Tetraurea calix[4]arenes with sulfur functions: synthesis, dimerization to capsules, and self-assembly on gold

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Various calix[4]arene derivatives, fixed in the cone conformation by decylether groups and functionalized at their wide rim by urea residues, were synthesized. In two compounds (**4f**,**g**) sulfur functions were attached to the urea groups *via* different spacers in order to allow binding to metal surfaces. While they exist as single molecules in polar solvents, tetraurea calix[4]arenes of this type (**4**) combine to form dimeric capsules in aprotic, apolar solvents. A solvent molecule is usually included in such a capsule, if no guest with a higher affinity is present. In the presence of an equimolar amount of the tetratosylurea **5**, the exclusive formation of heterodimers, consisting of one molecule of **4** and **5**, is observed. The homo- and heterodimerization of the newly prepared derivatives **4f**,**g** were studied by ^{1}H NMR to establish the conditions under which they exhibit the desired dimerization behaviour. Self-assembled monolayers (SAMs) were formed using the single calix[4]arenes **4f**,**g** and the heterodimeric capsules **4g**·**5**. Chloroform, dichloromethane and ferrocenium cations were used as guests in these immobilized heterodimeric capsules. The particular supramolecular architecture of the heterodimers should ensure that, after the immobilization on the metal surface, decomposition of the capsules and release or exchange of the guest is impossible or at least hindered. The self-assembly process and the stability of SAMs formed by capsules filled with ferrocenium cations in electrolyte solutions were tested with surface plasmon spectroscopy. The inclusion of guests, such as dichloromethane or ferrocenium, in the immobilized capsules were confirmed by classical surface plasmon spectroscopy, by gold nanoparticle absorption spectroscopy and by time-of flight secondary ion mass spectrometry (ToF-SIMS). The film stability and quality was tested by cyclic voltammetry.

Introduction

Molecular guest–host systems have attracted enormous interest in recent years.[1–6] Inclusion of a guest without covalent binding into a host material can serve many purposes, such as solubility enhancement, protection against degradation by light or oxygen, separation by chromatography[2] or simply removing undesired substances from a mixture, and is widely used in industrial products. Typically, most guest–host systems consist of an open cavity (the host) which allows molecules (the guest) to adsorb and bind and to desorb again according to chemical equilibrium. This equilibrium depends on the accessibility of the cavity, the concentration of the guest and the host and their affinity for each other.[7–10]

However, a "guest" molecule may also be more or less permanently included in cage-type molecules of the carcerand or hemicarcerand type,[11,12] or reversibly encapsulated in hollow assemblies held together by electrostatic forces,[13] by metal coordination[14] or by hydrogen bonding.[15] In so far as hydrogen bonding is concerned, dimeric capsules from calix[4]arenes (substituted at their wide rim by four (aryl) urea groups) have been extensively studied[16] in solution[17] and characterized by several single crystal X-ray structures.[18] If such a tetraurea is decorated by suitable sulfur functions, the formation of SAMs on gold should be possible. In addition, the attachment to the gold surface may lead to the permanent inclusion of a guest molecule; similar to carcerands.

Self-assembled monolayers (SAMs) are ordered molecular assemblies spontaneously formed by the adsorption of an active surfactant on a solid surface. In particular, the self-assembly of organosulfur adsorbates on gold has attracted considerable attention in recent decade(s).[19] The high specificity of the sulfur–gold interaction (which is strong but reversible) allows for the introduction of various functional groups into such monolayers without interfering with the adsorption process. The number of surface active organosulfur compounds that form monolayers has increased in recent years. These include dialkyl sulfides[20] and disulfides,[21] mercaptans,[22] thiophenols,[23] and various mercapto-substituted aromatic compounds,[23,24] to mention just a few examples.

Dialkyl sulfide groups were attached to calix[4]arenes,[25] to resorcarenes[26] and to resorcarene-derived cavitands[26] in order to obtain the respective SAMs on gold. Similar monolayers were

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obtained from carceplexes[27] and hemicarceplexes,[28] The attachment of a thioether residue to one of the melamine residues of a bis-melamine-substituted calix[4]arene made the construction of hydrogen-bonded "double rosettes" in self-assembled monolayers on the gold surface possible.[29]

As illustrated in Fig. 1, the attachment of sulfur functions to the ether residues should allow for a more or less unhindered decomposition of the capsules from the monolayer, leading to a loss or exchange of guests. Attachment of the sulfur functions to the urea residues, however, suggests the possibility that such immobilized capsules cannot fall apart, even if the hydrogen bonds are broken. The interdigitating urea residues in the dimer should prevent its disentanglement and keep the guest molecules bound to the surface, even when equilibrium conditions and osmotic pressure dictate a release.

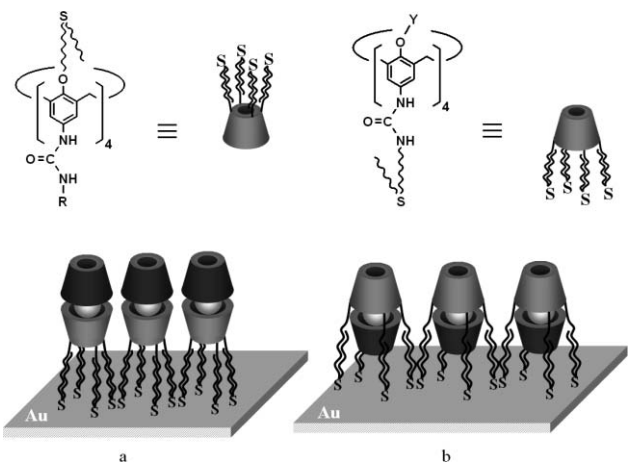


Fig. 1 Schematic representation of SAMs formed by hydrogen-bonded heterodimers. a) Attachment of sulfur functions to the ether residues of the narrow rim; b) attachment of sulfur functions to the urea residues at the wide rim.

Thus, we envisaged tetraaryl urea derivatives substituted by sulfur functions in the urea residues as target. If their heterodimers with a suitable partner, *e.g.* with a tetratosylurea calix[4]arene, would form SAMs on gold, it should be possible that an included guest can be permanently trapped. In the following report we describe the synthesis of these target compounds and the study of the self-assembly of their monomers or heterodimers on gold surfaces. We finally try to give a first answer to the question of whether or not the attachment to the surface makes dissociation of the capsules, and hence the release of the included guest, impossible.

Results and discussion

A. Syntheses

There are various methods for introducing sulfur-containing residues into a molecule and, as a result, enabling its self-assembly on gold surfaces. Lipoic acid, for instance, is frequently used, since it is commercially available and can be easily bound/attached to amino groups *via* amide linkages.[30] Thioether groups offer another possibility and have been applied to the functionalization of calixarenes,[25] resorcarenes[26] and cavitands[26] or carcerands[27,28] derived from them.

The synthesis of such tetraurea calix[4]arenes with sulfur functions is summarized in Scheme 1. To attach the four urea groups, the tetraamino calix[4]arene **1** was converted to an active urethane **2** by acylation with *p*-nitrophenyl chloroformate (81%), which was subsequently treated with the anilines **3a–c** (75–90%). The precursors **4a–c** were thus available in yields between 60–70%. While **3a** is commercially available, **3b** was prepared in four steps by *O*-alkylation of *p*-nitrophenol with *N*-(δ-bromobutyl)phthalimide, followed by hydrazinolysis, acylation with Boc-anhydride, and hydrogenation of the nitro group (overall ~50%). [This exchange of the protective group (phthalimido against Boc) was necessary, since a tetraurea obtained analogously with phthalimido groups could not be deprotected by hydrazine, leaving the urea functions intact.] To obtain **3c**, *p*-hydroxyacetanilide was *O*-alkylated with 11-bromoundecene followed by alkaline hydrolysis (overall ~80%), since the selective hydrogenation of a nitro group is not possible in this case.

Scheme 1 also indicates the further modification of **4a–c**. After the usual deprotection (cleavage of the Boc group) acylation with α-lipoic acid anhydride gave **4d** and **4f**, while **4e** was prepared for comparison with acetic acid anhydride. Addition of decylmercaptan in the presence of 9-borabicyclo[3.3.1]nonane converted **4c** into **4g** in 60% yield.

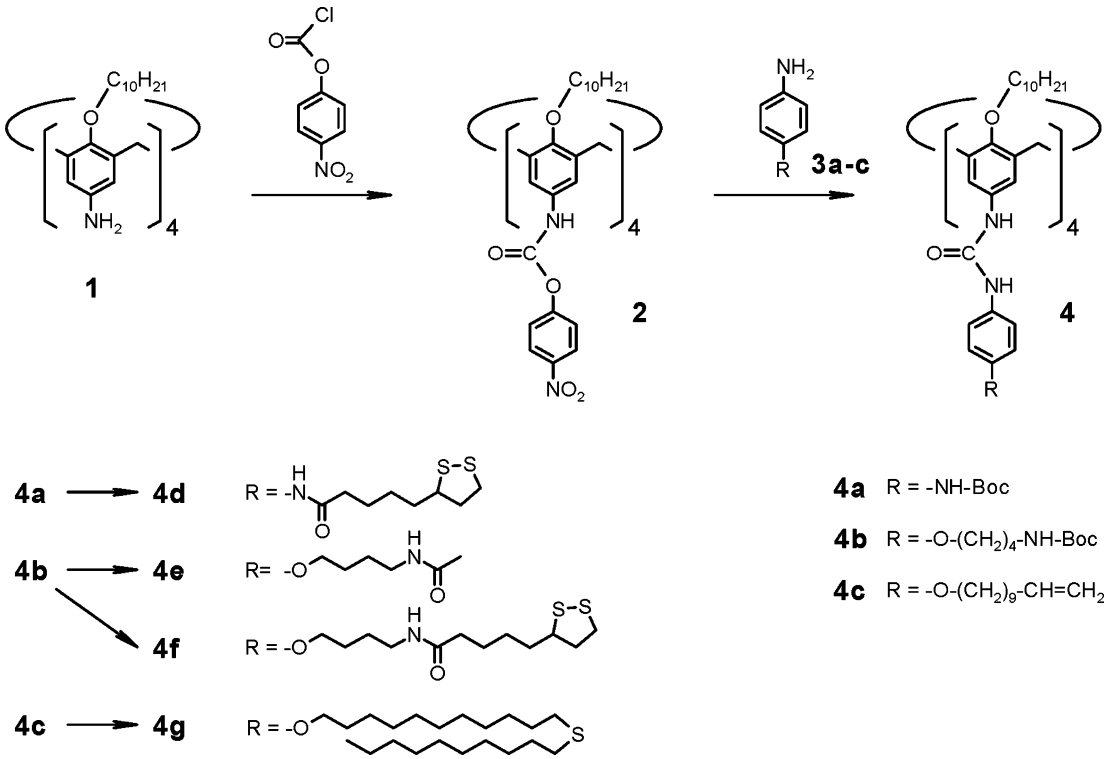
All tetraurea derivatives **4** were chromatographically pure (TLC). They were characterized mainly by their ^{1}H NMR spectra, which confirmed their C_{4v}-symmetrical structure in hydrogen-bond-breaking solvents, while their dimerization in apolar solvents led to more complicated spectra reflecting an S_8-symmetry for homodimers and a C_4-symmetry for heterodimers. In all relevant cases the molecular mass was confirmed by ESI-MS or FD-MS.

B. Dimerization studies

The dimerization of tetratolylurea (**4**, R = CH_3) with the inclusion of cobaltocenium as guest was shown using dichloroethane as a solvent.[31] However, this is not suitable for the intended electrochemical studies. Thus, conditions under which dimeric capsules with cobaltocenium as a guest are quantitatively formed within reasonable times had to first be established. For tetratolylurea, this has been shown in CD_2Cl_2, where the signals for homo- or heterodimers (**5** and **6**, respectively)[32] are seen in the NMR spectra recorded immediately after the dissolution of a stoichiometric mixture.[33] On the other hand, $CDCl_3$, a better guest itself, shows slower kinetics, and after 20 h an equilibrium mixture exists where approximately 15% of the capsules contain $CDCl_3$.

Among the compounds with sulfur functions foreseen for the formation of SAMs, **4d** was practically insoluble in all relevant solvents (CD_2Cl_2, $CDCl_3$, C_6D_6) at room temperature. In 1,1,2,2-tetrachloroethane (TCE) at 75 °C, the monomer can be seen in addition to irregular aggregates, while with the tetraloop compound **6** heterodimers are predominantly formed.

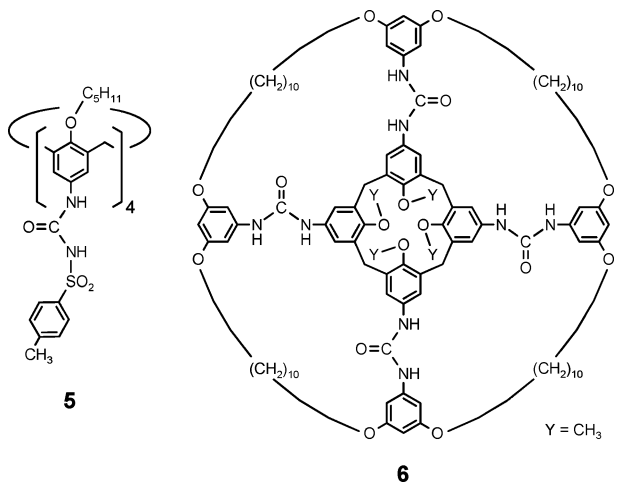
Compounds **4f** and **4e** (as a simpler model) have only slightly improved solubility, and conditions for the (exclusive) formation of the desired dimers were not found. Heterodimers of **4f** with **5** or **6** in different solvents and homodimers with cobaltocenium as a guest in CD_2Cl_2 were accompanied by irregular aggregates. Interestingly, in TCE, homodimers of **4f** are in equilibrium with the



Scheme 1 Syntheses of tetraurea calix[4]arenes bearing sulfur functions.

monomeric species at higher temperatures (75–100 °C) and with less defined species/aggregates at room temperature. It seems that the additional amide functions in **4f** are detrimental to controlled dimerization (although amide functions as such did not prevent the dimerization), as shown, for instance, by the formation of "polycaps".[34,35] The difference may be due to the fact that the amide-containing residues are bound to the urea functions (at the wide rim) in **4f**, which are essential for the dimerization, and not to the phenolic oxygens at the narrow rim.

Tetraurea **4g** not only forms homodimers, but also heterodimers with **5** or **6** (Scheme 2) in $CDCl_3$ or C_6D_6. In CD_2Cl_2, the inclusion of cobaltocenium occurs rapidly, and heterodimers with **5** or **6** and cobaltocenium cations as guests are exclusively formed in stoichiometric mixtures. Thus, given these observations, **4g** seems to be the most appropriate derivative to form SAMs of heterodimeric capsules on a gold surface.



Scheme 2 Chemical structure of compounds **5** and **6**.

In general, these results demonstrate that, except under limited conditions, the selective formation of dimeric capsules from tetraurea calix[4]arenes containing additional functional groups and the desired guest may be a demanding problem. However, as also shown, this problem can be solved using a wide variety of structural modifications.

C. SAMs: formation and properties

The SAMs were usually formed from 10 μM solutions of the calixarenes **4g** or **4f** or of their stoichiometric mixture with **5**. THF was used as a solvent for SAMs of a single calixarene (**4g** or **4f**), and chloroform (or dichloromethane) for heterodimeric capsules containing the solvent as guest. SAMs of capsules including ferrocenium as a guest were formed from dichloromethane. Here the concentration of both calixarenes (*e.g.* **4g** and **5**) was increased to 0.1 mM, and a 20% excess of the ferrocenium salt was added ($c = 0.12$ M) in order to shift the equilibrium from solvent-filled to ferrocenium-filled capsules. Since the gold substrate was immersed in the pre-fabricated solution, we assume that the capsules are formed in solution and that the SAMs are formed from completely filled capsules.

The SAM formation was investigated by surface plasmon resonance (SPR) spectroscopy, by monitoring the shift of the surface plasmon resonance while forming the SAM. Details are reported elsewhere.[7–9,36] From these plasmon resonance angle shifts, the thickness and the refractive index of the various SAMs on the gold surface were simulated.[7–9,36,37] The SPR results for

Table 1 Data analysis of SPR experiments for SAMs of **4g**, **4f**, capsule **4g·5** and capsule **4f·5**, filled with solvent or ferrocenium from the resonance angle shift $\Delta\theta$; n is the refractive index and ε is the dielectric constant at 632.8 nm wavelength

SAM	Thickness of SAM/Å	ε (SAM)	n (SAM)	n (solvent)
4g (in THF)	46.5	2.03	1.425	1.407
4f (in THF)	48	2.14	1.463	1.407
Capsule **4g·5** (in $CHCl_3$)	48	2.14	1.463	1.446
Capsule **4f·5** (in $CHCl_3$)	54	2.27	1.507	1.446
Capsule **4g·5** (in CH_2Cl_2)	50	2.19	1.480	1.424
Capsule **4g·5** + ferrocenium (in CH_2Cl_2) assembled in a 0.1 mM solution	50	2.15	1.466	1.424
Capsule **4g·5** + ferrocenium (in CH_2Cl_2) assembled in a 1 mM solution	50	2.162	1.47	1.424

SAMs of **4g**, **4f**, and the capsules **4g·5** and **4f·5** filled with chloroform, dichloromethane and ferrocenium are summarized in Table 1.

The theoretical sizes of the molecules bound to the gold and the maximum thickness of the SAMs were calculated using an idealized model. The estimated size/thickness of both **4g** and the capsule **4g·5** is 52 Å, since the urea groups of **4g** and **5** interdigitate when the capsule is formed and the back-folded alkyl chains of the dialkyl sulfide groups in **5** do not contribute to the size of the capsule. However, they increase the overall density of the film and, hence, the refractive index. Thus, we expect a slightly higher refractive index for the capsules in comparison to SAMs of pure **4g** or **4f**.

Both capsules (**4g·5**, **4f·5**) are filled with solvent when they are in solution. Therefore, the refractive index of the SAMs made up of capsules must depend on the refractive index of the guest solvent. Single molecules **4g** and **4f** are not necessarily filled with a solvent molecule, since they probably assume a "pinched cone" conformation.

SAMs of **4g** or **4f** obtained in THF, the solvent with the lowest refractive index used ($n = 1.407$), show a refractive index of 1.425 with a thickness of 46.5 Å, or 1.463 with a thickness of 48 Å, respectively. The higher refractive index for the **4f** SAM is due to a higher density because of the back-folding alkyl chains.[38] SAMs of the capsules **4g·5** and **4f·5**, which cannot be formed in the hydrogen-bond-breaking THF, but can be in $CHCl_3$,[39] show a thickness of 48 Å and 54 Å, respectively. The increase in refractive index to 1.463 and 1.507 can be attributed to the inclusion of a $CHCl_3$ guest molecule ($n = 1.446$) and to the above mentioned interdigitation.

Surprisingly, the refractive index of SAMs of capsules **4g·5** filled with dichloromethane increased in comparison to chloroform-filled SAMs of **4g·5**, although dichloromethane has a smaller refractive index ($n = 1.424$). They also have a slightly larger film thickness of 50 Å. It has been shown recently[40] that heterodimers of tetraaryl/tetratosylurea calix[4]arenes may contain two guest dichloromethane molecules. Aside from the better packing in the SAMs assembled from dichloromethane, it might also be possible that two dichloromethane molecules are encapsulated in **4g·5**. Both effects should yield a higher film density, and therefore an increased refractive index relative to the chloroform-filled film.

Although the proper formation of SAMs of **4f** and **4f·5** seems to be possible (despite the fact that **4f·5** is in equilibrium with its monomers), we decided to concentrate our further studies on capsule **4g·5**.

Filling the capsule **4g·5** with ferrocenium in dichloromethane does not change the thickness of its SAM but decreases its refractive index slightly to 1.466. It is known that tetraurea calix[4]arene dimers formed in a ferrocenium solution contain one ferrocenium cation as a guest, while ferrocene itself is not included.[31] The ferrocenium ion exhibits cation–π interactions with the aromatic groups of the cavity, which compensates for the weakened hydrogen bonding caused by the large guest molecule. This cation–π stabilization is missing in the case of the neutral molecule ferrocene.

In the case of the ferrocenium-filled capsule **4g·5**, if SAMs were formed at an elevated concentration of 1 mM, the film thickness remained unchanged at 50 Å; however, a minor increase in refractive index could be observed. This is attributed to a slightly more densely packed film due to an enhanced amount of available material.

In order to confirm the difference in the SAMs made of capsules containing dichloromethane or ferrocenium, which should have a higher refractive index than dichloromethane[41,42] as a guest, we did UV-Vis absorption spectroscopy on gold nanoparticles, both uncapped and capped with the SAMs under consideration. The position of the plasmon band of a SAM-capped nanoparticle yields information about the dielectric constant of the capping material. Fig. 2 shows a discrete dipole approximation (DDA)[43] calculation for hemispherical gold nanoparticles with a radius of 7 nm and a cap of 7 nm of *e.g.* an organic material, in an aqueous environment. The refractive index of the cap is systematically varied from $n = 1.33$, the blank particle in water, to $n = 3.33$. It can clearly be seen that the plasmon band absorption maximum shifts to higher wavelengths with the increasing refractive index of the capping material. The double peak structure appearing first at a refractive index of $n = 2$ is due to the dipolar and quadrupolar contributions of the plasmon band, which start to be separated spectrally under these conditions.[44]

We prepared simple gold nanoparticle samples by sputtering gold onto a microscope glass slide with a mean gold film thickness of 15 nm. These samples were used to prepare SAMs of a dichloromethane- and a ferrocenium-filled capsule **4g·5**. Their absorption spectra in air are shown in Fig. 3 along with a blank gold nanoparticle sample. A plasmon band around 545 nm can clearly been seen for the blank gold nanoparticles. The SAM of the ferrocenium-filled capsule **4g·5** shows a plasmon resonance at around 560 nm, whereas that of the dichloromethane-filled capsule **4g·5** has a plasmon band maximum at the longer wavelength of 570 nm. Again we find that the SAM of ferrocenium-filled capsules shows a smaller dielectric constant than that of the dichloromethane-filled one. Assuming the capsule itself does not change when assembled in dichloromethane, and that one ferrocenium is located in the capsule **4g·5**, two dichloromethane molecules

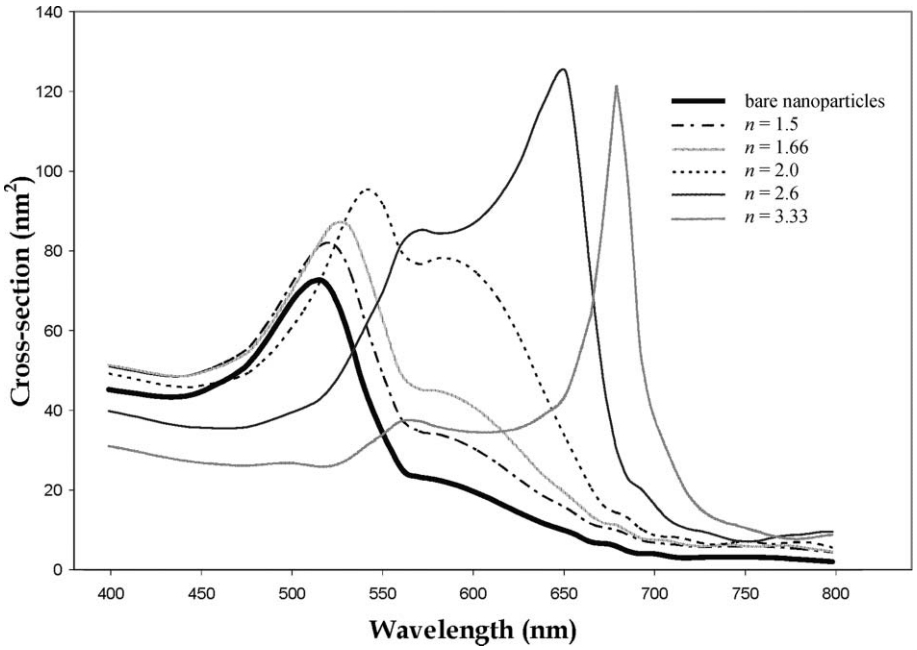


Fig. 2 DDA calculation of hemispherical gold nanoparticles (radius = 7 nm, cap = 7 nm) for capping materials with different refractive indices.

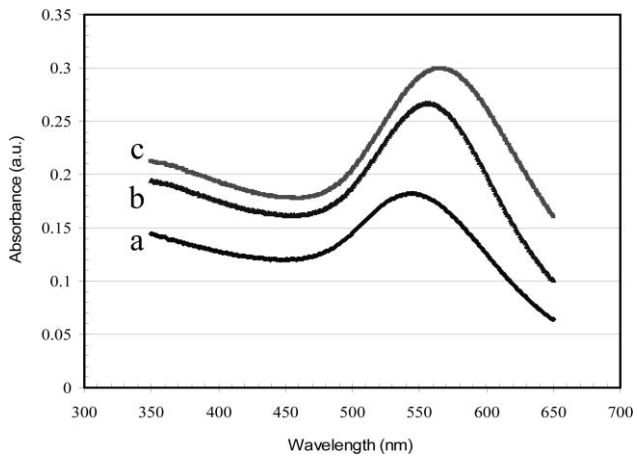


Fig. 3 UV-Vis spectra of SAMs of (a) pure gold; (b) **4g**·**5** filled with ferrocenium on gold nanoparticles, and (c) **4g**·**5** filled with dichloromethane on gold nanoparticles.

should be encapsulated in the case of the pure dichloromethane assembly.

D. ToF-SIMS investigations: is ferrocenium present in the SAMs?

Both sets of surface plasmon data only indirectly confirm the presence of the ferrocenium in the capsules. Therefore, in a second, direct approach with ToF-SIMS, the presence of the ferrocenium was studied by examining the iron signal of the ferrocenium. Fig. 4 depicts two ToF-SIMS spectra of SAMs of capsule **4g**·**5** assembled with ferrocenium at two capsule concentrations: 0.1 mM and 1 mM. Both spectra clearly show the most dominant Fe isotope (91.720%) with a peak at $m/z = 55.935$ u for SAMs of capsule **4g**·**5** assembled with ferrocenium. No mass peak of iron is obtained in ToF-SIMS spectra for SAMs formed with CH_2Cl_2 as guests, in the

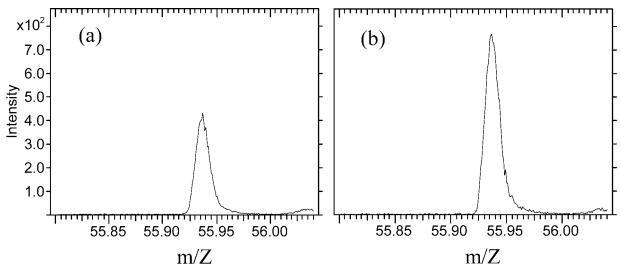


Fig. 4 ToF-SIMS spectra of SAMs of ferrocenium-filled capsules of **4g**·**5** on gold, formed from (a) a 0.1 mM solution; (b) a 1 mM solution.

absence of ferrocenium (data not shown). The Fe mass peak of the SAMs assembled from 1 mM **4g**·**5** with ferrocenium is about twice as high as that of the 0.1 mM encapsulated ferrocenium. ToF-SIMS is a quantitative and linear method; we therefore conclude that in the samples obtained from the more concentrated solution, about twice the amount of ferrocenium is present in the SAM due to a shift in the equilibrium between ferrocenium- and dichloromethane-filled capsules towards the ferrocenium-filled capsules.

E. Stability of 4g·5 SAMs in electrolytes

Given the previous results, we can conclude that we are able to fabricate SAMs of capsule **4g**·**5** filled with ferrocenium, *viz.* encapsulated, immobilized ferrocenium. The next question which has to be addressed is the stability of these SAMs in a liquid environment, *e.g.* in water, in an aqueous electrolyte or in dichloromethane with tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The stability was tested with SPR spectroscopy by taking spectra (always in dichloromethane) of SAMs formed by capsule **4g**·**5** filled with dichloromethane or with ferrocenium before and after immersion in pure Milli-Q-water, in 0.1 M KCl aqueous solution, in pure CH_2Cl_2 and in 0.15 M or 0.06 M $TBAPF_6$ in CH_2Cl_2 for 2 days.

Fig. 5 displays as an example the plasmon spectra of an SAM of capsule **4g·5** filled with ferrocenium (a) before and (b) after immersion in 0.1 M aqueous KCl solution. Clearly, in this case the plasmon resonance had shifted slightly towards smaller coupling angles with the immersion, indicating a loss of material from the film. Under these conditions the SAM is obviously not stable.

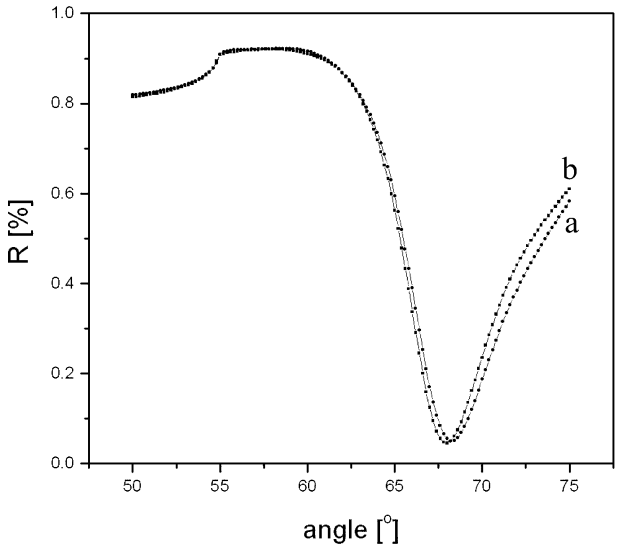


Fig. 5 Plasmon spectra (taken in dichloromethane) of a capsule **4g·5** SAM with ferrocenium immersed for 2 days in 0.1 M aqueous KCl solution: (a) before and (b) after immersion.

For all aqueous solutions this instability was found for the SAMs of ferrocenium-filled capsules. A very minor shift in the surface plasmon resonance curve was found for the SAM of the ferrocenium -filled capsule **4g·5** with 0.15 M $TBAPF_6$, but no shift is observed with 0.06 M $TBAPF_6$. The SAMs of dichloromethane-filled capsules did not yield any shifts in the tested solvents and were always stable for at least 2 days. Given that the SAMs of the ferrocenium-filled capsule **4g·5** are not stable in an aqueous environment, but are stable in dichloromethane with 0.06 M $TBAPF_6$, it should be possible to perform electrochemical experiments, such as cyclic voltammetry, in dichloromethane with 0.06 M $TBAPF_6$ and, possibly, with 0.15 M $TBAPF_6$.

F. Coverage of gold by SAMs of 4g·5: electrochemistry

Oxidation/reduction reactions of a redox couple in solution are often used for probing the coverage and quality of monolayers on a metal surface.[7,44] In our case, ferrocene/ferrocenium–methanol was used. After monolayer formation on the electrode surface, the current flow through the SAM was probed by cyclovoltammetry. A closely packed monolayer can block this current between the electrode with the monolayer and the electrolyte solution dramatically. This technique is highly sensitive to monolayer defects.[7,44]

In Fig. 6 the cyclic voltammogram of an electrode covered by a SAM fabricated from **4g** is shown. The electrochemical data for SAMs of dichloromethane-filled capsules **4g·5** and ferrocenium-filled capsules **4g·5** look identical (not shown). The very distinct cyclic voltammograms (a) depict the pure gold surface with the

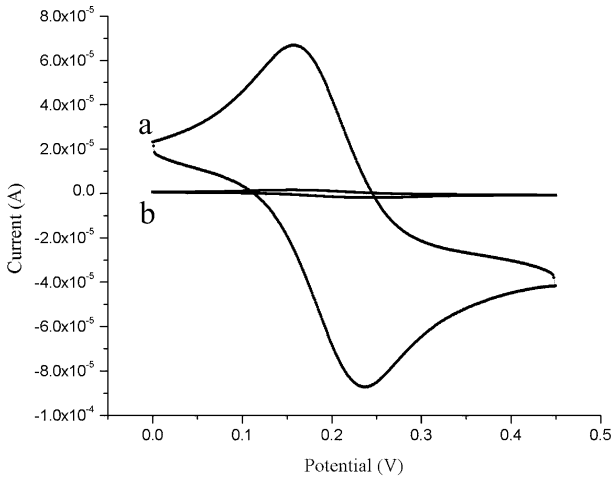


Fig. 6 Cyclic voltammetric current response *vs.* applied potential for (a) a pure gold surface and (b) for **4g** SAM/Au. Scan rate: 20 mV s^{-1}.

oxidation peak of the ferrocene–methanol and the reduction peak of the ferrocenium–methanol. The curve (b) depicts the response of the gold electrode with the SAM. Clearly, the electrochemical reactions are hindered and a basically flat, nearly featureless current–voltage behavior is found. This indicates that the SAMs blocked the electron transfer between redox couple and the electrode very well in aqueous solution. The low currents (around 1.5% of that for the bare gold case) from those voltammograms indicate that the SAMs are well-packed at the electrode. Sweeping the voltage several times did not change the electrochemical response, indicating the SAMs are stable over the duration of these electrochemical tests.

Conclusions

We were able to fabricate stable SAMs of the "monomeric" calix[4]arenes **4g** and **4f** by adsorption from a hydrogen-bond-breaking solvent (ethanol–chloroform 6 : 4, THF), and of the heterodimeric capsules **4g·5** and **4f·5** by adsorption from chloroform, which is also included as a guest. Since independent ^1H NMR studies showed that capsule **4f·5** is in equilibrium with its monomers and does not exclusively form heterodimers, we concentrated on capsule **4g·5** for our in-depth studies. The ferrocenium cation is encapsulated in **4g·5** and captured (see Fig. 1b) when the guest–host system is immobilized by self-assembly from dichloromethane. The SAMs of capsule **4g·5** filled with ferrocenium are unstable in water, probably because hydrogen bonds are broken, but are stable in dichloromethane with salt concentrations up to 0.15 M $TBAPF_6$. Electrochemistry has shown densely packed films, which are stable to electrochemical experiments in an aqueous environment for a few minutes.

The entanglement of the urea residues in heterodimers of capsule **4g·5** obviously is not sufficient for continued stabilization of the capsules and of their SAMs when the hydrogen bonds of the dimers are broken. Therefore, our future studies will focus on heterodimers formed by tetraureas of type **4g** with the tetraloop tetraureas of type **6**, in which the capsules after binding to the surface have a four-fold rotaxane (with Au as "stopper") or catenane structure (with Au as a connection between urea arms).

The capsules may then still be opened if the hydrogen bonds are broken, but they cannot fall apart. Under appropriate geometrical conditions (*e.g.* length of the spacer, size of the loops) this may lead to a permanent encapsulation of an included guest.

Experimental

Syntheses and dimerization

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*-Tetraaminocalix[4]arene tetradecylether **1** and *p*-tosyltetraurea tetrapentyl ether **5** were prepared according to published procedures.[45] Tetraloop-tetraurea calix[4]arenes **6** were prepared as described.[46]

***p*-(*N*-Phthalimidobutyloxy)nitrobenzene.** A suspension of *p*-nitrophenol (2.02 g, 14.5 mmol), potassium carbonate (2.21 g, 16 mmol) and bromobutylphthalimide (4.51 g, 16 mmol) in acetonitrile (80 ml) was refluxed for 24 hours. The hot mixture was filtered to remove potassium salts, and the filtrate was evaporated. The oily residue was recrystallized from acetonitrile (50 ml) to give the product (4.15 g, 84%) as white needles. Mp 120 °C (lit.,[47] 119 °C); ^{1}H NMR ($CDCl_3$), δ: 8.16 (2 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 7.89–7.78 (2 H, m, Ar-*H*), 7.77–7.65 (2 H, m, Ar-*H*), 6.91 (2 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 4.08 (2 H, br t, -OCH_2-), 3.77 (2 H, br t, -OCH_2-), 1.97–1.78 (4 H, m, -CH_2-). *m*/*z* (FD): 340.3 (M^+).

***p*-(Aminobutyloxy)nitrobenzene.** A slurry of *p*-(phthalimidobutyloxy)nitrobenzene (1.00 g, 2.92 mmol) and hydrazine hydrate (7.2 ml, 147 mmol) in ethanol (50 ml) was refluxed for 4 hours. After evaporation the product was extracted from the residue with dichloromethane. The extract was washed with aqueous sodium hydroxide and water and dried ($MgSO_4$). Evaporation finally gave the amine (0.50 g, 80%) as a yellow solid, which was used for the next step without further purification. Mp 40 °C; ^{1}H NMR ($CDCl_3$), δ: 8.18 (2 H, d, $^3J_{HH}$ 9.2 Hz, Ar-*H*), 6.93 (2 H, d, $^3J_{HH}$ 9.2 Hz, Ar-*H*), 4.06 (2 H, t, $^3J_{HH}$ 6.2 Hz, -OCH_2-), 2.80 (2 H, t, $^3J_{HH}$ 6.8 Hz, -CH_2NH$_2$), 1.93–1.57 (6 H, m, -CH_2-, -NH_2). *m*/*z* (FD) 210.1 (M^+).

***p*-(*tert*-Butyloxycarbonylamidobutyloxy)nitrobenzene.** A solution of *p*-(aminobutyloxy)nitrobenzene (1.50 g, 7.13 mmol) and Boc-anhydride (1.56 g, 7.13 mmol) in THF (80 ml) was stirred at rt for 24 h. The solvent was evaporated to give an oily residue, which solidified after drying under vacuum (oil pump). The solid was triturated with hexane, filtered and dried to give the *N*-Boc-protected product (1.87 g, 84%) as yellowish powder. Mp 58–60 °C; ^{1}H NMR ($CDCl_3$), δ: 8.18 (2 H, d, $^3J_{HH}$ 9.2 Hz, Ar-*H*), 6.93 (2 H, d, $^3J_{HH}$ 9.2 Hz, Ar-*H*), 4.57 (1 H, br s, -N*H*-), 4.06 (2 H, t, $^3J_{HH}$ 6.2 Hz, -OCH_2-), 3.25–3.13 (2 H, m, -CH_2NH-), 1.90–1.80 (2 H, m, -CH_2-), 1.72–1.62 (2 H, m, -CH_2-), 1.43 (9 H, s, -CH_3). *m*/*z* (FD) 310.1 (M^+).

***p*-(*tert*-Butyloxycarbonylamidobutyloxy)aniline 3b.** *p*-(*tert*-Butyloxycarbonylamidobutyloxy)nitrobenzene (1.80 g, 5.80 mmol) was dissolved in toluene (50 ml), a catalytic amount of Raney-Ni was added and the mixture was vigorously stirred in a hydrogen atmosphere at rt for 6–8 hours (the conversion may be monitored by TLC). The catalyst was filtered off and the solvent was removed in vacuum to give the pure aniline (1.38 g, 85%) as yellowish solid. Mp 46–47 °C; ^{1}H NMR ($CDCl_3$), δ: 6.72 (2 H, d, $^3J_{HH}$ 8.7 Hz, Ar-*H*), 6.62 (2 H, d, $^3J_{HH}$ 8.5 Hz, Ar-*H*), 4.62 (1 H, br s, N-*H*), 3.88 (2 H, t, $^3J_{HH}$ 6.1 Hz, -OCH_2-), 3.40 (2 H, br s, -NH_2), 3.25–3.07 (2 H, m, -CH_2-), 1.86–1.54 (4 H, m, -CH_2-), 1.43 (9 H, s, -CH_3). *m*/*z* (FD) 280.1 (M^+).

4-(10′-Undecenyloxy)acetamide. A suspension of 4-acetamidophenol (3.00 g, 19.8 mmol) and potassium carbonate (5.49 g, 39.7 mmol) in acetonitrile (150 ml) was refluxed for 1 hour. 11-Bromo-1-undecene (6.02 g, 25.8 mmol) was then added and the mixture was refluxed for 48 hours. After evaporation the product was extracted with $CHCl_3$. The organic solution was washed with aqueous sodium carbonate and water, and dried ($MgSO_4$). The residue obtained by evaporation was recrystallized from acetonitrile–methanol, yielding the product (5.35 g, 89%). Mp 89.5 °C; ^{1}H NMR ($CDCl_3$), δ: 7.35 (2 H, d, $^3J_{HH}$ 8.1 Hz, Ar-*H*), 7.02 (1 H, s, N-*H*), 6.83 (2 H, d, $^3J_{HH}$ 8.1 Hz, Ar-*H*), 5.88–5.73 (1 H, m, -C*H*=CH$_2$), 5.04–4.86 (2 H, m, -CH=CH_2), 3.91 (2 H, t, $^3J_{HH}$ 6.2 Hz, -OCH_2-), 2.14 (3 H, s, -CH_3), 2.08–1.96 (2 H, m, -OCH$_2$CH_2-), 1.82–1.67 (2 H, m, -CH_2-), 1.49–1.17 (12 H, m, -(CH_2)$_6$-). *m*/*z* (FD) 303.2 (M^+).

4-(10′-Undecenyloxy)aniline 3c. A mixture of the *O*-alkylated acetamide (5.35 g, 17.6 mmol) and sodium hydroxide (24.7 g, 617 mmol) was refluxed in EtOH (100 ml) and H_2O (10 ml) for 12 h. The solvent was evaporated and the residue was partitioned between ether and H_2O. The organic layer was washed twice with aqueous sodium carbonate and water and dried ($MgSO_4$). The residue obtained by evaporation, a brown solid (4.30 g, 93%), was analytically pure and used in further reactions without additional purification. Mp 37–38 °C; ^{1}H NMR ($CDCl_3$), δ: 6.74 (2 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 6.62 (2 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 5.96–5.68 (1 H, m, -C*H*=CH$_2$), 5.12–4.85 (2 H, m, -CH=CH_2), 3.86 (2 H, t, $^3J_{HH}$ 6.6 Hz, -OCH_2-), 3.39 (2 H, br s, -NH_2), 2.18–1.92 (2 H, m, -OCH$_2$CH_2-), 1.87–1.56 (2 H, m, -CH_2-), 1.54–1.15 (12 H, m, -(CH_2)$_6$-). *m*/*z* (FD) 261.2 (M^+).

Calix[4]arene 2. The solution of tetraamine **1** (2.00 g, 1.91 mmol) in THF (15 ml) was added to the stirred solution of 4-nitrophenylchloroformate (2.55 g, 12.6 mmol) in $CHCl_3$ (22 ml). The reaction mixture was refluxed for 12 hours. After evaporation, the residue was triturated with ethyl acetate and stored in a refrigerator for 4–8 hours. The solid was filtered off, washed with ethyl acetate and dried to give the pure product (2.65 g, 81%) as light-yellow powder. Mp 181 °C; ^{1}H NMR (DMSO-d_6), δ: 9.93 (4 H, s, N-*H*), 8.18 (8 H, d, $^3J_{HH}$ 7.0 Hz, Ar-*H*), 7.35 (8 H, d, $^3J_{HH}$ 6.6 Hz, Ar-*H*), 6.90 (8 H, s, Ar-*H*), 4.33 (4 H, d, $^2J_{HH}$ 10.6 Hz, ArCH_2Ar), 3.78 (8 H, br s, -OCH_2-), 3.08 (4 H, d, $^2J_{HH}$ 10.3 Hz, ArCH_2Ar), 1.87 (8 H, br s, -OCH$_2$CH_2-), 1.54–1.03 (56 H, m, -CH_2-), 0.84 (12 H, t, $^3J_{HH}$ 6.8 Hz, -CH_3). *m*/*z* (FD) 1706.0 (M^+).

Calix[4]arene 4a. *N*-Boc-1,4-phenylene diamine (0.081 g, 0.387 mmol), and diisopropylethylamine (0.050 g, 0.387 mmol) in DMF (5 ml) were added to a stirred solution of **2** (0.132 g, 0.0774 mmol) in DMF (5 ml). The mixture was stirred at rt for 24 hours. The product was precipitated with water, filtered off

and washed several times with water. The crude product was triturated with acetonitrile and the white powder was purified by reprecipitation from THF–methanol, yielding the product (0.137 g, 89%). Mp >195 °C (decomposition); ^{1}H NMR (DMSO-d_6), δ: 9.11 (4 H, s, N-*H*), 8.17 (4 H, s, N-*H*), 8.12 (4 H, s, N-*H*), 7.29 (8 H, d, $^3J_{HH}$ 8.4 Hz, Ar-*H*), 7.21 (8 H, d, $^3J_{HH}$ 9.2 Hz, Ar-*H*), 6.78 (8 H, s, Ar-*H*), 4.31 (4 H, d, $^2J_{HH}$ 12.1 Hz, ArCH_2Ar), 3.80 (8 H, br t, -OCH_2-), 3.08 (4 H, d, $^2J_{HH}$ 12.5 Hz, ArCH_2Ar), 1.90 (8 H, m, -OCH$_2$CH_2-), 1.45 (36 H, s, -CH_3), 1.42–1.15 (56 H, m, -CH_2-), 0.85 (12 H, br t, -CH_3). *m/z* (ESI) 2005.3 (M + Na$^+$), 1014.2 (M + 2Na$^+$).

Calix[4]arene 4b. Prepared as described above for **4a** from **2** (0.195 g, 0.114 mmol), aniline **3b** (0.130 g, 0.464 mmol) and diisopropylethylamine (0.070 g, 0.510 mmol) in DMF (10 ml); reprecipitation from THF–acetonitrile. Yield: 0.195 g (75%). Mp >165 °C (decomposition); ^{1}H NMR (DMSO-d_6), δ: 8.11 (4 H, s, N-*H*), 8.09 (4 H, s, N-*H*), 7.21 (8 H, d, $^3J_{HH}$ 8.9 Hz, Ar-*H*), 6.88–6.69 (20 H, m, Ar-*H*, N-*H*), 4.31 (4 H, d, $^2J_{HH}$ 11.9 Hz, ArCH_2Ar), 3.87 (8 H, t, $^3J_{HH}$ 6.3 Hz, -OCH_2-), 3.79 (8 H, br t, -OCH_2-), 3.07 (4 H, d, $^2J_{HH}$ 12.3 Hz, ArCH_2Ar), 3.02–2.87 (8 H, m, -NHCH_2-), 1.90 (8 H, m, -OCH$_2$CH_2-), 1.70–1.58 (8 H, m, -CH_2-), 1.56–1.16 (100 H, m and s (1.36) overlapped, -CH_2-, -CH_3), 0.85 (12 H, br t, $^3J_{HH}$ 6.3 Hz, -CH_3). *m/z* (ESI) 2293.6 (M + Na$^+$), 1158.3 (M + 2Na$^+$).

Dimer (4b)$_2$. ^{1}H NMR (CDCl$_3$), δ: 9.20 (8 H, s, N-*H*), 7.70 (8 H, d, $^3J_{HH}$ 8.9 Hz, Ar-*H*), 7.60 (8 H, s, Ar-*H*), 7.03 (8 H, s, N-*H*), 6.87 (16 H, d, $^3J_{HH}$ 8.9 Hz, Ar-*H*), 5.96 (8 H, s, Ar-*H*), 4.59 (8 H, br s, N-*H*), 4.22 (8 H, d, $^2J_{HH}$ 11.6 Hz, ArCH_2Ar), 3.97–3.85 (16 H, m, -OCH_2-), 3.65 (16 H, t, $^3J_{HH}$ 7.8 Hz, -OCH_2-), 3.24–3.06 (16 H, m, -NHCH_2-), 2.82 (8 H, d, $^2J_{HH}$ 11.9 Hz, ArCH_2Ar), 2.02–1.87 (16 H, m, -CH_2-), 1.84–1.71 (16 H, m, -CH_2-), 1.69–1.53 (16 H, m, -CH_2-), 1.43 (72 H, s, -CH_3), 1.38–1.19 (112 H, m, -CH_2-), 0.88 (24 H, t, $^3J_{HH}$ 6.8 Hz, -CH_3).

Calix[4]arene 4c. Prepared as described above for **4a** from **2** (0.72 g, 0.42 mmol), aniline **3c** (0.50 g, 1.9 mmol) and diisopropylethylamine (0.27 g, 2.1 mmol) in DMF (35 ml). Trituration with acetonitrile gave the analytically pure product (0.63 g, 68%) as a white powder. Mp 155 °C (decomposition); ^{1}H NMR (DMSO-d_6, 80 °C), δ: 7.89 (4 H, s, N-*H*), 7.84 (4 H, s, N-*H*), 7.21 (8 H, d, $^3J_{HH}$ 8.7 Hz, Ar-*H*), 6.80 (8 H, s, Ar-*H*), 6.77 (8 H, d, $^3J_{HH}$ 8.7 Hz, Ar-*H*), 5.87–5.73 (4 H, m, C*H*=CH$_2$), 5.04–4.87 (8 H, m, CH=CH_2), 4.38 (4 H, d, $^2J_{HH}$ 12.6 Hz, ArCH_2Ar), 3.97–3.81 (16 H, m, -OCH_2-), 3.09 (4 H, d, $^2J_{HH}$ 12.9 Hz, ArCH_2Ar), 2.07–1.97 (8 H, m, -OCH$_2$CH_2-), 1.96–1.83 (8 H, m, -OCH$_2$CH_2-), 1.74–1.62 (8 H, m, -CH_2-), 1.49–1.19 (104 H, m, -CH_2-), 0.88 (12 H, br t, -CH_3). *m/z* (ESI) 2217.7 (M + Na$^+$).

Dimer (4c)$_2$. ^{1}H NMR (CDCl$_3$), δ: 9.22 (8 H, s, N-*H*), 7.71 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 7.60 (8 H, d, $^2J_{HH}$ 2.4 Hz, Ar-*H*), 7.02 (8 H, s, N-*H*), 6.87 (16 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 5.94 (8 H, d, $^2J_{HH}$ 2.4 Hz, Ar-*H*), 5.86–5.74 (8 H, m, C*H*=CH$_2$), 5.02–4.88 (16 H, m, CH=CH_2), 4.20 (8 H, d, $^2J_{HH}$ 11.2 Hz, ArCH_2Ar), 3.94–3.82 (16 H, m, -OCH_2-), 3.64 (16 H, br t, $^3J_{HH}$ 8.1 Hz, -OCH_2-), 2.81 (8 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 2.07–1.99 (16 H, m, -CH_2-), 1.98–1.87 (16 H, m, -CH_2-), 1.78–1.67 (16 H, m, -CH_2-), 1.48–1.19 (208 H, m, -CH_2-), 0.88 (24 H, t, $^3J_{HH}$ 6.8 Hz, -CH_3).

Calix[4]arene 4d. A solution of calixarene **4a** (0.137 g, 0.0691 mmol) in dichloromethane (10 ml) and trifluoroacetic acid (4 ml) was stirred at rt for 2 h. The solvent was evaporated and the residue was triturated with Et$_2$O. A solid was filtered off, washed with Et$_2$O and dried. The salt obtained was dissolved in THF (10 ml), treated with an excess of Et$_3$N (0.5 ml) and with α-lipoic acid anhydride (prepared from α-lipoic acid (0.071 g, 0.345 mmol) and DCC (0.036 g, 0.173 mmol) in benzene (5 ml) as described in the literature[48]). The reaction mixture was stirred at rt for 2 h. The solvent was evaporated and the residue was triturated with methanol to give the pure product (0.120 g, 74%) as a yellowish powder. Mp >190 °C (decomposition); ^{1}H NMR (DMSO-d_6), δ: 9.07 (s, N-*H*, 4 H), 8.23 (4 H, s, N-*H*), 8.14 (4 H, s, N-*H*), 7.43 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 7.25 (8 H, d, $^3J_{HH}$ 8.4 Hz, Ar-*H*), 6.79 (8 H, s, Ar-*H*), 4.31 (4 H, d, $^2J_{HH}$ 11.0 Hz, ArCH_2Ar), 3.90 (8 H, m, -OCH_2-), 3.90 (4 H, m, -SC*H*-), 3.23–2.97 (12 H, m, -SCH_2-, ArCH_2Ar), 2.50–2.35 (8 H, m, -CH_2-), 2.26 (8 H, br t, -CH_2C(O)-), 2.02–1.80 (8 H, m, -CH_2-), 1.78–1.48 (16 H, m, -CH_2-), 1.49–1.14 (64 H, m, -CH_2-), 0.85 (12 H, br t, -CH_3). *m/z* (ESI) 2358.3 (M + Na$^+$), 1190.7 (M + 2Na$^+$).

Calix[4]arene 4e. A solution of calixarene **4b** (0.100 g, 0.0440 mmol) in dichloromethane (10 ml) and trifluoroacetic acid (1 ml) was stirred at rt for 2 h. The solvent was evaporated, the residue dissolved in THF (15 ml), and then treated with an excess of diisopropylethylamine (0.114 g, 0.880 mmol) and acetic anhydride (0.045 g, 0.440 mmol). The reaction mixture was stirred for 12 h at rt and evaporated. The oily residue was triturated with acetonitrile; the solid was filtered off and dried to give the pure product (0.083 g, 93%) as a white powder. Mp >150 °C (decomposition); ^{1}H NMR (DMSO-d_6), δ: 8.13 (4 H, s, N-*H*), 8.11 (4 H, s, N-*H*), 7.82 (4 H, br t, $^3J_{HH}$ 5.1 Hz, N-*H*), 7.22 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-*H*), 6.86–6.71 (16 H, m, Ar-*H*), 4.31 (4 H, d, $^3J_{HH}$ 12.2 Hz, ArCH_2Ar), 3.88 (8 H, t, $^3J_{HH}$ 6.4 Hz, -OCH_2-), 3.79 (8 H, br t, -OCH_2-), 3.14–3.00 (12 H, m, -NHCH_2-, ArCH_2Ar), 1.98–1.84 (8 H, m, -CH_2-), 1.78 (12 H, s, -CH_3), 1.72–1.60 (8 H, m, -CH_2-), 1.57–1.46 (8 H, m, -CH_2-), 1.46–1.17 (52 H, m, -CH_2-), 0.86 (12 H, br t, $^3J_{HH}$ 6.6 Hz, -CH_3). *m/z* (ESI) 2061.4 (M + Na$^+$), 1042.2 (M + 2Na$^+$).

Calix[4]arene 4f. Prepared as described above for **4d** from calixarene **4b** (0.195 g, 0.0859 mmol), α-lipoic acid (0.100 g, 0.504 mmol) and DCC (0.050 g, 0.252 mmol) in benzene (5 ml) and THF (8 ml). When the oily product was triturated with acetonitrile a solid formed, which was filtered off and dried to give the pure product (0.156 g, 59%) as a white powder. Mp >145 °C (decomposition); ^{1}H NMR (DMSO-d_6), δ: 8.12 (s, N-*H*, 4 H), 8.09 (4 H, s, N-*H*), 7.78 (4 H, br t, N-*H*), 7.22 (8 H, d, $^3J_{HH}$ 8.2 Hz, Ar-*H*), 6.94–6.63 (16 H, m, Ar-*H*), 4.43–4.17 (4 H, br d, ArCH_2Ar), 3.97–3.66 (16 H, m, -OCH_2-), 3.58 (4 H, m, -SC*H*-), 3.20–2.89 (12 H, m, -SCH_2-, ArCH_2Ar), 2.50–2.28 (8 H, m, -CH_2-), 2.04 (8 H, br t, -CH_2C(O)-), 1.96–1.74 (8 H, m, -CH_2-), 1.73–1.05 (80 H, m, -CH_2-), 0.85 (12 H, br t, -CH_3). *m/z* (MALDI-ToF) 2623.4 (M$^+$).

Heterodimer 4f·5. ^{1}H NMR (TCE), δ: 10.62 (4 H, s, N-*H*), 8.12 (8 H, d, $^3J_{HH}$ 8.0 Hz, Ar-*H*), 8.02 (4 H, s, N-*H*), 7.91 (8 H, s, N-*H*, Ar-*H*), 7.59 (8 H, d, $^3J_{HH}$ 8.3 Hz, Ar-*H*), 6.50 (8 H, d, $^3J_{HH}$ 8.4 Hz, Ar-*H*), 7.41 (4 H, s, N-*H*), 6.98 (8 H, s, Ar-*H*), 6.66 (8 H, d, $^3J_{HH}$ 9.1 Hz, Ar-*H*), 7.48 (4 H, t, $^3J_{HH}$ 5.6 Hz, N-*H*), 5.26 (4 H, s, Ar-*H*), 4.54 (4 H, d, $^2J_{HH}$ 11.5 Hz, ArCH_2Ar), 4.09

(4 H, d, $^2J_{HH}$ 11.1 Hz, ArCH_2Ar), 4.01–3.65 (16 H, m, -OCH_2-), 3.65–3.48 (10 H, m, -OCH_2-, -SC*H-), 3.38 (4 H, d, $^2J_{HH}$ 11.1 Hz, ArCH_2Ar), 3.32–3.08 (18 H, m, -NHCH_2-, -SCH_2-, -SC*H-), 2.71 (4 H, d, $^2J_{HH}$ 12.5 Hz, ArCH_2Ar), 2.59–2.32 (20 H, m and s (2.52) overlapped, -CH_3, -CH_2-), 2.22–2.02 (16 H, m, -CH_2-), 2.00–1.10 (120 H, m, -CH_2-), 1.00–0.78 (24 H, m, -CH_3).

Calix[4]arene 4g. The solution of calixarene **4c** (0.31 g, 0.14 mmol), 1-decanethiol (0.30 g, 1.7 mmol) in THF (10 ml) was degassed with nitrogen and cooled to 0–5 °C. Then a 0.5 M solution of 9-BBN in THF (0.2 ml, 0.1 mmol) was added and the reaction mixture was stirred for 24 h while being allowed to warm to rt. The residue obtained after evaporation was triturated with acetonitrile. The solid formed was filtered off and dried to give the pure sulfide (0.25 g, 60%) as a white powder. Mp 104 °C (decomposition); ^{1}H NMR (DMSO-d_6/$CDCl_3$), δ: 8.02 (8 H, s, N-H), 7.18 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 6.76 (8 H, s, Ar-H), 6.71 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 4.33 (4 H, d, $^2J_{HH}$ 12.7 Hz, ArCH_2Ar), 4.00–3.59 (16 H, m, -OCH_2-), 3.04 (4 H, d, $^2J_{HH}$ 11.7 Hz, Ar-CH_2-Ar), 2.41 (16 H, t, -SCH_2-), 1.90 (8 H, m, -OCH$_2$CH_2-), 1.77–0.99 (192 H, m, -CH_2-), 0.96–0.70 (24 H, m, -CH_3). *m/z* (ESI) 2915.4 (M + Na^+), 1469.2 (M + 2Na^+).

Homodimer (4g)$_2$. ^{1}H NMR ($CDCl_3$), δ: 9.22 (8 H, s, N-H), 7.71 (8 H, d, $^3J_{HH}$ 8.2 Hz, Ar-H), 7.60 (8 H, s, Ar-H), 7.02 (8 H, s, N-H), 6.87 (16 H, d, $^3J_{HH}$ 8.2 Hz, Ar-H), 5.94 (8 H, s, Ar-H), 4.21 (8 H, d, $^2J_{HH}$ 11.0 Hz, ArCH_2Ar), 3.99–3.79 (16 H, m, -OCH_2-), 3.64 (16 H, br t, -OCH_2-), 2.81 (8 H, d, $^2J_{HH}$ 11.0 Hz, ArCH_2Ar), 2.48 (32 H, t, $^3J_{HH}$ 7.0 Hz, -SCH_2-), 2.03–1.84 (16 H, m, -CH_2-), 1.81–1.65 (16 H, m, -CH_2-), 1.65–1.02 (368 H, m, -CH_2-), 1.00–0.75 (48 H, m, -CH_3).

Heterodimer 4g·5. ^{1}H NMR (C_6D_6), δ: 11.10 (4 H, s, N-H), 8.66 (4 H, s, N-H), 8.56 (4 H, s, Ar-H), 8.53 (4 H, s, N-H), 8.19 (8 H, d, $^3J_{HH}$ 7.8 Hz, Ar-H), 7.96 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 7.85 (4 H, s, N-H), 7.77 (4 H, s, Ar-H), 7.51 (4 H, s, Ar-H), 6.78 (8 H, d, $^3J_{HH}$ 8.3 Hz, Ar-H), 6.68 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 5.55 (4 H, s, Ar-H), 4.92 (4 H, d, $^2J_{HH}$ 11.2 Hz, ArCH_2Ar), 4.28 (4 H, d, $^2J_{HH}$ 11.2 Hz, ArCH_2Ar), 4.07 (8 H, t, $^3J_{HH}$ 7.6 Hz, -OCH_2-), 3.96 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 3.57 (8 H, t, $^3J_{HH}$ 7.8 Hz, -OCH_2-), 3.53–3.43 (4 H, m, -OCH_2-), 3.43–3.32 (4 H, m, -OCH_2-), 3.01 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 2.50–2.39 (16 H, m, -SCH_2-), 2.38–2.25 (8 H, m, -CH_2-), 2.02–1.90 (8 H, m, -CH_2-), 1.85 (12 H, s, -CH_3), 1.69–1.09 (208 H, m, -CH_2-), 1.03–0.95 (24 H, m, -CH_3), 0.92 (12 H, t, $^3J_{HH}$ 7.1 Hz, -CH_3).

Heterodimer 4g·6. ^{1}H NMR (C_6D_6), δ: 10.08 (4 H, s, N-H), 9.75 (4 H, s, N-H), 8.22 (4 H, s, Ar-H), 8.17 (4 H, s, Ar-H), 8.08 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 7.97 (4 H, s, Ar-H), 7.49 (4 H, s, N-H), 7.27 (4 H, s, Ar-H), 7.01 (4 H, s, N-H), 6.84 (8 H, d, $^3J_{HH}$ 8.3 Hz, Ar-H), 6.54 (4 H, s, Ar-H), 6.36 (4 H, s, Ar-H), 6.31 (4 H, s, Ar-H), 4.45 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.32 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.15–3.40 (44 H, m, -OCH_2-, -OCH_3), 3.33–3.08 (8 H, m, ArCH_2Ar), 2.43 (16 H, m, -SCH_2-), 2.15–1.94 (8 H, m, -CH_2-), 1.80–1.04 (256 H, m, -CH_2-), 1.03–0.82 (24 H, m, -CH_3).

Complex of dimer (4g)$_2$ with cobaltocenium. ^{1}H NMR (CD_2Cl_2), δ: 9.03 (8 H, s, N-H), 7.75 (24 H, d and s overlapped, $^3J_{HH}$ 8.4 Hz, Ar-H), 6.99 (16 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 6.74 (8 H, s, N-H), 5.64 (8 H, br s, Ar-H), 4.34 (8 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 3.98–3.82 (16 H, m, -OCH_2-), 3.74 (16 H, t, $^3J_{HH}$ 7.1 Hz, -OCH_2-), 2.93 (8 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 2.82 (10 H, s, included cobaltocenium), 2.48 (32 H, t, $^3J_{HH}$ 7.1 Hz, -SCH_2-), 2.00–1.86 (16 H, m, -CH_2-), 1.78–1.66 (16 H, m, -CH_2-), 1.62–1.48 (16 H, m under water peak, -CH_2-), 1.48–1.14 (352 H, m, -CH_2-), 0.98–0.82 (48 H, m, -CH_3).

Complex of dimer (4g)$_2$ with tetraethylammonium. ^{1}H NMR (CD_2Cl_2), δ: 8.95 (8 H, s, N-H), 7.79 (24 H, d and s overlapped, $^3J_{HH}$ 9.3 Hz, Ar-H), 7.00 (16 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 6.36 (8 H, s, N-H), 5.61 (8 H, br s, Ar-H), 4.33 (8 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 3.90 (16 H, m, $^3J_{HH}$ 6.1 Hz, -OCH_2-), 3.76 (16 H, t, $^3J_{HH}$ 8.1 Hz, -OCH_2-), 2.97 (8 H, d, $^2J_{HH}$ 12.2 Hz, ArCH_2Ar), 2.47 (32 H, t, $^3J_{HH}$ 7.3 Hz, -SCH_2-), 2.03–1.86 (16 H, m, -CH_2-), 1.78–1.64 (16 H, m, -CH_2-), 1.62–1.48 (16 H, m under water peak, -CH_2-), 1.48–1.17 (352 H, m, -CH_2-), 1.14 (4 H, br s, included Et_4N^+, N-CH_2-), 0.98–0.82 (48 H, m, -CH_3), 0.50 (4 H, br s, included Et_4N^+, N-CH_2-), –0.15 (6 H, br s, included Et_4N^+, N-CH_3), –3.29 (6 H, br s, included Et_4N^+, N-CH_3).

Complex of heterodimer 4g·5 with cobaltocenium. ^{1}H NMR (CD_2Cl_2), δ: 11.16 (4 H, s, N-H), 8.40 (4 H, s, N-H), 8.14 (8 H, d, $^3J_{HH}$ 8.3 Hz, Ar-H), 7.93 (4 H, s, N-H), 7.84 (4 H, br s, Ar-H), 7.59 (8 H, d, $^3J_{HH}$ 9.3 Hz, Ar-H), 7.53 (8 H, d, $^3J_{HH}$ 8.3 Hz, Ar-H), 7.50 (4 H, s, N-H), 7.11 (4 H, br s, Ar-H), 7.00 (4 H, br s, Ar-H), 6.69 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 4.86 (4 H, br s, Ar-H), 4.64 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.09 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.04–3.87 (8 H, m, -OCH_2-), 3.80–3.65 (8 H, m, -OCH_2-), 3.56 (8 H, t, $^3J_{HH}$ 7.8 Hz, -OCH_2-), 3.37 (4 H, d, $^2J_{HH}$ 12.2 Hz, ArCH_2Ar), 3.05 (10 H, s, included cobaltocenium), 2.69 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 2.53 (12 H, s, -CH_3), 2.52–2.44 (16 H, t (2.49) and t (2.48) overlapped, $^3J_{HH}$ 7.3 Hz and $^3J_{HH}$ 7.3 Hz, -SCH_2-), 2.14–2.00 (8 H, m, -CH_2-), 2.85–1.72 (8 H, m, -CH_2-), 1.66–1.49 (8 H, m, -CH_2-), 1.48–1.16 (200 H, m, -CH_2-), 1.00–0.78 (36 H, m, -CH_3).

Complex of heterodimer 4g·6 with cobaltocenium. ^{1}H NMR (CD_2Cl_2), δ: 9.14 (4 H, s, N-H), 9.01 (4 H, s, N-H), 7.81 (4 H, s, Ar-H), 7.79 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 7.67 (4 H, s, Ar-H), 7.44 (4 H, s, Ar-H), 7.06 (4 H, s, N-H), 7.03 (8 H, d, $^3J_{HH}$ 8.8 Hz, Ar-H), 6.71 (4 H, s, Ar-H), 6.52 (4 H, s, N-H), 6.19 (4 H, s, Ar-H), 5.68 (4 H, s, Ar-H), 5.43 (4 H, s, Ar-H), 4.25 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.27 (4 H, d, $^2J_{HH}$ 11.7 Hz, ArCH_2Ar), 4.09–3.61 (44 H, m, -OCH_2-, -OCH_3), 2.98 (4 H, d, $^2J_{HH}$ 12.1 Hz, ArCH_2Ar), 2.86–2.73 (14 H, d and s of included cobaltocenium overlapped, ArCH_2Ar), 2.48 (16 H, m, $^3J_{HH}$ 6.6 Hz, -SCH_2-), 1.99–1.65 (32 H, m, -CH_2-), 1.62–0.98 (232 H, m, -CH_2-), 0.97–0.80 (24 H, m, -CH_3).

Preparation and physical characterization of SAMs

The necessary gold substrates (99.99%, the Royal Canadian Mint) for surface plasmon spectroscopy and electrochemistry were prepared using an e-beam sputtering system (HOSER) at a pressure around 5×10^{-6} torr.

For the formation of SAMs, the gold films were immersed for 15–25 h into the following solutions: a) 10 μM of **4g** or **4f** in THF for SAMs of a single calix[4]arene; b) 10 μM of **4g** or **4f**, and **5**, in chloroform or dichloromethane for SAMs of the heterodimeric capsules **4g·5** and **4f·5** with the solvent as guest; c) for heterodimeric capsules **4g·5** with ferrocenium cation as guest, a 0.1 mM solution in dichloromethane was used, which

was prepared with 15% excess of **5** and 20% excess of ferrocenium hexafluorophosphate.

Surface plasmon spectroscopy experiments were performed using a home-built surface plasmon spectrophotometer, which is described elsewhere.[7–9,40,41] Absorption spectra were measured with a Perkin Elmer Lambda 850 spectrometer with clean glass as reference. A ToF-SIMS (model VI of ION-ToF GmbH, Germany) with a primary ion beam of Cs at 9 keV was used to obtain the mass data.

For the electrochemical coverage measurements, a solution was made of 0.9 mM ferrocene in methanol and 0.1 M KCl as supporting electrolyte in Milli-Q-water. The electrochemical cell consisted of a Teflon cylinder with a working electrode at the bottom. The measurements were performed on an electrochemical analyzer (CH610A, CH Instruments, Austin, Texas) in a three-electrode system: gold working electrode (0.845 cm^2), a platinum counter-electrode, and a Ag/AgCl reference electrode. The scan rate was 20 mV s^{-1}, and the potential range (*vs*. Ag/AgCl) was 0.45 V.

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