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Self-Assembled Monolayers of Carceplexes on Gold

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Symmetrical carceplexes, hosts with permanently present guests, have been extensivlely investigated by Cram and others.[1] We have recently reported nonsymmetrical carceplexes by combination of functionalized calix[4]arenes and resorcin[4]-arenes that exhibit a novel type of stereoisomerism as the result of two different orientations of the incarcerated guest.[2] The energy barrier between the two states depends on the structure of both the cavity and of the incarcerated guest.[3]

Self-assembled monolayers are an attractive platform to order and orient such molecules in two dimensions.[4,5] Previously, we have shown that self-assembly of molecules in monolayers is a tool to control the orientation of molecular recognition sites.[6,7] Essential in the design of these adsorbates is that the eight alkyl chains fill the space under the recognition site. This is realized via four sulfides and back folding of the alkyl chain.[8] Thus, highly-ordered monolayers on gold were obtained of resorcin[4]arene[9] and calix[4]arene[10] derivatives.

Similarly, a modified carcerand might be oriented in space via the controlled assembly on gold. This will orient the carcerand, while the guest remains free to adopt two positions. In principle two different diastereometric surfaces can be formed.

In this communication we report the successful confinement of such a resorcin[4]arene-based carceplex (**1·DMF**) in a self-assembled monolayer on gold.

The synthesis of **1·DMF** (Scheme 1) is based on the coupling of calixarene **2** and resorcinarene **3** in MeCN at 80 °C in the presence of Cs_2CO_3 and KI.[11] Subsequent removal of the phthalimido groups with hydrazine monohydrate in EtOH, followed by selective acylation of the amino groups with chloroacetyl chloride in CH_2Cl_2 gave **4** in 22% overall yield. The intramolecular alkylation was achieved quantitatively in DMF at 80 °C in the presence of Cs_2CO_3 and KI.[12] The resulting DMF carceplex was reacted with 1-decanethiol in the presence of a catalytic amount of 9-borabicyclo[3.3.1]nonane (9-BBN) in THF, giving tetrasulfide carceplex **1·DMF** in 64% yield.[13] The ^1H NMR spectrum of **1·DMF** in $CDCl_3$ exhibits three singlets of the incarcerated DMF molecule at 4.84, 0.66, and −0.90 ppm for C(O)H and the two CH_3 groups, respectively. Those signals are shifted upfield by 3.16, 2.25, and 3.69 ppm, respectively, in comparison with the signals of free DMF, which clearly proves that DMF is complexed in the carcerand.[2] Moreover, the presence of DMF was confirmed by MS-FAB (*m*-nitrobenzyl alcohol as a matrix) showing a distinct peak of carceplex **1·DMF** at 2736.9 (calcd 2737.0).

Self-assembled monolayers of carceplex **1·DMF** on gold were prepared from an 0.1 mM ethanol solution.[14] Since in previous experiments[9] the temperature appeared to have great influence on the order in the layer, the adsorption was studied both at room temperature and at 60 °C. The monolayers were characterized by XPS, ellipsometry, electrochemical methods, contact angle measurements, and grazing incidence FTIR.[15] XPS data are fully consistent with the proposed structure (Table 1). The measured percentages of the atoms are in good agreement with the calculated numbers. The C 1s peak is broadened up to 287 eV due to the variety of atoms linked to the carbon atoms (like C−N, C−S, and C−O in addition to C−C and C═C). A separate maximum is observed for the carbonyl carbon atoms. The O 1s peak of the carbonyl appears as a shoulder at 532 eV.[16] An ellipsometrical thickness of 28 Å was determined, which is in good agreement with what can be expected for these monolayers oriented almost perpendicular to the surface. The advancing contact angle of 89° shows that the surface is hydrophobic, while the receding contact angle (66°) indicates slight disorder. This is expected, as the area per molecule is covered by eight alkyl chains, while only four propyl groups are directed to the outer interface, resulting in a loose packing of the top few angstroms. In contrast to the resorcin[4]arene monolayers,[9] no distinct difference in quality is observed between layers prepared at room temperature or at 60 °C. The same was observed for the calix[4]arene monolayers.[10] That overall a well-ordered monolayer is obtained is evident from electrochemical measurements; a high resistance of 25 kΩ was determined with electrochemical impedance spectroscopy.[17] Also the infrared data (Table 2) indicate a high degree of order,

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[1] For an overview of symmetrical carcerands, see: Cram, D. J.; Cram, J. M. In *Container Molecules and their Guests* in *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, MA, 1994; Vol. 4. A non-symmetrical carceplex was published recently: Fraser, J. R.; Borecka, B.; Trotter, J.; Sherman J. C. *J. Org. Chem.* **1995**, *60*, 1207−1213.

[2] Timmerman, P.; Verboom, W.; van Veggel, F. C. J. M.; van Duynhoven, J. P. M.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2345−2348.

[3] Van Wageningen, A. M. A.; van Duynhoven, J. P. M.; Verboom, W.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1995**, 1941−1942.

[4] For a recent review, see: (a) Dubois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437−463. (b) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991.

[5] For examples of monolayers with recognition sites, see: (a) Rojas, M. T.; Köninger, R.; Stoddart, J. F.; Kaifer, A. E. *J. Am. Chem. Soc.* **1995**, *117*, 336−343. (b) Adams, H.; Davis, F.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 2527−2529.

[6] Thoden van Velzen, E. U.; Engbersen, J. F. J.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1994**, *116*, 3597−3598.

[7] Schierbaum, K.-D; Weiss, T.; Thoden van Velzen, E. U.; Engbersen, J. F. J.; Reinhoudt, D. N.; Göpel, W. *Science* **1994**, *265*, 1413−1415.

[8] Porter recently reported on the S−C bond cleavage of sulfides upon adsorption to gold (Zhong, C.-J.; Porter, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 11616−11617). We have evidence that C−S cleavage does not occur in our case, as we will discuss in a forthcoming paper.

[9] Thoden van Velzen, E. U.; Engbersen, J. F. J.; de Lange, P. J.; Mahy, J. W. G.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1995**, *117*, 6853−6862.

[10] Huisman, B.-H.; Thoden van Velzen, E. U.; van Veggel, F. C. J. M.; Engbersen, J. F. J.; Reinhoudt, D. N. *Tetrahedron Lett.* **1995**, *36*, 3273−3276.

[11] Compound **2** was prepared by stepwise selective functionalization of tetrapropoxycalix[4]arene via 1,2-nitration, 3,4-iodination, and phthalimide insertion at the 3,4-positions, followed by reduction of the nitro groups and subsequent chloroacetylation (five steps). Tetrol **3** was synthesized from the corresponding resorcinarene via bromination of both the aromatic rings and the double bonds, selective debromination (recovering the double bonds), bridging of the octol, and bromo−lithium exchange, followed by quenching with trimethylborate and oxidation with hydrogen peroxide to the tetrol (four steps). Details of the synthesis will be published elsewhere.

[12] The general procedure for the preparation of similar carceplexes and their properties have recently been published, see ref 2 and references cited therein.

[13] Selected spectral data for **1·DMF**: ^1H NMR ($CDCl_3$) δ 7.65 (s, 4 H), 6.92 (s, 8 H), 6.74 (s, 4 H), 5.76, 3.98 (AB, $J = 7.0$ Hz, 8 H), 4.84 (s, 1 H), 4.81 (s, 8 H), 4.62 (t, $J = 8.0$ Hz, 4 H), 4.40, 3.18 (AB, $J = 13.0$ Hz, 8 H), 3.76 (t, $J = 7.5$ Hz, 8 H), 2.43 (t, $J = 7.5$ Hz, 16 H), 2.2−2.0 (m, 8 H), 1.9−1.7 (m, 8 H), 1.5−1.1 (m, 124 H), 0.98 (t, $J = 8.0$ Hz, 12 H), 0.82 (t, $J = 7.5$ Hz, 12 H), 0.66 (s, 6 H), −0.90 (s, 6 H); MS-FAB *m/z* 2736.9 $[(\mathbf{1} + \mathrm{DMF})]^+$, calcd for $C_{163}H_{243}O_{21}N_5S_4$ 2737.0], 2586.4 $[(\mathbf{1} + \mathrm{DMF} - (CH_2)_{10}SH + \mathrm{Na})]^+$, calcd 2587.0].

[14] Identical substrates and conditions were applied as decribed before in ref 9.

[15] Experimental details of the analytical techniques were described in ref 9 (electrochemical analysis, contact angle measurements) and ref 10 (IR). Ellipsometry was performed on a Plasmos Ellipsometer ($\lambda = 633$ nm) assuming a refractive index of 1.50 for the monolayer. For XPS an Escalab 220 XL was used with an Al Kα monochromized source.

[16] *Practical Surface Analysis*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; Wiley: Chichester, 1990; Vol. 1.

[17] Resistances of <5 kΩ were determined for disordered monolayers, while the resistance of highly-ordered layers was on average 300 kΩ, and incidentally up to 800 kΩ (unpublished results).

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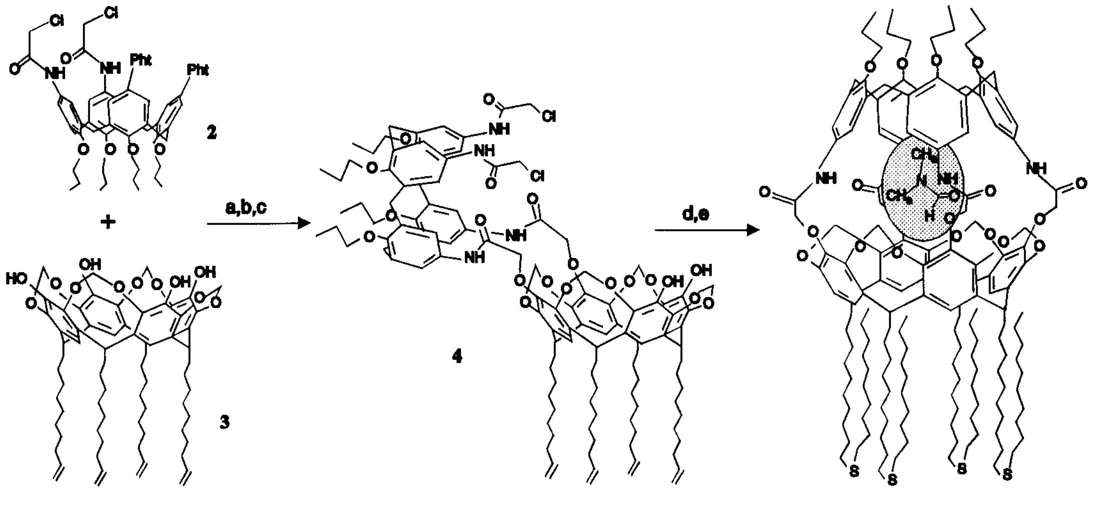
Scheme 1



(a) Cs_2CO_3, KI, 80 °C, MeCN, high dilution; (b) $N_2H_4 \cdot H_2O$, EtOH; (c) $ClCH_2C(O)Cl$, CH_2Cl_2;

(d) Cs_2CO_3, KI, 80 °C, DMF, high dilution; (e) $CH_3(CH_2)_9SH$, 9-BBN, THF.

Table 1. XPS Data for Carceplex **1·DMF** Monolayer

		atom %	
peak	center [eV]	measured	calcd
O 1s	533.2	11.4	10.9
N 1s	400.3	2.2	2.6
C 1s	284.7	84.8	84.5
S 2p	161.9	1.5	2.1

Table 2. Selected Infrared Peak Positions [cm^{-1}] for Carceplex **1·DMF** in the Bulk and the Monolayer

vibration	bulk	monolayer
$-CH_2-$, symmetrical	2853	2853
$-CH_2-$, asymmetrical	2924	2926
amide-I	1696	not obsd
amide-II	1526	1537

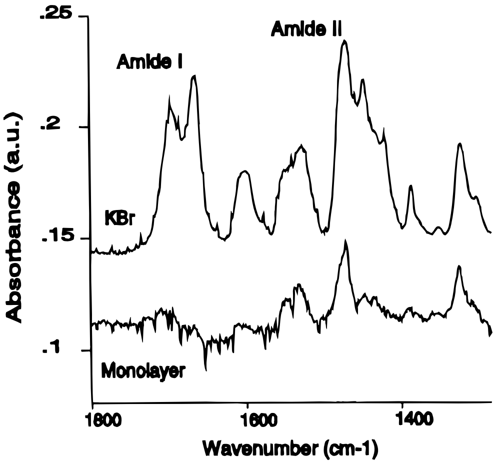


Figure 1. Infrared spectra from 1800−1250 cm^{-1} of carceplex **1·DMF** in KBr (top) and as a monolayer (bottom).

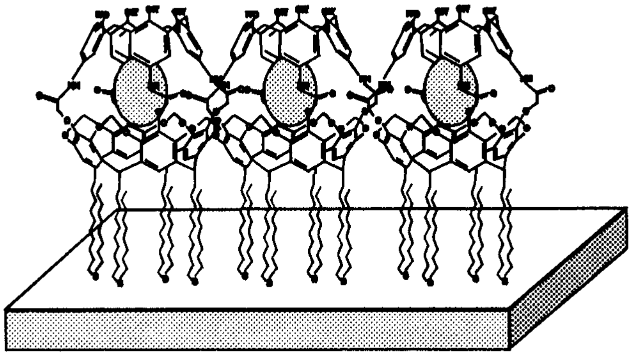


Figure 2. Schematic representation of carceplex **1·DMF** monolayer on gold.

as the maxima of the methylene C−H stretching modes in the monolayer are very similar to the bulk maxima. The infrared spectra further provide information about the orientation of the carceplex **1·DMF** on the monolayer. As presented in Figure 1 and Table 2, the amides in the carceplex clearly appear in the infrared bulk spectrum as both amide-I (predominantly C=O stretch) and amide-II bands (mainly C−N stretch and N−H bending).[18] In the monolayer spectrum, however, only an amide-II band appears at 1537 cm^{-1}, while amide-I is very weak or absent. This implies that the orientation of the transition dipole of the amide-I band is perpendicular to the p-polarization of the infrared beam, i.e. the carbonyl bonds are approximately parallel to the gold surface. This proves that the orientation of the carceplex **1·DMF** is perpendicular as schematically depicted in Figure 2.

In conclusion, asymmetric carceplexes can be ordered and positioned by means of self-assembly on gold. The high molecular order and the 2D confinement provide in principle the possibility of switching the incarcerated guests without affecting the orientation of the host. Currently, the possibilities to influence the orientation of the guest (and other guests) and switching this orientation are under investigation.

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[18] Hadzi, D. In *Infrared Spectroscopy and Molecular Structure*; Davies, M., Ed.; Elsevier: Amsterdam, 1963.