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PAPER

Preparation, reactivity and controlled release of SAMs of calix[4,6]arenes and calix[6]arene-based rotaxanes and pseudorotaxanes formed on polycrystalline Cu†

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Specific and reversible binding of guest molecules from a solution to a surface pre-treated with host molecules is a recent and active field of research. Self-assembled monolayers may result from supramolecular interactions, adding distinct functionalities to the surface. In this frame, the first compared study is given here of the anchoring on the technologically relevant Cu surface of calix[4]arene receptors and calix[6]arene-based rotaxanes and pseudorotaxanes. These molecules, which belong to the most representative classes of compounds in supramolecular chemistry, have been chosen for their synthetic accessibility and versatility, which make them useful building blocks for the synthesis of new advanced supramolecular structures. Covalent functionalisation of calix[4,6]arenes on Cu was reached *via* a dip-coating procedure, optimizing the various synthetic aspects in order to obtain good coverages and copper passivation. Molecular adhesion has been demonstrated by the presence and relative quantitation of XPS signals from specific elements in the molecules. We have successfully tested the combination of different functionalities by producing a mixed film, prepared by ligand exchange of calix[4]arene with undecanethiol. The availability of the calix[4]arene cavity to reversibly host further species after anchoring on Cu has been demonstrated by a sequence of uptake and release cycles with pyridinium salts. Rotaxane and pseudorotaxane species, composed of a calix[6]arene wheel functionalized with *N*-phenylurea groups on the upper rim, and a viologen-containing axle, have been anchored on Cu *via* the SH-termination of the axle. XPS demonstrated the successful self-assembly of fully threaded rotaxanes and pseudorotaxanes from their solutions and the controlled release upon biasing of full rotaxanes and of the pseudorotaxane wheel.

Introduction

In the frame of supramolecular studies, the combination of suitable molecules and surfaces of inorganic solids which have been pre-organized to produce a host–guest interaction is relatively new and may lead to materials with new and tuneable properties for perspective applications. These hybrid materials generally own more attractive properties, compared with their separate counterparts. By covering metal surfaces and metal nanoparticles with an organic stabilizing shell, very interesting examples of hybrid materials are obtained.[1] 2D self-assembled monolayers (2D-SAMs) or monolayer-protected clusters (MPCs or 3D-SAMs) can be obtained, respectively. The enticing aspect of these systems is that the nature of both the metal and the organic layer can influence the properties of the resulting hybrid material. During the last decade, it became progressively clear that supramolecular chemistry, through the application of a "bottom-up approach", opens virtually unlimited possibilities to the design of nanomaterials and nanoscale objects.[2] The controlled production of organic SAMs on metal surfaces started in 1983, and is now a mature field. Early studies reported the behaviour of alkanethiols and dialkyl sulfides or disulfides on Au.[3] Various examples of functional species have thereafter been proposed, such as redox species,[4–6] biomolecules or selective receptors.[7,8] The use of model surfaces of a high technological impact, such as Cu, to investigate molecular recognition reactions can provide great insights into different classes of phenomena. In molecular electronics, a critical issue is the establishment of a robust and

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reliable metal contact without damage of the organic layer and contamination of the interface. Cu is a metal of choice for vias. In the literature, a few different methods are described to this aim, as producing Cu deposits on self-assembled monolayers (SAMs) covalently attached to a semiconductor as Si,[9] or depositing Cu nanoparticles on semiconductor surfaces.[10] We are interested in a selective functionalisation procedure of a substrate as a key-step towards controlled deposition of suitable metals (also as nanoparticles) on semiconductors. In the case of Cu and Si, distinct and selective anchoring groups towards the two moieties are needed in case a bridging bond should be established between, *e.g.*, Cu nanoparticles and a pre-patterned Si surface. Moreover, investigations on the reactivity of polycrystalline Cu surfaces can be considered as preliminary to Cu single-crystal studies.[11] We have been investigating for several years the reactivity of organics and organometallics both on Si oriented surfaces, also exploring molecular recognition reactions, and on single crystals and polycrystalline copper.[12,13] We made use primarily of photoemission spectroscopies, coupled with EXAFS and other synchrotron-radiation based techniques, because of their effectiveness in evidencing formation and stimulated evolution of chemical bonds. Among the several macrocyclic synthetic hosts that have been used as receptors in supramolecular chemistry, calixarenes have found wide application as molecular platforms, on which a large variety of binding sites can be inserted and oriented in space, or as tridimensional receptors able to include into their aromatic cavities either neutral or charged species.[14] Calix[6]arene derivatives functionalized with *N*-phenylureido groups have been recently employed as active components for the preparation of prototypes of molecular machines.[15] Owing to their particular shape and size, these macrocycles can act as asymmetric wheels for *N*,*N*′-dialkyl-4,4′-dipyridinium salts (viologens), to give rise to self-assembled species belonging to the class of rotaxanes and pseudorotaxanes.[14*b*–*f*] These latter are supramolecular complexes characterized by high thermodynamic stability, which can be reversibly disassembled in solution by external electrochemical stimuli.[2]

We report here the first surface study on the application of supramolecular systems on Cu. The molecular species here selected are the very versatile calix[4,6]arenes, which have been studied together with rotaxanes and pseudorotaxanes as important applications. The characterization of the bonding interactions, of the reactivity of the anchored systems towards host–guest interactions, and of the effectiveness of controlled release upon biasing have been all conducted by the use of XPS.

Experimental section

Synthesis

All reactions were carried out under nitrogen; all solvents were freshly distilled under nitrogen and stored over molecular sieves for at least 3 h prior to use. ^{1}H and ^{13}C NMR spectra were recorded on instruments operating at 300 and 75 MHz, respectively. Mass spectra were recorded in the ESI mode. Melting points are uncorrected. Calix[4]arene **3**,[16] calix[6]arene **6**,[15*f*] *N*-hydroxymethyl-*N*-phenylurea,[17] 1,6-bis(toluene-4-sulfonyloxy)-hexane,[18] pentyl tosylate **8**,[19] and undec-10-enyl tosylate[20] were synthesized according to reported procedures. All other reagents were of reagent grade quality as obtained from commercial suppliers and were used without further purification.

Calix[4]arene (4). A solution of calix[4]arene **3** (1.2 g, 1.4 mmol) and *N*-hydroxymethyl-*N*-phenylurea (0.23 g, 1.4 mmol) in dry CH_2Cl_2 (100 mL) was cooled at 0 °C with an external ice bath. After stirring for 15 min, $AlCl_3$ (0.4 g, 3 mmol) was added and the resulting mixture was stirred for further 30 min. The external ice bath was removed and the mixture was left to react at room temperature under stirring for 2.5 h. After this period, the reaction was quenched by adding 100 mL of distilled water. The resulting organic phase was separated, washed with water up to neutrality, dried over Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was purified by column chromatography (eluent: hexane/ethyl acetate = 7/3) to afford 0.6 g of **4** (40%) as a white solid (found: C, 72.10; H, 7.59; N, 2.69; S, 6.06. $C_{62}H_{80}N_2O_7S_2$ requires: C, 72.37; H, 7.78; N, 2.72; S, 6.22%); mp 45.5 °C–46.5 °C; δ_H (300 MHz, $CDCl_3$) 8.33 (s, 1H), 8.27 (s, 1H), 7.3–6.6 (m, 16H), 6.3 (bs, 1H), 4.9 (bt, 1H), 4.4–4.2 (m, 6H), 3.99 (t, 4H, J = 6.5 Hz), 3.37 and 3.35 (2d, 4H, J = 13 Hz), 2.84 (t, 4H, J = 7.2 Hz), 2.30 (s, 6H), 2.2–2.0 (m, 4H), 1.8–1.2 (m, 32H); δ_C (75 MHz, $CDCl_3$) 196.5, 156.1, 153.3, 152.6, 151.9, 138.9, 133.4, 133.3, 129.1, 128.9, 128.7, 128.4, 128.1, 128.0, 125.2, 122.7, 119.7, 119.0, 76.7, 43.9, 31.4, 31.3, 30.4, 30.0, 29.6, 29.5 (2 resonances), 29.2, 28.8, 25.9; *m*/*z* (ESI) 1051 (M + Na$^+$, 100), 1052 (M + Na$^+$, 70).

Calix[4]arene (5). CH_3ONa (0.2 g, 4 mmol) was added to a solution of calix[4]arene **4** (0.4 g, 0.4 mmol) in a 1 : 1 mixture of CH_3OH : THF (50 mL) kept under argon atmosphere. After stirring for 15 min, 1,4-dithioerythritol (0.36 g, 2.3 mmol) was added. After stirring at room temperature for 3 h, 0.5 g of activated DOWEX-H$^+$ was added to the reaction mixture. The solution was filtered, evaporated to dryness under reduced pressure. The solid residue was purified by column chromatography (eluent: CH_2Cl_2/ethyl acetate = 95/5) to yield 0.26 g of **5** (70%) as a white solid (found: C, 73.53; H, 8.30; N, 2.86; S, 6.71. $C_{58}H_{76}N_2O_5S_2$ requires: C, 73.72; H, 8.05; N, 2.97; S, 6.78%); mp 67.5–68.5 °C; δ_H (300 MHz, $CDCl_3$) 8.32 (s, 1H), 8.25 (s, 1H), 7.3–6.6 (m, 16H), 6.2 (bs, 1H), 4.9 (bt, 1H), 4.4–4.2 (m, 6H), 3.99 (t, 4H, J = 6.5 Hz), 3.37 and 3.35 (2d, 4H, J = 13 Hz), 2.51 (m, 4H), 2.2–2.0 (m, 4H), 1.8–1.2 (m, 16H); δ_C (75 MHz, $CDCl_3$) 155.6, 153.3, 152.7, 151.9, 138.4, 133.4, 133.2, 129.0, 128.9, 128.7, 128.5, 128.4, 128.1, 128.0, 125.1, 123.5, 120.6, 119.0, 76.7, 44.1, 34.0, 31.4, 31.3, 29.9, 29.6 (2 resonances), 29.5, 29.4, 29.1, 28.3, 25.9, 24.6; *m*/*z* (ESI) 967 (M + Na$^+$, 100), 968 (M + Na$^+$, 65).

6-(3,5-Di-*tert*-butylphenoxy)hexyl tosylate (7). A solution of 1,6-bis(toluene-4-sulfonyloxy)hexane (10 g, 0.02 mol), 3,5-di-*tert*-butylphenol (4.4 g, 0.02 mol) and K_2CO_3 (3.2 g, 0.02 mol) in CH_3CN (200 mL) was refluxed and stirred for 48 h. After this period, the solvent was completely evaporated under reduced pressure and the solid residue was taken up with

CH_2Cl_2 and H_2O. The separated organic layer was washed with H_2O, dried over Na_2SO_4, and evaporated to dryness. Purification of the solid residue by column chromatography (silica gel, hexane 70%–ethyl acetate 30%) afforded 7.8 g of tosylate **7** (85%) as a white solid (found: C, 70.77, H, 8.42, S, 7.22. $C_{27}H_{40}O_4S$ requires: C, 70.39, H, 8.75, S, 6.96%); mp 79–80 °C; δ_H ($CDCl_3$, 300 MHz) 7.79 (d, 2H, $J = 8.3$ Hz), 7.33 (d, 2H, $J = 8.3$ Hz), 7.01 (t, 1H, $J = 1.5$ Hz), 6.73 (d, 2H, $J = 1.5$ Hz), 4.04 (t, 2H, $J = 6.4$ Hz), 3.92 (t, 2H, $J = 6.4$ Hz), 1.8–1.6 (m, 4H), 1.5–1.3 (m, 4H), 1.30 (s, 18H); δ_C ($CDCl_3$, 75 MHz) 152.1, 129.7, 127.8, 114.8, 108.7, 70.5, 67.3, 34.9, 31.4, 28.7, 29.2, 25.5, 25.1; m/z (ESI) 483 (M + Na^+, 100).

General procedure for the synthesis of the monotosylate salts **9**·*TsO and* **10**·*TsO*. A solution of the proper tosylate (**7** or **8**, 0.01 mol) and 4,4′-bipyridyl (1.6 g, 0.01 mol) in CH_3CN (300 mL) was refluxed with stirring for 48 h. After cooling to room temperature, the solvent was completely evaporated under reduced pressure and the sticky residue was taken up with hot ethyl acetate. After cooling to room temperature, the desired pure monotosylate salt was recovered as a white solid by suction filtration.

9·TsO: 4 g (65%) (found: C, 71.84, H, 7.84, N, 4.54, S, 5.20. $C_{37}H_{48}N_2O_4S$ requires: C, 72.04, H, 8.11, N, 4.24, S, 4.89%); mp 59–60 °C; δ_H ($CDCl_3$, 300 MHz) 9.21 (d, 2H, $J = 6.5$ Hz), 8.73 (d, 2H, $J = 5.4$ Hz), 8.18 (d, 2H, $J = 6.5$ Hz), 7.73 (d, 2H, $J = 8$ Hz), 7.55 (d, 2H, $J = 8$ Hz), 7.08 (d, 2H, $J = 8$ Hz), 6.99 (t, 1H, $J = 1.5$ Hz), 6.70 (d, 2H, $J = 1.5$ Hz), 4.75 (t, 2H, $J = 6$ Hz), 3.87 (t, 2H, $J = 6$ Hz), 2.25 (s, 3H), 2.0–1.9 (m, 2H), 1.7–1.6 (m, 2H), 1.5–1.4 (m, 2H), 1.28 (s, 20H); δ_C ($CDCl_3$, 75 MHz) 158.4, 153.1, 152.1, 151.2, 150.6, 145.7, 143.5, 140.9, 139.4, 128.7, 125.8, 125.6, 121.4, 114.8, 108.6, 67.0, 61.5, 34.9, 31.4, 31.1, 29.5, 25.6, 25.4, 21.2; m/z (ESI) 445 (M − TsO, 100).

10·TsO: 3 g (75%) (found: C, 66.62, H, 7.68, N, 6.91, S, 8.14. $C_{22}H_{26}N_2O_3S$ requires: C, 66.30, H, 7.58, N, 7.03, S, 8.05%); mp 155.5–156.5 °C; δ_H (CD_3OD, 300 MHz) 9.08 (d, 2H, $J = 6.8$ Hz), 8.79 (d, 2H, $J = 5.9$ Hz), 8.46 (d, 2H, $J = 6.7$ Hz), 7.96 (d, 2H, $J = 6.2$ Hz), 7.66 (d, 2H, $J = 8$ Hz), 7.19 (d, 2H, $J = 8$ Hz), 4.65 (t, 2H, $J = 7.6$ Hz), 2.33 (s, 3H), 2.2–2.0 (m, 2H), 1.5–1.3 (m, 4H), 0.94 (t, 3H, $J = 6.6$ Hz); δ_C (CD_3ODCl_3, 75 MHz) 155.1, 152.1, 146.8, 144.0, 143.9, 142.0, 130.2, 128.5, 127.4, 127.2, 123.8, 63.0, 32.5, 32.4, 29.6, 23.5, 21.6, 14.5; m/z (ESI) 227 (M − TsO, 100).

S-11-(Tosyloxy)undecyl ethanethioate (11). To a solution of undec-10-enyl 4-methylbenzenesulfonate (5 g, 0.015 mol) and thioacetic acid (5.9 g, 77 mmol) in dry toluene (200 mL), a tip of spatula of AIBN was added. After refluxing for 5 h, the reaction was quenched by addition of water (200 mL). The separated organic phase was dried over Na_2SO_4. After the removal of the solvent under reduced pressure, the solid residue was purified by column chromatography (eluent: hexane/ethyl acetate = 9/1) to afford 5.7 g of **11** (95%) as a yellowish solid (found: C, 59.57; H, 8.15; S, 16.23. $C_{20}H_{32}O_4S_2$ requires: C, 59.96; H, 8.05; S, 16.01%); mp 28.0–29.5 °C; δ_H (300 MHz, $CDCl_3$) 7.78 (d, 2H, $J = 8.3$ Hz), 7.34 (d, 2H, $J = 8.3$ Hz), 4.01 (t, 2H, $J = 6.6$ Hz), 2.85 (t, 2H, $J = 7.2$ Hz), 2.44 (s, 3H), 2.32 (s, 3H), 1.8–1.5 (m, 4H), 1.4–1.1 (m, 14H); δ_C (75 MHz, $CDCl_3$) 195.0, 144.4, 140.3, 130.5, 128.3, 70.0, 32.5, 30.5, 29.7 (2 resonances), 29.5 (2 resonances), 29.3 (2 resonances), 28.8 (2 resonances), 25.8, 21.3; m/z (ESI) 432 (M + Na^+, 100).

General procedure for the synthesis of viologens **12**·*2TsO and* **14**·*2TsO*. A solution of the monotosylate salt (**9**·TsO or **10**·TsO, 3.3 mmol) and S-11-(tosyloxy)undecyl ethanethioate **11** (1.4 g, 3.3 mmol) in CH_3CN (70 mL) was refluxed for 72 h at 95 °C in a sealed glass autoclave. After cooling to room temperature, the reaction mixture was evaporated to dryness under reduced pressure. Recrystallization of the solid residue from CH_3CN affords the desired viologen salt as a white solid.

12·2TsO: 1.7 g (50%) (found: C, 67.55, H, 8.53, N, 2.99, S, 9.10. $C_{57}H_{80}N_2O_8S_3$ requires: C, 67.23, H, 8.65, N, 2.75, S, 9.45%); mp 160–162 °C; δ_H (CD_3OD, 300 MHz) 9.27 (bt, 4H), 8.66 (d, 4H, $J = 6.7$ Hz), 7.70 (d, 4H, $J = 8$ Hz), 7.23 (d, 4H, $J = 8$ Hz), 7.03 (t, 1H, $J = 1.5$ Hz), 6.70 (d, 2H, $J = 1.5$ Hz), 4.8–4.7 (m, 4H), 3.99 (t, 2H, $J = 6$ Hz), 2.86 (t, 2H, $J = 7$ Hz), 2.38 (s, 6H), 2.31 (s, 3H), 2.2–2.0 (m, 4H), 1.9–1.7 (m, 2H), 1.7–1.3 (m, 38H); δ_C ($CDCl_3$, 75 MHz) 158.5, 152.0, 148.7, 146.1, 143.3, 139.6, 128.8, 127.3, 125.7, 114.8, 108.6, 67.2, 61.9, 34.9, 31.4, 30.6, 29.4, 29.3, 29.2, 29.0, 28.9, 28.7, 26.0, 25.9, 25.5, 21.2; m/z (ESI) 337 (M − 2TsO, 100).

14·2TsO: 1.7 g (65%) (found: C, 63.07, H, 7.12, N, 3.44, S, 11.87. $C_{42}H_{58}N_2O_7S_3$ requires: C, 63.13, H, 7.32, N, 3.51, S, 12.04%); mp 145.0–146.0 °C; δ_H (DMSO-d_6, 300 MHz) 9.38 (d, 4H, $J = 5.7$ Hz), 8.77 (d, 4H, $J = 6.7$ Hz), 7.46 (d, 4H, $J = 8$ Hz), 7.10 (d, 4H, $J = 8$ Hz), 4.68 (t, 4H, $J = 7$ Hz), 2.80 (t, 2H, $J = 7.2$ Hz), 2.31 (s, 3H), 2.28 (s, 6H), 2.1–1.9 (m, 4H), 1.6–1.2 (m, 20H), 0.88 (t, 3H, $J = 6.7$ Hz); δ_C (DMSO-d_6, 75 MHz) 195.1, 148.3, 145.6, 145.5, 137.5, 127.9, 126.4, 125.3, 60.7, 33.2, 30.7, 30.4, 30.3, 29.0, 28.7, 28.6, 28.4, 28.3, 28.2, 28.0, 27.6, 27.4, 25.3, 23.6, 21.4, 20.6, 13.6; m/z (ESI) 228 (M − 2TsO, 100).

General procedure for the synthesis of the thiolate viologen axles **13**·*2TsO and* **15**·*2TsO*. To a solution of the viologen salt (**12**·2TsO or **14**·2TsO, 2 mmol) in EtOH (150 mL), toluene-4-sulfonic acid (0.5 g, 2.5 mmol) was added. The resulting mixture was refluxed under stirring for 48 h. After this period, the solvent was evaporated under reduced pressure. The solid residue was triturated with hot ethyl acetate. After cooling to room temperature, the desired thiolate viologen axle was recovered as a pure white solid by suction filtration.

13·2TsO: 1.35 g (70%) (found: C, 67.91, H, 7.85, N, 3.18, S, 10.13. $C_{55}H_{78}N_2O_7S_3$ requires: C, 67.72, H, 8.06, N, 2.90, S, 9.86%); mp 189–191 °C; δ_H ($CDCl_3$, 300 MHz) 9.21 (bt, 4H), 8.79(d, 4H, $J = 6.6$ Hz), 7.70 (d, 4H, $J = 8$ Hz), 7.10 (d, 4H, $J = 8$ Hz), 6.71 (d, 2H, $J = 1.5$ Hz), 6.99 (t, 1H, $J = 1.5$ Hz), 4.7–4.6 (m, 4H), 3.85 (t, 2H, $J = 6$ Hz), 2.6–2.4 (m, 2H), 2.26 (s, 6H), 1.9–1.8 (m, 4H), 1.7–1.5(m, 4H), 1.5–1.0 (m, 36H); δ_C NMR ($CDCl_3$, 75 MHz) 158.5, 152.1, 148.7, 145.8, 143.3, 139.6, 128.9, 127.3, 125.7, 114.8, 108.7, 67.2, 61.9, 34.9, 29.6, 29.4, 29.1, 29.0, 28.9, 28.7, 26.0, 25.9, 25.7, 25.5, 21.2; m/z (ESI) 316 (M − 2TsO, 100).

15·2TsO: 1 g (69%) yield (found: C, 63.32, H, 7.51, N, 3.60, S, 12.46. $C_{40}H_{56}N_2O_6S_3$ requires: C, 63.46, H, 7.46, N, 3.70, S, 12.71%); mp 236.0–237.0 °C; δ_H ($CDCl_3$, 300 MHz) 9.19 (d, 4H, $J = 6.3$ Hz), 8.85 (d, 4H, $J = 6$ Hz), 7.74 (d, 4H, $J = 8.1$ Hz), 7.16 (d, 4H, $J = 7.9$ Hz), 4.65 (bt, 4H), 2.5–2.4 (m, 2H), 2.33 (s, 6H), 2.0–1.8 (m, 4H), 1.7–1.5 (m, 2H), 1.5–1.1 (m, 18H), 0.85 (t, 3H, *J* = 6.7 Hz); δ_C (CD_3OD, 75 MHz) 151.5, 147.3, 144.0, 142.0, 130.2, 128.6, 127.2, 63.5, 40.0, 35.5, 32.9, 32.5, 30.9 (2 resonances), 30.8, 30.6, 30.5, 29.7 (2 resonances), 29.6, 27.5, 25.2, 23.5, 21.6, 14.5; *m*/*z* (ESI) 207 (M − 2TsO, 100).

General procedure for the synthesis of pseudorotaxanes **6**⊃**13**·*2TsO and* **6**⊃**15**·*2TsO*. To a stirred solution of calix[6]-arene **6** (0.01 g, 0.007 mmol) in toluene (10 ml), an excess of desired axle (0.02 mmol) was added. After few minutes, the colour of the toluene solution turns orange-red. The reaction mixture was stirred at room temperature for further 30 min and then filtered off to remove the solid suspension. The resulting toluene solutions containing the pseudorotaxanes (**6**⊃**13**·2TsO or **6**⊃**15**·2TsO) were used for the monolayer preparation without any further purification.

Monolayer preparation on copper. The polycrystalline Cu substrates (99.95%) were cleaned by immersion into the 32.5% nitric acid solution for 30 s followed by the immersion into 3.7% hydrochloric acid solution for 7 min. The samples were eventually rinsed with large amounts of distilled water, and immediately dipped into the appropriate thiol solution for 4 h. Toluene and CH_2Cl_2 were the solvents used for surface adsorption. We used a 0.2 mM solution for calixarenes, 0.4 mM for rotaxane and pseudorotaxane, in order to maintain the same concentration of sulfur. As a reference, a copper surface was covered with undecanethiol (45 mM solution for 17 h, to form a self-assembled monolayer). A mixed film was prepared by ligand exchange: the copper substrate functionalized with calix[4]arene was immersed in the undecanethiol solution for 4 h. XPS analysis was accomplished to evaluate the monolayer composition.

The reactivity of the rotaxane and pseudorotaxane was investigated in toluene and dichloromethane, in order to possibly evidence the influence of a different polarity of the solvent on the threading of the adducts and their assembling on the Cu surface. The kinetics of formation of the adducts is favored in a dichloromethane solution,[15e] but the larger solubility of the charged axle may favor the anchoring of the bare axle directly to the surface. The overall behavior of the adducts in the two solvents was found closely comparable. In toluene we observed a closer match between theoretical and experimental atomic ratios for both NH/N^+ and C/S, but the surface coverage was much lower.

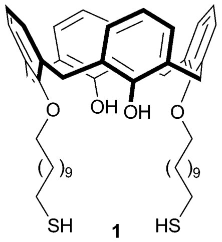
X-Ray photoelectron spectroscopy. XPS results were obtained on an experimental apparatus in UHV consisting of a modified Omicron NanoTechnology MXPS system, with an XPS chamber equipped with a dual X-ray anode source (Omicron DAR 400) and an Omicron EA-127 energy analyzer, and an attached VT-atomic force and scanning tunneling microscope. Sample transfer between the various experimental areas was conducted by means of linear magnetic transfer rods or manipulators. All measurements were conducted in the least possible time after sample preparation. Samples were produced directly on cleaned polycrystalline Cu sample holders. No sizeable sign of sample degradation under the acquisition times under the X-rays was observed for the samples. MgKα and AlKα photons were employed ($h\nu$ = 1253.6 and 1486.6 eV, respectively), generated operating the anode at 14–15 kV, 10–20 mA. BE values were derived from experimentally determined kinetic energies (KEs) from the relation: $BE = h\nu - KE$, after spectrometer energy calibration with metal standards. XPS atomic ratios for the bipyridine-functionalized hybrids were estimated from experimentally determined area ratios of the relevant core lines, corrected for the corresponding theoretical atomic cross-sections and for a square-root dependence of the photoelectrons kinetic energies. All reported spectra were acquired at a photoelectron take-off angle of 11° measured from the surface normal. Surface coverage was estimated by making use of eqn (1) and (3) in the model for the substrate attenuation of core line intensity exerted by an alkanethiol monolayer on Au.[21] The values for S 2p and Cu 2p inelastic mean free path (IMFP) at the photon energy employed were taken from ref. 20.

Cyclic voltammetry. Cyclic voltammetry was performed in 0.1 M $NBut_4ClO_4$ (tetrabutylammonium perchlorate, TBAP) in dry CH_3CN. The electrolyte solution contained no deliberately added electroactive species. All electrochemical measurements were performed with a three-electrode cell using an Autolab Electrochemical Analyzer (model PGSTAT 12, Eco Chemie BV, The Netherlands). The counter electrode was a platinum coil wire, and a silver wire immersed in 0.01 M $AgNO_3$/0.1 M TEAP in CH_3CN, separated from the main solution by a porous fritted glass + agar plug, served as a reference electrode. All potentials reported will be henceforth referred to this reference.

Results and discussion

Production and characterization of calix[4,6]arenes on Cu

The functionalization of polycrystalline copper surfaces with calixarene-based receptors requires the introduction on the calixarene macrocycle of suitable "anchoring points". The high affinity of sulfur for copper has been largely documented;[22] therefore, calix[4]arene **1** and calix[6]arene **2**, characterized by the presence of two and three ω-alkylthiolate chains on their lower rims, respectively, were chosen as active coating agents of the copper surface.[23]



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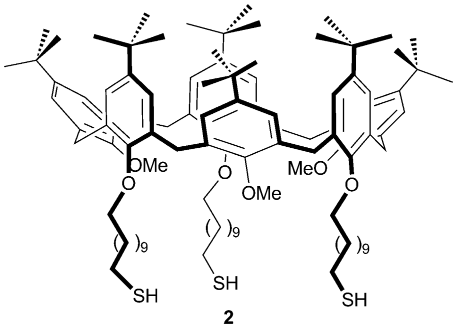


2

The chemisorption experiments were systematically conducted on polycrystalline Cu surfaces, which were preliminarily characterized by XPS. The relevant region of adsorbed calixarenes **1** and **2** is S 2p, which is reported in Fig. 1, together with the spectrum of undecanethiol ($C_{11}SH$), which we took as the reference compound for the present investigation, since it is known to form a nearly ideal SAM on Cu.[24] Two S 2p spin–orbit split doublets were always evident, which refer to the formation of thiolate and, at a higher binding energy (BE), to the presence of residual thiol groups. These last could belong to calixarenes chemisorbed *via* a different thiol group and/or to purely physisorbed molecules. The amount of this component did not exceed ~10% for calixarenes **1** and **2**, and it was much smaller in the case of $C_{11}SH$ (3%).

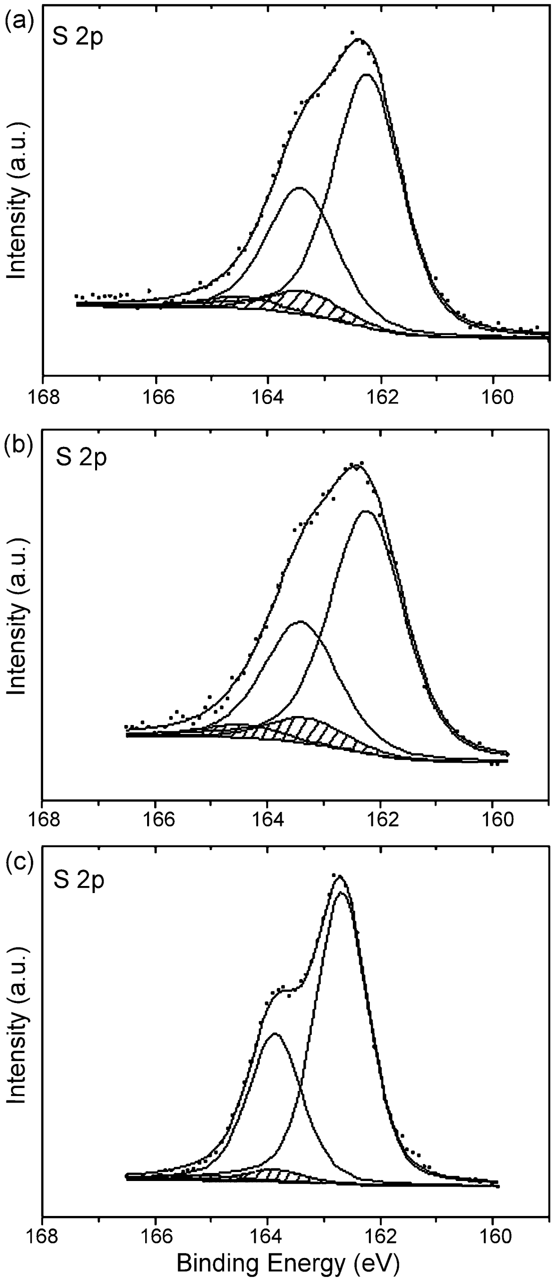


Fig. 1 S 2p XPS spectra taken at 11° from the surface normal of the Cu/thiolate ligand. The main spin–orbit split component is due to thiolate. The cross-hatched areas identify the component due to SH. (a) **1**, (b) **2** and (c) undecanethiol ($C_{11}SH$).

Table 1 XPS peak positions and quantitative ratios (±10%), and values of surface coverage (σ) for Cu/calixarene, Cu/C_{11}SH and mixed film

	S 2p (eV)	SCu/Cu	σ/nm^{-2}	SH/SCu	C/S (theor.)
1	162.7 163.9	0.45	3.1	0.12	28 (25)
2	162.2 163.3	0.47	3.2	0.10	34 (34)
$C_{11}H_{23}SH$	162.2 163.3	0.51	3.8	0.03	12 (11)
2 + C_{11}[a]	162.3 163.3	0.49	3.4	0.12	17

[a] Mixture of **2** and $C_{11}H_{23}SH$.

The surface coverage, σ, was estimated by means of a literature model,[21,25] by making use of the SCu(thiolate)/Cu ratio (columns 2 and 3 in Table 1). The atomic ratios of calixarenes are, within the experimental error, closely similar to the case of $C_{11}SH$. The coverages fall in the same range, hinting at a close-to-ideal monolayer coverage. These results are consistent with the passivation of Cu surfaces. In fact, only Cu(0) and Cu(I) components are present in the Cu LMM Auger spectra, while a Cu(II) component was never found in the Cu 2p spectrum (Fig. 2).

A clear indication that molecules adsorb intact on the surface with no added contamination comes from inspection of column 5 in Table 1, where a superposition can be seen between theoretical and experimental C/S ratios. We took this encouraging result as a reference in our study of a mixed

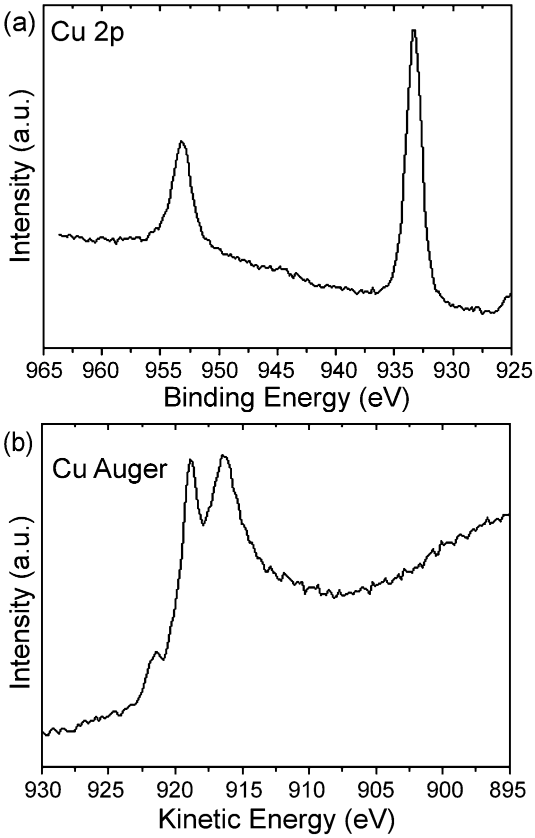


Fig. 2 Cu 2p and Cu LMM Auger lines of Cu/calixarenes **1** and **2**.

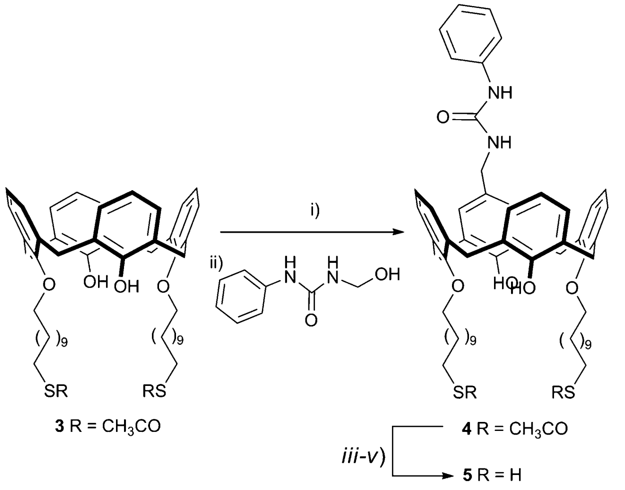
monolayer, which we produced in order to demonstrate the feasibility of a double functionalization. Such a monolayer was obtained by ligand exchange, starting from a Cu/calix[4]-arene **1** surface, which was eventually contacted with $C_{11}SH$. The experimental C/S value is 17, right in between calix[4]arene **1** and $C_{11}SH$, which hints at a 1 : 1 monolayer on Cu.

Recognition reactions of *N*-methylpyridinium ion-pairs towards anchored heteroditopic calix[4]arene receptors

We tested the reactivity of heteroditopic calixarenes anchored on Cu with a series of experiments. To this aim, we selected the heteroditopic calix[4]arene **5** in order to extend to surfaces our solution studies on its reactivity towards *N*-methylpyridinium and *N*,*N*′-dimethylviologen salts.[26] **5** was synthesized in *ca.* 30% of the overall yield following the pathway described in Scheme 1.

In previous studies,[27] we evidenced how a phenylureido group in the upper rim of a calixarene macrocycle allows for a combined effect (a cooperative heteroditopic effect[28]) on the recognition of a salt. The combination of a hard H-bond, which can be established by the urea group with an anion, with a soft calix-cation π-bond,[29] through the methyl group of the pyridinium, reduces the ionic interaction in the salt, as testified, *e.g.*, by the fact that *N*-methyl pyridinium chloride (NMPCl), when it acts as a guest, is a ligand-separated ion pair, in the solid state.[26b] By testing a series of NMP salts with different anions, such as tosylate, Cl^-, I^-, trifluoroacetate, we determined the binding constants at RT for the formation of 1 : 1 adducts in $CHCl_3$, which evidenced that the phenylurea group increases the affinity for the NMPX salt by up to two orders of magnitude with respect to the monotopic receptor.[26a]

A sequence of N 1s XPS spectra of Cu/calix[4]arene **5** is reported in Fig. 3. They were obtained after a first cycle of immersion in a CH_2Cl_2 solution of *N*-methyl pyridinium iodide (NMPI), followed by rinsing in CH_3OH acidified with HCl and by a second immersion in the solution of the pyridinium salt.‡ Each N 1s spectrum of this sequence is complex, and three components result from curve fitting. The main component, also present in the initial sample, before complexation, is assigned to the calixarene phenylureido group, on the basis of the literature.[30] A second peak



Scheme 1 *Reactions and conditions*: (i) $AlCl_3$, CH_2Cl_2, 15 min, $T = 0\ ^\circ C$; (ii) 3 h, $T = 25\ ^\circ C$; (iii) CH_3OMe, THF/MeOH, $T = 25\ ^\circ C$, 15 min; (iv) 1,4-dithioerythritol, THF/MeOH, $T = 25\ ^\circ C$, 3 h; (v) activated DOWEX-H^+, THF/MeOH.

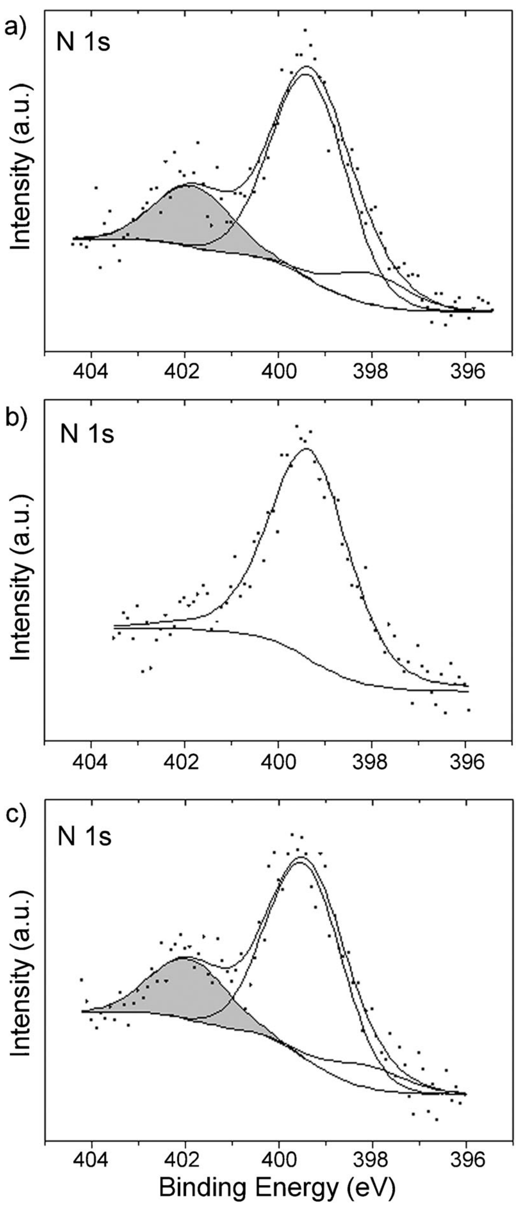


Fig. 3 Sequence of N 1s XPS spectra taken at 11° from the surface normal of Cu/**5**, after immersion in a CH_2Cl_2 solution of NMPI (a), after subsequent rinsing in a CH_3OH solution, acidified with HCl (b), after a new immersion in the above solution (c) (the gray areas identify the component due to N^+).

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‡ The N 1s XPS spectra for Cu/calix[4]arene **5** before and after immersion in the pyridine solution are closely similar, as a result of the presence of adventitious NH_4^+ ions (presumably coming from DOWEX-H^+ resin used in the deprotection step) in the former. In this sample, the rinsing procedure applied to the sequence of samples in Fig. 3 was not effective in removing ammonium, because of the poor solubility of this cation in CH_3OH. We recall here that water rinsing cannot be applied. Notice that the N^+ component in the two cases comes from distinct species, ammonium and pyridinium, respectively.

component at a higher BE, characteristic for N^+,[31] appears after each immersion cycle, while it is absent upon rinsing with acidified CH_3OH. Such component necessarily relates to the coordination of the pyridinium cation by the calix[4]arene (Fig. 3a and c). The minor component at ~398 eV is assigned to a direct coordination to the Cu surface of neutral pyridine molecules,[32] an impurity which may accompany the synthesis of methylpyridinium. This assignment of the component is further supported by its disappearance upon acid rinsing in CH_3OH.

We have established the extent of such a recognition reaction by taking the experimental relative atomic ratios between the two N 1s components, reported in Table 2. Such ratios differ from the value expected from stoichiometry, indicating that the filling of the calix sites by the pyridinium amounted to 60–70%. The establishment of the recognition reaction and the molecular integrity are confirmed by the close match, within the experimental error, of experimental and theoretical C/N values (Table 2).

The S 2p spectrum of Cu/**5** is reported in Fig. 4, where the two spin–orbit split doublets, already assigned above, are present in a SH/SCu 0.27 ratio. The larger amount of physisorbed molecules, with respect to the simpler calix[4]arene, is expected because of the presence of the phenylureido group. A coverage of 0.43 nm^{-2} can be calculated from the SCu/Cu ratio.[21,25]

Table 2 XPS peak positions and NH/N^+ quantitative ratios (±10%) for Cu/**5** as prepared and as a function of progressive NMP^+ uptake from a solution and rinsing

	S 2p (eV)	N 1s (eV)	NH/N^+ (theor.)	C/N (theor.)
Cu/**5** + NMPI[a] (1st cycle)	161.9	398.0	3.0 (2)	21.2 (21.3)
	163.2	399.3		
		401.8		
After rinsing	161.9	398.0	—	27.4 (29)
	163.2	399.3		
		401.8		
Cu/**5** + NMPI[a] (2nd cycle)	161.9	398.0	2.6 (2)	24.1 (21.3)
	163.2	399.3		
		401.8		

[a] CH_2Cl_2 solution of NMPI.

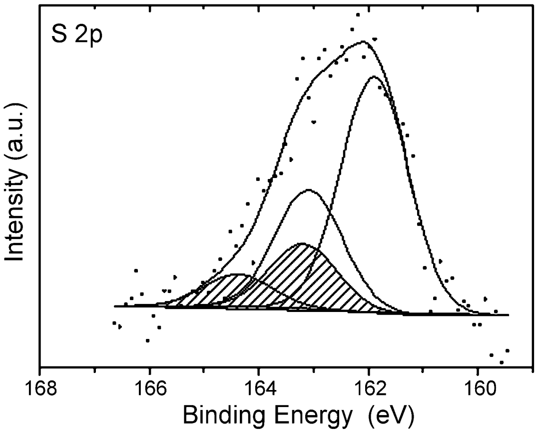


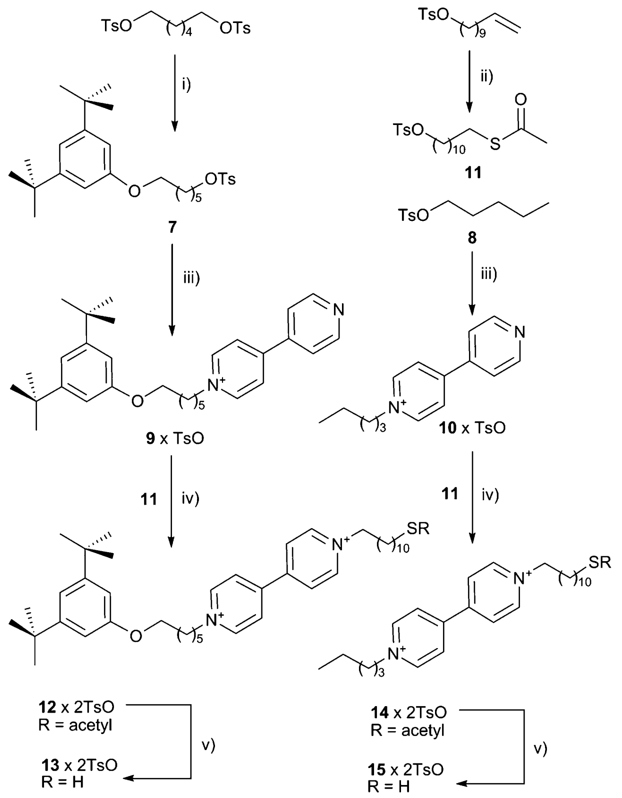
Fig. 4 S 2p XPS spectrum taken at 11° from the surface normal of Cu/**5**. The main spin–orbit split component is due to thiolate. The cross-hatched areas identify the component due to SH.

The reduction in surface coverage with respect to the case of calix[4]arene **1** could result from a larger surface disorder, due to the combined effects of polarity and flexibility of the phenylureido group.

As for the I^- anion, its quantitative ratio to N^+ was lower than that expected for the anchored calix[4]arene **5**. The N^+/I^- ratio further diminished after rinsing, and a Cl^- peak became visible in the XPS spectrum. We interpret this as a result of the anion exchange, which takes place during the rinsing cycle in a CH_3OH solution acidified with HCl to free the aromatic cavity of **5**.

Self-assembly of rotaxane and pseudorotaxane species on Cu

The recognition in a CH_2Cl_2 solution of *N*,*N*′-dialkylviologen-based "axles" **13**·2TsO and **15**·2TsO, synthesized as depicted in Scheme 2, with triphenylureidocalix[6]arene-based "wheel" **6**,[15f] followed by immersion of Cu in the above solution, resulted in the first self-assembly example, to our knowledge, of rotaxane and pseudorotaxane species on Cu. To this aim, two similar though conceptually different pre-formed systems were used. As shown in previous studies[15b,f] and here verified, the pseudorotaxane **6**⊃**13**·2TsO that originates by threading, in low polar solvent such as toluene, the wheel **6** with the



Scheme 2 *Reactions and conditions*: (i) 3,5-di-*tert*-butylphenol, K_2CO_3, CH_3CN, reflux, 48 h; (ii) CH_3COSH, AIBN, toluene, reflux, 5 h; (iii) CH_3CN, reflux, 48 h; (iv) CH_3CN, reflux, 72 h (autoclave); (v) TsOH, EtOH, reflux, 48 h.

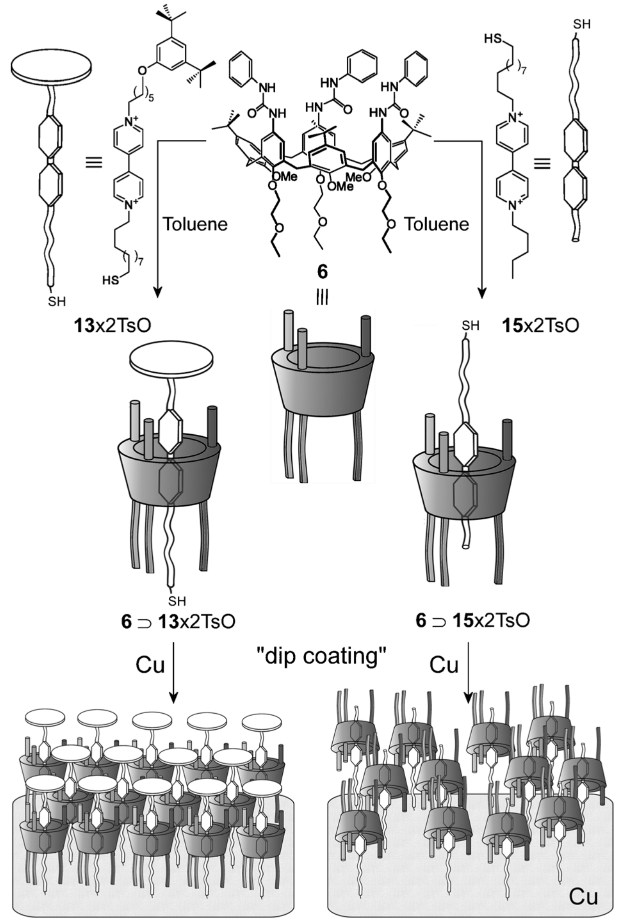


Fig. 5 Schematic representation of the threading reaction between "wheel" **6** and axles **13**·2TsO and **15**·2TsO. In toluene, axles **13**·2TsO and **15**·2TsO give rise to solutions of oppositely oriented pseudorotaxanes $\mathbf{6}\supset\mathbf{13}\cdot 2\mathrm{TsO}$ and $\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$, respectively. These solutions resulted in different coverages of polycrystalline Cu surfaces.

mono-stoppered axle **13**·2TsO is an oriented pseudorotaxane bearing the phenyl stopper at the upper and the –SH function at the lower rim (see Fig. 5).

The threading reaction carried out by using the axle **15**·2TsO, that lacks the stopper, yields the pseudorotaxanes $\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$, which have the SH function oriented towards the upper rim of the macrocycle (see Fig. 5). This means that the anchoring of these two different systems yields in one case an oriented polyrotaxane, in which the copper surface acts as a stopper, and a reversely oriented polypseudorotaxane in the other (see Fig. 5).

The assembly on Cu of preformed pseudorotaxanes was preferred to a 2-step reaction (adsorption of axles on Cu followed by threading of the calix by reacting Cu with its solution) because of the poor adsorption of *N*,*N*′-dialkylviologen on the surface, likely due to repulsive interactions between the positive charges of the axle. This same approach was followed for closely related molecular systems on Si(100).[13g] Fig. 6 reports the N 1s and S 2p peaks of the rotaxane Cu/$\mathbf{6}\supset\mathbf{13}\cdot 2\mathrm{TsO}$ and pseudorotaxane Cu/$\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$ adducts, respectively. NH and N$^+$ peak components are again present, indicating the anchoring of these species at the Cu surface. The NH/N$^+$ ratio is in the range of 3, as expected from the stoichiometric value in the absence of dethreading (Table 3).

We also found no sizeable dethreading of the pseudorotaxanes from the values of the NH/N$^+$ and C/N ratios, which fall in the range expected for intact chemisorbed rotaxanes. The S 2p photoemission region displays the two couples of spin–orbit components with the same meaning and assignment reported above, apart from the presence at high BE of the peak component related to the tosylate counterion. The relative intensity of this last peak to the rest of the S 2p signal follows the stoichiometry of the salt.

Controlled release of rotaxane and pseudorotaxane species from Cu surfaces

We investigated in detail the controlled release of rotaxanes and pseudorotaxanes by application of a suitable potential. It is known from solution studies[15e] that the reduction of bipyridinium N$^+$ induces the dethreading of the wheel from the viologen axle in pseudorotaxanes. We first measured the reduction potentials of pseudorotaxane $\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$ chemisorbed on an Au microelectrode *via* CV. An Au microelectrode was preferred to Cu because of the high reduction current displayed by the latter. We found two well separated peaks at −0.7 and −1.2 V (*vs.* Ag/Ag$^+$ in acetonitrile), which we assigned, on the basis of the literature,[15e,33] to the two N$^+$ reductions of the viologen-based axle **15**·2TsO. We compared the behaviour of rotaxane $\mathbf{6}\supset\mathbf{13}\cdot 2\mathrm{TsO}$ and pseudorotaxane $\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$ on Cu by keeping the two samples biased at −1.7 V (*vs.* Ag/Ag$^+$ in acetonitrile) for 1 min.

XPS results before and after polarization can be compared in Table 4. The diminishing of the thiolate component of S 2p in the case of rotaxane $\mathbf{6}\supset\mathbf{13}\cdot 2\mathrm{TsO}$ (see ESI†) is a clear indication of the release of approximately half of the rotaxanes, induced by the breaking of Cu–S bonds. This is accompanied by the drastic fall of intensity displayed by the tosylate anion, likely due to its reduction, in addition to the loss of rotaxane. The nearly constant ratio between the NH group from the triphenylurea and the S of the anchored species, NH/(SH + S–Cu) in Table 4 indicates the residual presence of intact rotaxanes at the surface. The reduction of the viologen N$^+$ appears in the N 1s spectrum as a new component at ∼398.9 eV (see ESI†). Its energy separation with respect to triphenylureido N is consistent with the electron-withdrawing effect exerted on N by the C=O group in the latter.

The more complex case represented by pseudorotaxane $\mathbf{6}\supset\mathbf{15}\cdot 2\mathrm{TsO}$ can be deduced by inspection of Table 4 and Fig. 7. A clear evidence for dethreading of the wheel as the largely prevailing effect of biasing comes from the sizeable lowering of the ratio NH/(SH + S–Cu) in Table 4. Notice the constancy in the S–Cu/Cu atomic ratio, which excludes loss of the whole pseudorotaxane. We still notice the drastic loss of the tosylate anion, with the same meaning as above (see Fig. 7). This general trend is further confirmed by extending the biasing to 3 min. Inspection of Fig. 7b and Table 4 evidences that the low BE component in the N 1s spectrum increases with respect to 1 min biasing. The absence of any further dethreading of the wheel after 1 and 3 min comes from the comparable decrease of the NH/(SH + S–Cu) ratio.

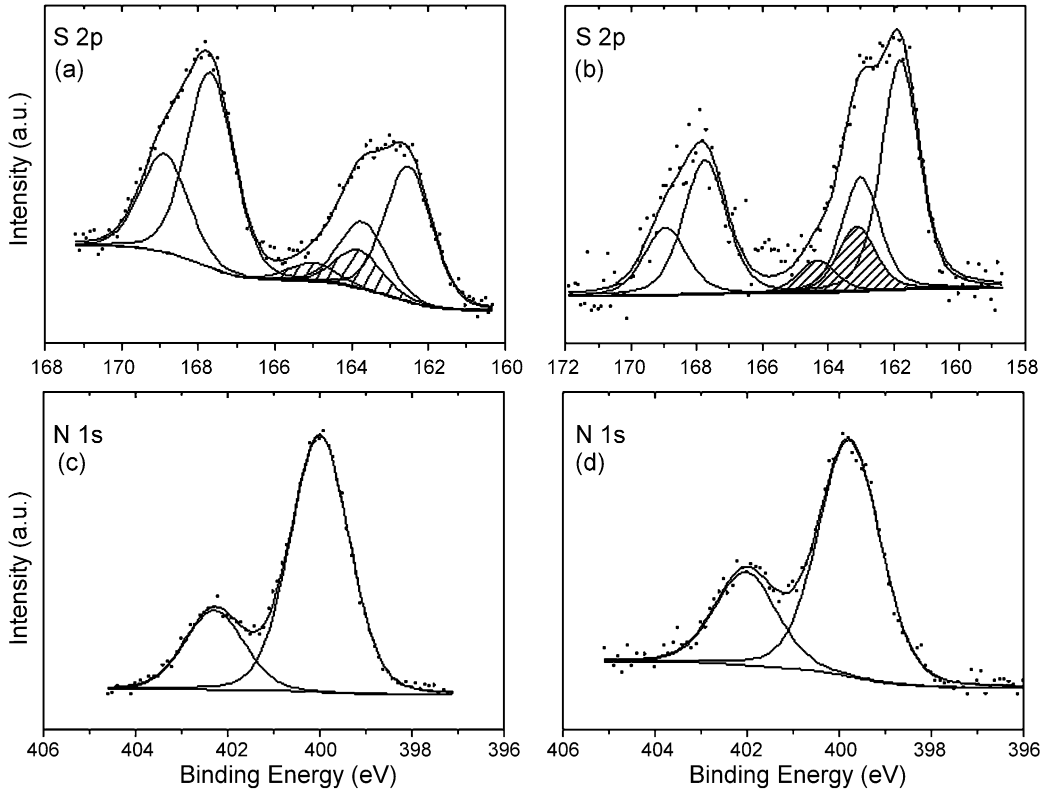


Fig. 6 S 2p and N 1s XPS spectra taken at 11° from the surface normal of Cu/**6**⊃**13**·2TsO (a and c) and Cu/**6**⊃**15**·2TsO (b and d). For the S 2p spectra, the main spin–orbit split component is due to thiolate and the cross-hatched areas identify the component due to SH; the doublet at high BE is assigned to tosylate. For the N 1s spectra, the experimental curve is displayed as dotted line, with the NH and N^+ peak components, resulting from curve-fitting, as solid lines.

Table 3 XPS peak positions and experimental and theoretical (reported in brackets) quantitative ratios (±10%) and surface coverage for rotaxane Cu/**6**⊃**13**·2TsO and pseudorotaxane Cu/**6**⊃**15**·2TsO

	S 2p (eV)	N 1s (eV)	NH/N^+ (theor.)	C/N (theor.)	SCu/Cu	θ/nm^{-2}
Cu/**6**⊃**13**	162.5 163.8 167.7	400.0 402.3	2.8(3)	15.3(18.1)	0.32	1.6
Cu/**6**⊃**15**	161.8 163.1 167.7	399.8 402.0	3.4(3)	16.4(16.2)	0.44	2.8

Table 4 XPS quantitative ratios (±10%) for rotaxane Cu/**6**⊃**13**·2TsO and pseudorotaxane Cu/**6**⊃**15**·2TsO before and after biasing

	OTs^-/Cu	S–Cu/Cu	NH/(SH + SCu)	N^+/(SH + SCu)
Cu/**6**⊃**13**	0.17	0.18	3.8	0.89
Cu/**6**⊃**13**[a]	0.03	0.11	3.0	0.74
Cu/**6**⊃**15**	1.1	0.44	4.5	1.3
Cu/**6**⊃**15**[a]	0.10	0.43	1.9	0.57
Cu/**6**⊃**15**	0.96	0.40	5.3	1.5
Cu/**6**⊃**15**[b]	0.10	0.38	2.8	0.64

[a] 1 min bias. [b] 3 min bias.

We interpret this last result as due to the second reduction of the $\mathbf{15}^{\bullet +}$ radical cation axle, from which the wheel has departed after the first reduction.[15e]

Conclusions

We have reported the first study on supramolecular systems self-assembled on polycrystalline Cu surfaces. SAMs of calixarenes, rotaxanes and pseudorotaxanes were produced and characterized by means of XPS. Covalent functionalization of calix[4,6]arenes on Cu was reached using a dip-coating procedure which allowed for good surface coverages and copper passivation. Molecular adhesion was demonstrated by the presence and relative quantitation of XPS signals from specific elements in the molecules. We successfully tested the combination of different functionalities by producing a mixed film, prepared by ligand exchange of calix[4]arene with undecanethiol. The availability of the calix[4]arene cavity to reversibly host further species after anchoring on Cu was demonstrated by a sequence of uptake and release cycles with pyridinium salts.

Pseudorotaxane species, composed of a calix[6]arene wheel derivatized with *N*-phenylureido groups on the upper rim, and viologen-containing axle, were anchored on Cu *via* the SH-termination of the axle. XPS demonstrated the successful self-assembling of fully threaded rotaxanes and pseudorotaxanes and the effectiveness of controlled release upon biasing of full rotaxanes and of the pseudorotaxane wheel. This will allow for more complex species to be produced on Cu, by the use of suitably substituted calixarenes.

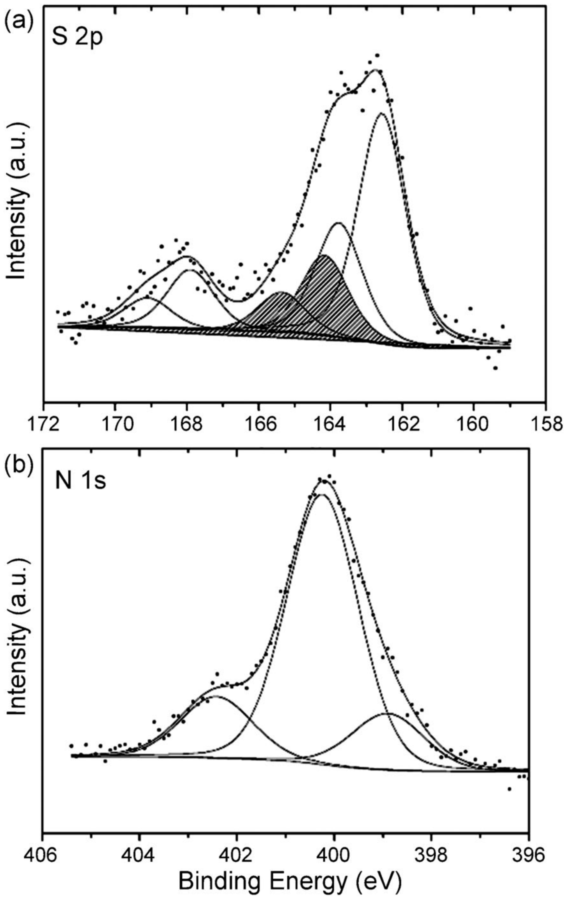


Fig. 7 S 2p and N 1s XPS spectra taken at 11° from the surface normal of Cu/**6**⊃**15**·2TsO after 3 min biasing. The main spin–orbit split S 2p component in (a) is due to thiolate and the cross-hatched areas identify the component due to SH.

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