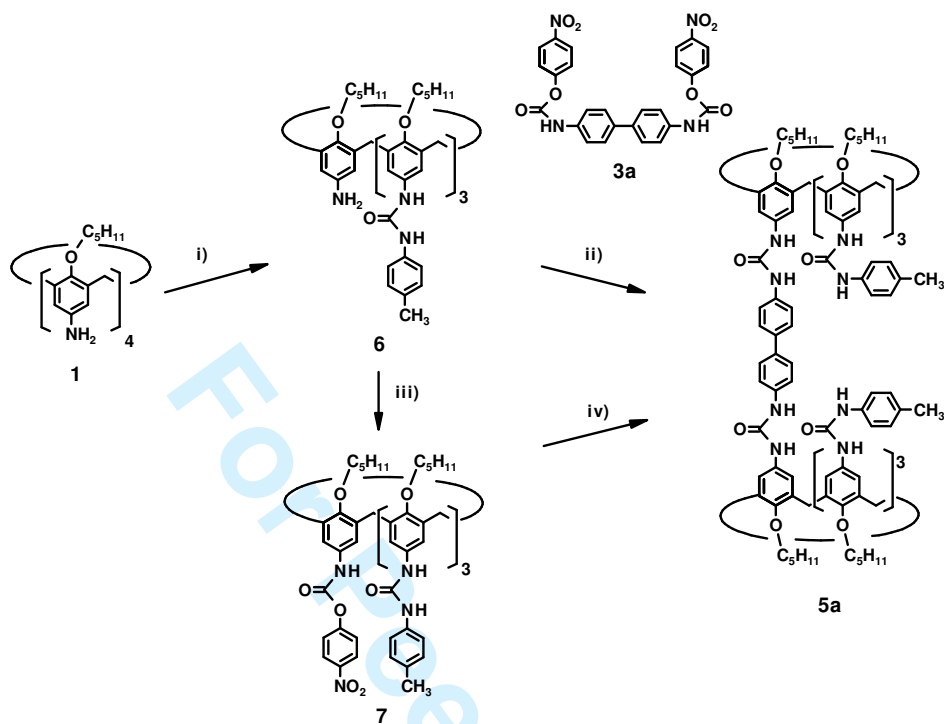


FIGURE 1

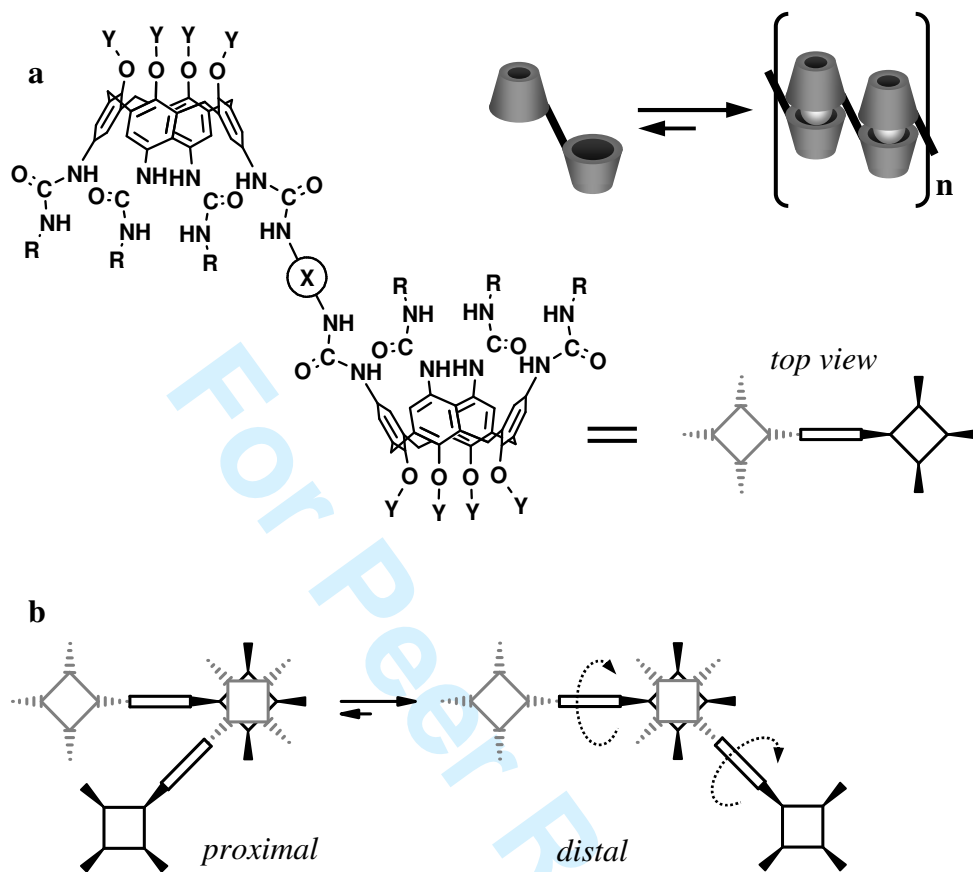


FIGURE 2

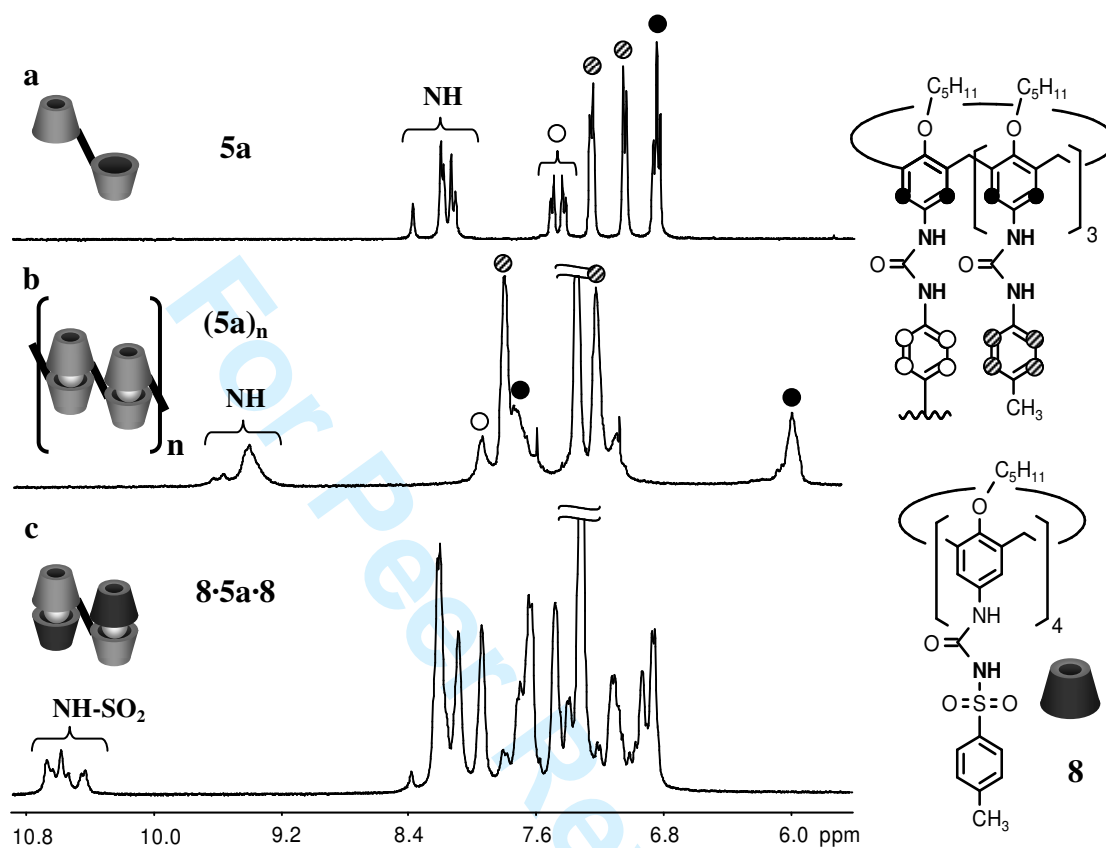


FIGURE 3

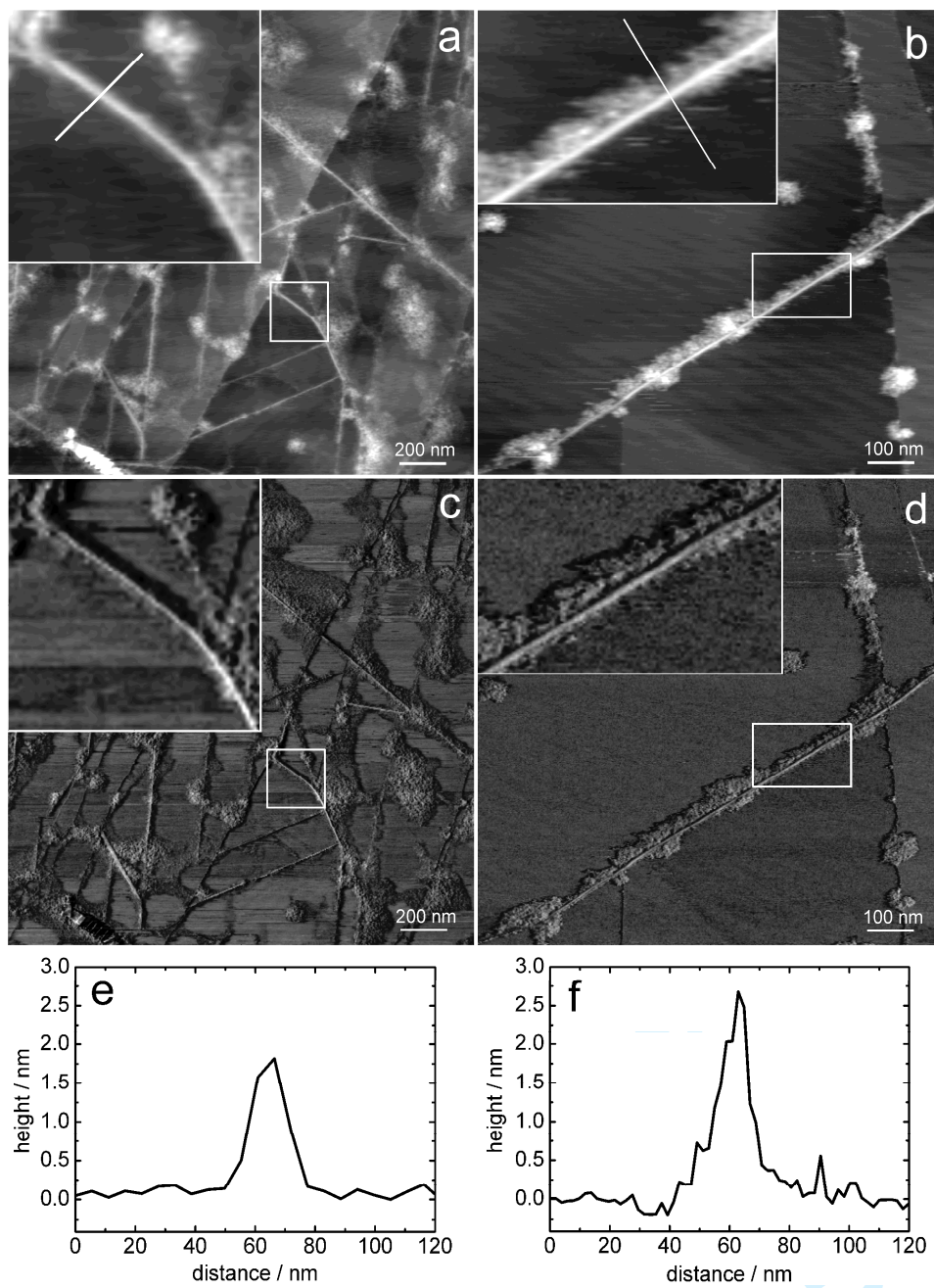
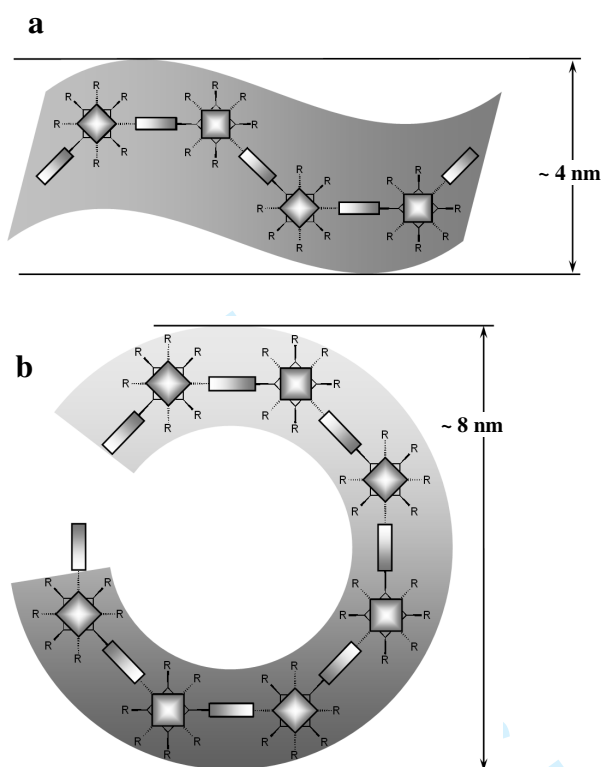


FIGURE 4



List of scheme captions

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4 SCHEME 1 Pathways to *bis*(tetra-urea calix[4]arenes). i) Boc₂O, CH₂Cl₂; ii) *i*-Pr₂EtN,
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6 DMF or THF; iii) CF₃COOH, CH₂Cl₂; iv) *i*-Pr₂EtN, **R**-NCO or **R**-NH(CO)-*p*-O-C₆H₄-
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8 NO₂, THF.
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10 SCHEME 2 An alternative approach to *bis*(tetra-urea calix[4]arenes) attempted for **5a**.
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12 i) *p*-tolylisocyanate, CH₂Cl₂; ii) Et₃N, DMF; iii) *p*-nitrophenol chloroformate, CHCl₃;
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16 iv) benzidine, *i*-Pr₂EtN, DMF.
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22 List of figure captions

23
24 FIGURE 1 Schematic representation of the dimerisation of *bis*-tetra-urea calix[4]arenes.
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27 FIGURE 2 ¹H NMR spectra of *bis*-calixarene **5a**. a) **5a** in DMSO-d₆, 50°C; b) **5a** in
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29 CDCl₃, rt; c) **5a** and tetra-tosylurea calix[4]arene **8** in the ratio 1 : 2; CDCl₃, rt (*bis*-
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31 heterodimer **8•5a•8**).
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34 FIGURE 3 AFM height (a,b) and phase images (c,d) of the *bis*-calixarene **4b** on HOPG
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36 prepared by spin-coating of solutions C = 0.01 mg/ml. (a) CHCl₃; (b) CHCl₃ + 5% *p*-
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38 difluorobenzene; (c) CHCl₃; (d) CHCl₃ + 5% *p*-difluorobenzene; (e) cross section along
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40 the line shown in (a); (f) cross section along the line shown in (b).
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44 FIGURE 4 Idealized representation of a polymeric assembly in a “stretched” (a) or
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46 “helical” (b) arrangement.
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