FULL PAPER

# Assembly of Gold Nanoparticles on Functionalized Si(100) Surfaces through Pseudorotaxane Formation

## Alice Boccia,<sup>[a]</sup> Fabio D'Orazi,<sup>[a]</sup> Elena Carabelli,<sup>[b]</sup> Rocco Bussolati,<sup>[b]</sup> Arturo Arduini,<sup>[b]</sup> Andrea Secchi,<sup>\*[b]</sup> Andrea G. Marrani,<sup>[a]</sup> and Robertino Zanoni<sup>\*[a]</sup>

**Abstract:** The assembly of gold nanoparticles (AuNPs) on a hydrogenated Si(100) surface, mediated by a series of hierarchical and reversible complexation processes, is reported. The proposed multi-step sequence involves a redox-active ditopic guest and suitable calix[n]arene-based hosts, used as functional organic monolayers of the two inorganic components. Surface reactions and controlled release of AuNPs have been monitored by application of XPS, atomic force microscopy (AFM), field-emission scanning electron microscopy (FESEM) and electrochemistry.

#### Introduction

The anchoring of nanoparticles at specific surface sites is a process of large basic and technological importance, since it can modulate relevant properties such as those exhibited by nanowires, semiconductors, nanocapacitors and nanomagnets. Consider, for example, the social impact of the development of new flash memories based on metallic nanoparticles, devices that are nano-miniaturised, that have low power consumption and could store an entire database in ultra-small spaces.<sup>[1]</sup> Moreover, an important step toward the generation of novel integrated devices is based on the postulated possibility to transport light under the diffraction limit by using ordered arrays of close-spaced metal nanoparticles placed on technologically relevant surfaces such as silicon (plasmonic waveguides).<sup>[2-4]</sup> Silicon is an attractive inorganic platform, as it offers the possibility to make robust and durable devices by forming stable Si-C covalent bonds.<sup>[5,6]</sup> Several reports on organic monolayers formed through a covalent Si-C bond have been published so far by several research groups,<sup>[7–9]</sup> including ours.<sup>[10,11]</sup>

Supramolecular interactions have now started to diffuse into the realm of Si-anchored receptors, thus extending the control of reversibility that is typical for this type of chemi-

 [a] Dr. A. Boccia, Dr. F. D'Orazi, Dr. A. G. Marrani, Prof. R. Zanoni Dipartimento di Chimica Università degli Studi di Roma "La Sapienza" Piazzale Aldo Moro 5, 00185 Roma (Italy) E-mail: robertino.zanoni@uniroma1.it

[b] Dr. E. Carabelli, Dr. R. Bussolati, Prof. A. Arduini, Prof. A. Secchi Dipartimento di Chimica Università degli Studi di Parma Parco Area delle Scienze 17/A, 43124 Parma (Italy) E-mail: andrea.secchi@unipr.it

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201204318.

**Keywords:** calixarenes • electrochemistry • gold • nanoparticles • surface chemistry

cal bonds.<sup>[12-14]</sup> The combination of a stable anchoring bond at the interface with the supramolecular interaction offered by the attached receptors leads to specific recognising systems, which can be considered prototypical of more complex inorganic-organic hybrids.[15-17] In the latter context, we have shown that ditopic bis-pyridinium-based guests are able to promote the self-assembly of calix[4]arene-protected gold nanoparticles (AuNPs) in low polar solvents.<sup>[18]</sup> More recent efforts have been aimed at bringing the properties of molecular-machine prototypes to the interface by anchoring calix[6]arene-based pseudorotaxanes onto inorganic surfaces through their axial component.<sup>[14,19]</sup> On this basis, we report herein the reversible assembly of gold nanoparticles on an Si(100) surface mediated by a series of hierarchical complexation processes. These last involve a redox-active ditopic guest and suitable calix[n] arene-based hosts that are used as functional organic monolayers of the two inorganic components.

#### **Results and Discussion**

**Design and synthesis**: Calix[6]arene  $Cx_6$  (see Scheme 1) was used for the covalent functionalisation of hydrogenated Si-(100) surfaces. This compound was identified as a good candidate for Si coating because it presents three  $\omega$ -unsaturated C11 alkyl chains on its lower rim. Such long arms act as anchoring points that favour an upward orientation of the aromatic cavity of  $Cx_6$ , which can thus retain its recognition properties.

Calix[6]arene  $Cx_6$  was synthesised in three steps starting from known compounds (see Scheme 1). Calix[6]arene **1** was alkylated to its phenolic groups with the undec-10-enyl tosylate **2** in 70% yield. The three nitro groups of **3** were then quantitatively reduced to amino groups in ethyl acetate under reflux conditions by using SnCl<sub>2</sub>·2 H<sub>2</sub>O as the regiose-

Chem. Eur. J. 2013, 19, 7999-8006

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

WILEY ONLINE LIBRARY

- 7999



Scheme 1. Reagents and conditions: i)  $K_2CO_3$ , CH<sub>3</sub>CN, reflux, 7 d; ii) SnCl<sub>2</sub>·2 H<sub>2</sub>O, AcOEt, reflux, 36 h; iii) C<sub>6</sub>H<sub>3</sub>NCO, CH<sub>2</sub>Cl<sub>2</sub>, RT, 3 h.

lective reducing agent. Reaction of the amino groups of 4 with phenylisocyanate yielded  $Cx_6$  in 20% overall yield. The <sup>1</sup>H NMR spectra of  $Cx_6$  dissolved in C<sub>6</sub>D<sub>6</sub> (see Figure S1 in the Supporting Information) shows evidence that in this sol-

vent the calix[6]arene macrocycle adopts a cone conformation on the NMR spectroscopic timescale. Indeed the six bridging methylene protons resonate as a typical AX system of two doublets at  $\delta = 4.72$  and 3.68 ppm with a coupling constant (*J*) of 15 Hz. The three  $\omega$  unsaturations give rise to a characteristic system of two doublets at  $\delta = 5.05$  and 4.5 ppm and a multiplet centred at  $\delta = 5.8$  ppm and thus indirectly confirmed the effectiveness of the regioselective reduction of the nitro groups with respect to the alkene terminations. As typical of these type of calix[6]arene "wheels",<sup>[20,21]</sup> the three methoxy groups present in the lower rim of the macrocycle experience a large shielding effect from the aromatic rings that bear the phenylurea groups, thus resonating at high fields ( $\delta = 2.87$  ppm).

**Grafting and characterisation of calix[6]arenes on the Si-**(100) **surface**: The starting material is the hydrogenated Si-(100) surface, which was always prepared immediately before use in the anchoring process, conducted in Schlenk tubes. The method adopted for the surface anchoring requires visible-light activation (see the Supporting Information).<sup>[10,11,22-24]</sup> This extra-mild approach preserves the integrity of the molecular species and effectively limits the surface oxidation of the silicon substrate.

The characterisation of the functionalised Si surface  $(Si/Cx_6)$  was carried out through XPS measurements (see Figure 1 and the Supporting Information). The Si 2p region of the XPS spectra (see Figure 1a) shows, in addition to the



Figure 1. a) Si 2p and b) N 1s XPS regions of Si/Cx<sub>6</sub> surface. N 1s XPS region after complexation reaction of Si/Cx<sub>6</sub> surface with c) viologen DOV, d) bifunctional guest 8 and e) after the hierarchical assembly of AuNPs NP(Cx<sub>4</sub>) ( $d \approx 5$  nm). f) Au 4f XPS region of Si/Cx<sub>6</sub>/8/NP(Cx<sub>4</sub>) ( $d \approx 5$  nm).

8000

www.chemeurj.org

© 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Chem. Eur. J. 2013, 19, 7999-8006

# **FULL PAPER**

Table 1. XPS relative quantitative ratios ( $\pm 10\%$ ) and binding energies (BE) for the Si/Cx<sub>6</sub> surface as prepared and after complexation reactions at the interface.<sup>[a]</sup>

							Si 2p		N 1s		Au 4f	
Designation	C/N	N/Si	NH/N+	Au/Si	Au/N(tot)	Au/N+	BE [eV]	Assignment	BE [eV]	Assignment	BE [eV]	Assignment
Si/Cx <sub>6</sub>	17 (18.5)	0.037	_	-	_	-	99.7	Si bulk	401.0	NH	-	-
							99.9	Si-C/Si-H				
							103.5	$Si_xO_y$				
Si/Cx <sub>6</sub> /DOV	17 (17.1)	0.042	2.9 (3)	_	_	_	99.7	Si bulk	401.0	NH	_	_
	. ,		. /				99.9	Si-C/Si-H	403.2	N <sup>+</sup>		
							103.5	$Si_xO_y$				
Si/Cx <sub>6</sub> /8	22 (15.9)	0.021	1.9 (2)	_	_	_	99.7	Si bulk	400.8	NH	_	_
							103.6	$Si_xO_y$	403.0	N <sup>+</sup>		
$Si/Cx_6/8/NP(Cx_4)^{[b]}$	38	0.030	2.0 (2)	0.009	0.28	1.3	99.7	Si bulk	400.7	NH	85.0	Au <sup>I</sup>
							103.6	$Si_xO_y$	403.2	N <sup>+</sup>		
$Si/Cx_6/8/NP(Cx_4)^{[c]}$	35	0.072	1.8 (2)	0.19	2.6	8.7	99.7	Si bulk	400.9	NH	84.3	$Au^0$
							103.8	$Si_xO_y$	403.0	N <sup>+</sup>	85.1	Au <sup>I</sup>
											86.5	Au <sup>III</sup>
Si/Cx <sub>6</sub> /NP(Cx <sub>4</sub> ) <sup>[c]</sup>	14	0.054	1.8 (2)	0.005	0.10	_	99.7	Si bulk	400.8	NH	84.4	$Au^0$
							103.5	$Si_xO_y$			85.4	Au <sup>I</sup>
								-			86.3	Au <sup>III</sup>

[a] Theoretical values in parentheses. [b] Mean core size of 1 nm as determined by TEM measurements. [c] Mean core size of 5 nm.

main  $2p_{3/2,1/2}$  spin-orbit doublet due to bulk Si, a second doublet with its main component located at 99.9 eV, assigned on the basis of the literature<sup>[25]</sup> to the superficial Si (Si-H<sub>2</sub> terminations) and the Si-C components. A small broad feature centred at 103.5 eV is due to a very limited oxidation of the Si surface that occurs upon reaction with  $Cx_6$ . The N 1s region (see Figure 1b) presents an NH peak component at 401 eV. This peak is diagnostic of the effective anchoring of  $Cx_6$  onto the Si surface.

The structural integrity of the attached monolayer and the covering degree of the Si surface was evaluated considering the relative quantitative ratios of diagnostic elements (see Table 1 and the Supporting Information). The calculated C/N ratio is, within the experimental error, in good agreement with the stoichiometry of  $Cx_6$ , thus confirming the mildness of the photoactivation process employed.

The functionalised Si/Cx<sub>6</sub> surface was then exposed to a solution of 1,1'-dioctyl-4,4'-bipyridinium diiodide (DOV) in 95:5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH. Indeed, it is known that this redoxactive viologen salt forms very stable and electrochemically switchable pseudorotaxane complexes with calix[6]arene macrocycles similar to those linked on the Si substrate.<sup>[26]</sup> The simultaneous presence in the N 1s region of two peak components (see Figure 1c) due to the NH groups of Cx<sub>6</sub> and the N<sup>+</sup> from the pyridine rings of **1**, respectively, indicates the establishment of the pseudorotaxane complex to an extent that was quantified by taking the experimental relative atomic ratios between the two N 1s components. The experimental NH/N<sup>+</sup> ratio matched the value expected from the pseudorotaxane stoichiometry (see Table 1).

The previous findings prompted us to explore the possibility of exploiting a series of successive and hierarchical complexation processes to promote the reversible assembly of gold nanoparticles (AuNPs) on the silicon substrate. To this end, the new supramolecular linker **8** was devised and synthesised in 50% overall yield (see Scheme 2). With respect to DOV, the redox-active 4,4'-bipyridinium core of **8** has been linked through a flexible dodecyl chain to another pyridinium ring. This latter structural motif has been indeed successfully used for the supramolecular grafting of calix[4]arene-protected AuNPs onto inorganic surfaces.<sup>[27]</sup>



Scheme 2. Reagents and conditions: i) pyridine, CH<sub>3</sub>CN, reflux, 48 h; ii) CH<sub>3</sub>CN, reflux, 48 h.

To demonstrate the feasibility of the whole process, a simple experiment was devised (see Scheme 3): the Si/ $Cx_6$  surface was exposed through a dip-coating process to a solution of guest 8 in 95:5 CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (see the Supporting Information for the experimental details). XPS measurements (see Figure 1d and the Supporting Information) verified that the outcome of the threading reaction at the interface was almost quantitative (see the NH/N<sup>+</sup> ratio in Table 1).

www.chemeurj.org

**CHEMISTRY** 

A EUROPEAN JOURNAL



Scheme 3. Schematic representation of the formation of pseudorotaxane complexes at the interface between a Si(100) surface coated with calix[6]-arene-based "wheels"  $Cx_6$  and the viologen-based "axle" (8) present in CH<sub>2</sub>Cl<sub>2</sub>/MeOH.

The complexed Si/Cx<sub>6</sub>/8 surface was successively dipped into a CH<sub>2</sub>Cl<sub>2</sub> solution that contained AuNPs (NP(Cx<sub>4</sub>)) protected with the thiolate calix[4]arene ligand Cx<sub>4</sub> (see Scheme 3) and with a mean core size of 1 nm. XPS measurements (see the Supporting Information) of the Si/Cx<sub>6</sub>/8/NP-(Cx<sub>4</sub>) ( $d \approx 1$  nm) system (see Table 1) showed an NH/N<sup>+</sup> ratio equal to the theoretical one, thereby confirming that the Cx<sub>6</sub>/8 assembly remained unchanged after grafting of NP(Cx<sub>4</sub>).

The core size of the nanoparticles used in the previous experiment was small enough for a surface-sensitive technique such as XPS to produce a meaningful relative quantification of the elements present in the assembled layers on the Si substrate. On the other hand, these AuNPs were too small for an accurate morphological investigation of the surface and, most importantly, they were not imbued with plasmonic properties. To overcome this problem, the assembly experiment was performed by exposing the Si/Cx<sub>6</sub>/8 surface to a solution of nanoparticles  $NP(Cx_4)$  with a mean core size of 5 nm in CH<sub>2</sub>Cl<sub>2</sub>. XPS characterisation confirmed the results obtained with the smaller AuNPs as to the NH/N<sup>+</sup> ratio (see Figure 1e, f, Table 1, and the Supporting Information), whereas a large increase in the Au/Si ratio was found relative to the case of Si/Cx<sub>6</sub>/8/NP(Cx<sub>4</sub>) ( $d \approx 1$  nm), which was expected on the basis of the larger number of Au atoms in the NP, along with a moderate decrease in the C/N ratio.<sup>[28]</sup>



Figure 2. a) AFM image (needle sensor, in an ultra-high vacuum) showing a portion  $(300 \times 300 \text{ nm})$  of the Si/**Cx**<sub>6</sub>/8 surface after its exposure to a solution of approximately 5 nm NP(**Cx**<sub>4</sub>) AuNPs; b) enlarged image ( $150 \times 150 \text{ nm}$ ) of the same area; c) FESEM image of the same sample taken at 600 KX magnification ( $500 \times 375 \text{ nm}^2$ ); d) enlarged image ( $190 \times 190 \text{ nm}$ ) of the same area showing a hexagonal motif in the packing symmetry.

After XPS characterisation, the  $Si/Cx_6/8/NP(Cx_4)$  (d  $\approx$ 5 nm) system was investigated through atomic force microscopy (AFM) and field-emission scanning electron microscopy (FESEM) measurements. In Figure 2a and b, a region of the Si surface (300×300 nm) is reported along with a detailed view  $(150 \times 150 \text{ nm})$ , which was analysed in ultra-high vacuum by needle-sensor AFM. In the image, the resolution of the instrument used for the measurements allowed us to detect structures with a size of approximately 10 nm, which is compatible with NPs approximately 5 nm in size protected by an organic layer approximately 2 nm thick. The average height calculated over the pixels of the whole image is 0.90 nm with a root-mean-square (RMS) roughness of 0.27 nm. The measured height value is lower than the overall diameter of the  $NP(Cx_4)$  unit, thereby suggesting that NPs are organised in self-assembled aggregates, probably reflecting the morphology underneath. The latter aspect prevents an accurate determination of the overall self-assembled monolayer (SAM) thickness. Height- and phase-contrast AFM images acquired in ambient air in tapping mode (see the Supporting Information) also confirm the presence of particles with a diameter of approximately 10 nm. Highresolution FESEM images (see Figure 2c,d) evidence a high coverage of dispersed NPs organised in aggregates with a hexagonal motif of packing symmetry. The origin of such a motif should be found in non-specific electrostatic interactions. Single NPs can be clearly identified and a narrow size distribution centred at 10 nm can be estimated, in agreement with AFM images.

To verify the role played by the calix[6]arene and the ditopic guest 8 units in the assembly of nanoparticles  $NP(Cx_4)$ ,

8002

# **FULL PAPER**

separate bare hydrogenated Si and Si/Cx<sub>6</sub> surface were dipped into a solution of approximately 5 nm NP(Cx<sub>4</sub>) in CH<sub>2</sub>Cl<sub>2</sub>. In principle, the resulting systems should not be covered at all by NP(Cx<sub>4</sub>), the interaction between the two parts being totally non-specific in this case. The comparison of the two Au/Si ratios (see Table 1) clearly indicates that the amount of NPs deposited on the substrate is more than an order of magnitude higher when NP(Cx<sub>4</sub>) are in contact with bare hydrogenated Si than with Si/Cx<sub>6</sub>. This is probably due to the relevant hydrophobic interaction between the H–Si surface and the organic fraction of AuNPs. On the other hand, the Au/Si ratio found in the Si/Cx<sub>6</sub>/NP(Cx<sub>4</sub>) ( $d \approx 5$  nm) system demonstrates that the presence of the ditopic guest **8** is mandatory for the construction of the supramolecular assembly presented here.

Electrochemical studies at the interface: Electrochemical investigations were carried out by means of cyclic voltammetry (CV) on the Si/Cx<sub>6</sub>/8 (Figure 3a) and Si/Cx<sub>6</sub>/8/NP(Cx<sub>4</sub>)-



Figure 3. Cyclic voltammograms of a) Si/ $Cx_6/8$ ; and Si/ $Cx_6/8/NP(Cx_4)$  with NPs with a mean core size of b) 5 nm and c) 1 nm. Measurements were run in CH<sub>3</sub>CN+0.1 M TBAP at a 0.8 V s<sup>-1</sup> scan rate under illumination with white light. On the left is a schematic representation of the electrochemical disassembly process.

functionalised surfaces, for which the code NP( $Cx_4$ ) identifies nanoparticles with a mean core size of either 5 or 1 nm (Figure 3b and c, respectively). Measurements were run in a nitrogen-purged CH<sub>3</sub>CN/tetrabutylammonium perchlorate (TBAP) solution under illumination with a low-intensity halogen lamp. In the dark no current signal was detected upon potential scanning, owing to the low concentration of negative charge carriers in the n-doped semiconductor. Under white-light irradiation, a significant photocurrent, depending on the photon flux, was detected as a consequence of the generation of electrons in the conduction band, which promoted a reduction process at the semiconductor surface. All the cyclic voltammograms of the three samples (see Figure 3) show a single reversible one-electron wave, probably associated with one of the reduction processes of the three N<sup>+</sup> groups of **8** in the supramolecular surface assembly.<sup>[20]</sup> The formal potentials ( $E^{\circ}$ ) recorded, estimated as the mean value between the anodic ( $E_{a}$ ) and the cathodic ( $E_{c}$ ) peak potentials, were -0.514, -0.550 and -0.407 V in voltammograms in Figure 3a–c, respectively. The three samples showed CV waves with a peak potential splitting ( $\Delta E_{pp} = E_{a} - E_{c}$ ) of 0.041, 0.028 and 0.003 V, in the series shown in Figure 3a–c. These values are very close to the 0 V splitting predicted for an ideal redox species confined at the surface of an electrode<sup>[29,30]</sup> and they indicate that the electron-transfer rate across the surface-bound molecular layer is faster than the 0.8 V s<sup>-1</sup> scan rate used here.

Due to the establishment of a surface photopotential of unknown value upon irradiation with white light, no definite correspondence can be drawn between the values of formal potentials in Ref. [20] (obtained from closely comparable systems in solution) and those reported here. Nevertheless,

> given that a single reduction of the axle unit is sufficient to induce the disassembly of one or more units of the whole assembly,<sup>[26]</sup> one could infer that the reduction-oxidation process evidenced by the CV can be associated with a reversible "unthreading-rethreading" movement of either 1) the unit NP- $(Cx_4)$  out and into the Si/Cx<sub>6</sub>/8 system, or 2) the  $8/NP(Cx_4)$  assembly out and into the Si/Cx<sub>6</sub> surface species. On this basis, to induce the release of AuNPs from the supramolecular surface assembly, the two  $Si/Cx_6/8/$ NP(Cx<sub>4</sub>) samples (AuNP mean core sizes of 5 and 1 nm) were polarised at a potential of -0.7 V for 2 min, then washed in CH<sub>3</sub>CN and examined with XPS again. In both samples, a sizeable decrease in intensity of the Au 4f signal was detected,

the Au 4f signal was detected, with a change in the Au/Si ratio from 0.0090 to 0.0046 and from 0.19 to 0.046 for the Au NPs with mean core sizes of 1 and 5 nm, respectively. This behaviour shows that the detachment of AuNP( $Cx_4$ ) units can be obtained. Its extent could probably be modulated by controlling both the polarisation potential and time.

## Conclusion

The synthesis and characterisation of novel hybrid systems on the basis of a supramolecular surface assembly of AuNPs onto an Si(100) surface have been performed. AuNPs have

www.chemeurj.org

been attached to and electrochemically detached from a Si-(100) surface that presents functional groups able to bind the nanoparticles through a hierarchical multi-step sequence of reactions. The proposed method involves suitable calix-[n]arene-based hosts, which have been used as the interface species for the assembly of the two inorganic moieties, and a bipyridinium-based redox-active ditopic guest. Surface reactions have been monitored at their various steps by application of XPS, AFM, FESEM and electrochemistry.

### **Experimental Section**

**Materials and synthetic methods**: All solvents were dried using standard procedures. All other reagents were of reagent-grade quality obtained from commercial suppliers and were used without further purification. NMR spectra were recorded at 400 and 300 MHz for <sup>1</sup>H and 100 and 75 MHz for <sup>13</sup>C. Melting points are uncorrected. Chemical shifts ( $\delta$ ) are expressed in ppm by using the residual solvent signal as internal reference. Mass spectra were recorded in ESI mode. Calix[6]arene **1**,<sup>[31]</sup> undec-10-enyl tosylate (**2**),<sup>[32]</sup> *N*-pentyl-4(4'-pyridyl) pyridinium bromide (7)<sup>[33]</sup> and the calix[4]arene-protected gold nanoparticles NP(C**x**<sub>4</sub>) with mean core sizes of 1<sup>[34]</sup> and 5 nm<sup>[18]</sup> were synthesised according to published procedures.

Synthesis of 3: This compound was synthesised by using an improved published procedure.<sup>[35]</sup> In a sealed glass autoclave, kept under a nitrogen atmosphere, a suspension of K2CO3 (1 g, 7 mmol) in a solution of calix[6]arene 1 (2 g, 2 mmol) and 2 (2.3 g, 7 mmol) in acetonitrile (150 mL) was heated at reflux for 3 days. After this period, the apparatus was cooled to room temperature and the solution was poured into a beaker that contained a mixture of HCl (10%, 100 mL) and ethyl acetate. The organic phase was separated, dried on Na2SO4 and evaporated to dryness under reduced pressure. The oily residue was purified by column chromatography on silica gel (n-hexane/ethyl acetate 9:1) to yield 3 as a yellowish solid (75%). M.p. 138–140°C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.67$ (brs, 6H), 7.21 (brs, 6H), 5.9-5.7 (m, 3H), 5.0-4.9 (m, 6H), 4.6-4.1 (m, 6H), 3.83 (brs, 6H), 3.7-3.4 (m, 6H), 2.86 (s, 9H), 2.1-2.0 (m, 6H), 1.85 (brs, 6H), 1.6–1.0 ppm (m, 53H);  $^{13}\mathrm{C}$  NMR (75 MHz, CDCl<sub>3</sub>):  $\delta\!=\!146.8,$ 143.6, 139.1, 127.8, 127.3, 123.1, 114.1, 77.4, 73.9, 59.9, 34.2, 33.7, 31.4, 31.2, 30.9, 30.5, 30.2, 29.4, 29.2, 29.0, 28.8, 26.0 ppm; MS-ESI: m/z: 1461.7  $[M+Na^+]$ 

Synthesis of Cx<sub>6</sub>: SnCl<sub>2</sub>·2H<sub>2</sub>O (1.4 g, 6 mmol) was added to a solution of calix[6]arene 3 (0.6 g, 0.4 mmol) in ethyl acetate (50 mL). The resulting heterogeneous mixture was heated at reflux for 36 h, cooled to room temperature and then quenched by addition of a saturated solution of Na<sub>2</sub>CO<sub>3</sub> (50 mL). The separated organic phase was washed with water until neutrality, dried over anhydrous Na2SO4 and evaporated to dryness under reduced pressure. The recovered amino compound 4 (0.5 g) was then dissolved in dry CH2Cl2 (100 mL) and treated with phenyl isocyanate (0.12 g, 1 mmol). After stirring at room temperature for 5 h, the solvent was evaporated to dryness under reduced pressure. Purification of the oily residue by column chromatography on silica gel (n-hexane/ethyl acetate 7:3) yielded calix[6]arene  $Cx_6$  (0.4 g, 55%) as a yellowish solid. M.p. 143–145 °C; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = 7.4$  (s, 6 H), 7.2 (d, <sup>3</sup>J = 7.8 Hz, 6H), 7.0 (brs, 3H), 6.98 (t, <sup>3</sup>J=7.8 Hz, 6H), 6.9 (brs, 3H), 6.8-6.7 (m, 9H), 5.8 (ddt,  ${}^{3}J_{1(trans)} = 17$  Hz,  ${}^{3}J_{2(cis)} = 10$  Hz,  ${}^{3}J_{3} = 7$  Hz, 3H), 5.05 (d,  ${}^{3}J_{1(trans)} = 17$  Hz, 3 H), 5.00 (d,  ${}^{3}J_{2(cis)} = 10$  Hz, 3 H), 4.72 (d,  ${}^{2}J = 15$  Hz, 6 H), 3.94 (t,  ${}^{3}J = 6$  Hz, 6H), 3.68 (d,  ${}^{2}J = 15$  Hz, 6H), 2.9 (brs, 9H), 2.0 (q,  ${}^{3}J =$ 7 Hz, 6H), 1.9–1.8 (m, 6H), 1.6–1.5 (m, 6H), 1.4–1.3 ppm (m, 57H);  $^{13}\text{C}$  NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta\!=\!155.2$  (2 resonances), 154.2, 151.7, 146.6, 138.9, 138.8, 136.0, 133.7, 133.6, 128.7, 123.0, 122.0, 120.2, 114.2, 72.9, 60.1, 34.0, 33.9, 31.4, 31.2, 30.6, 29.6, 29.5, 29.2, 29.0, 26.4 ppm; MS-ESI: m/z (%): 1744 (100) [M+Na<sup>+</sup>].

**Synthesis of 6**: In a sealed glass autoclave kept under a nitrogen atmosphere, a solution of 1,12-dibromo dodecane (**5**; 5 g, 15 mmol) and pyridine (0.2 g, 2.7 mmol) in acetonitrile (50 mL) was heated at reflux for

48 h. After cooling to room temperature, the solvent was evaporated to dryness under reduced pressure and the residue was dissolved in ethyl acetate. Pure compound **6** (95%; 1.1 g) was recovered from the solution by suction filtration as small white crystals. M.p. 52.2–56.3 °C; <sup>1</sup>H NMR (300 MHz, MeOD):  $\delta$ =9.05 (d, <sup>3</sup>*J*=7 Hz, 2H), 8.63 (t, <sup>3</sup>*J*=7 Hz, 1H), 8.15 (t, <sup>3</sup>*J*=7 Hz, 2H), 4.67 (t, <sup>3</sup>*J*=7 Hz, 2H), 3.45 (t, <sup>3</sup>*J*=7 Hz, 2H), 2.1–2.0 (m, 2H), 1.8–1.7 (m, 2H), 1.5–1.3 ppm (m, 14H); <sup>13</sup>C NMR (100 MHz, MeOD):  $\delta$ =145.5, 144.5, 128.1, 61.74, 48.0, 47.9, 47.6, 47.3, 47.0, 33.1, 32.6, 31.1, 29.1, 29.0, 28.7, 28.4, 27.7, 25.8 ppm; MS-ESI: *m/z* (%): 326.2 (100) [*M*-Br], 328.2 (97) [*M*-Br].

Synthesis of 8: In a sealed glass autoclave kept under a nitrogen atmosphere, a solution of 6 (0.5 g, 1.2 mmol) and *N*-pentyl-4(4'-pyridyl) pyridinium bromide (7; 0.7 g, 1.2 mmol) in acetonitrile (20 mL) was heated to reflux for 48 h. After cooling to room temperature, the resulting heterogeneous solution was diluted with ethyl acetate (15 mL) and filtered to recover 8 (0.6 g, 74%) as a yellow solid. M.p. 76.4–79.3 °C; <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]DMSO):  $\delta$ =9.49 (d, *J*=5.6 Hz, 4H), 9.32 (d, *J*=6.8 Hz, 2H), 8.87 (d, *J*=6.8 Hz, 4H), 8.7 (m, 1H), 8.18 (t, *J*=7 Hz, 2H), 4.75 (t, *J*=7 Hz, 4H), 4.65 (t, 2H, *J*=7 Hz), 2.0–1.8 (m, 26H), 0.88 ppm (t, *J*=7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, MeOD):  $\delta$ =149.3, 145.9, 144.9, 128.5, 127.1, 61. 6, 61.4, 31.1, 30.8, 29.1, 28.8, 28.7, 27.9, 25.8, 21.9, 14.1 ppm; MS-ESI: *m/z* (%): 237 (100) [*M*–3Br] (*z*=2).

**Preparation of hydrogenated silicon**: Si(100) wafers of 400 mm thickness, n-doped (phosphorus-doped, single-side polished, 10–50  $\Omega$  cm<sup>-1</sup> resistivity) and with areas of approximately 1 cm<sup>2</sup> were first washed in boiling 1,1,2-trichloroethane for 10 min and subsequently in methanol at room temperature with sonication for 5 min. They were then oxidised in H<sub>2</sub>O<sub>2</sub>/HCl/H<sub>2</sub>O (2:1:8) at 353 K for 15 min, rinsed copiously with water, etched with 10% aqueous HF for 10 min, rinsed with water again, dried under a stream of N<sub>2</sub> and immediately used in the functionalisation process.

**Photoimmobilisation of calix[6]arene Cx**<sub>6</sub> on hydrogenated silicon: Freshly etched Si samples were always used for anchoring. The functionalisation experiments on the surface-activated samples were carried out using standard preparative Schlenk-line procedures. After functionalisation, all samples were subjected to the same cleaning procedure, which consisted of two sonication cycles (5 min each) with dichloromethane and drying in a stream of N<sub>2</sub>. Hydrogen-terminated Si(100) wafers were dipped in solutions of calix[6]arene **Cx**<sub>6</sub> (10 mM) in toluene in Schlenk tubes under a N<sub>2</sub> atmosphere and subjected to a 35 mW cm<sup>-2</sup> visible irradiation for 4 h from a quartz–iodine lamp. The molecular solution was previously deoxygenated by three freezing–pumping–annealing cycles and kept under N<sub>2</sub> to prevent silicon from undergoing surface oxidation.

**Complexation reactions on Si/Cx**<sub>6</sub> **surface**: The feasibility of the threading reaction between the calix[6]arene-based "wheels" **Cx**<sub>6</sub> placed on the silicon surface and viologen-based "axles" was investigated in 9:1 dichloromethane/methanol, since it is known that the formation of these types of pseudorotaxane complexes is favoured in low-polar solvents.<sup>[21]</sup> Methanol was used as co-solvent to favour the solubility of the viologen axles in dichloromethane. In particular, a freshly prepared Si/Cx<sub>6</sub> surface was dipped in a 1 mM solution of axle (DOV or **8**), which was prepared by dissolving the salt in the minimum amount of methanol and then diluting with nine parts of dichloromethane. After 30 min the hydrogenated Si(100) wafer was removed from the solution of the viologen and then copiously rinsed with dry dichloromethane. After drying with an N<sub>2</sub> stream, the "complexed" silicon surfaces Si/Cx<sub>6</sub>/DOV and Si/Cx<sub>6</sub>/2 were submitted to XPS analysis.

Supramolecular anchoring of calix[4]arene-protected AuNPs on silicon: The calix[6]arene-loaded silicon surface previously treated with the ditopic guest 8 (Si/ $Cx_6/8$ ) was dipped in a solution of calix[4]arene-protected AuNPs with a mean core size of either 1 or 5 nm in dichloromethane. After 30 min, the treated Si(100) surfaces were rinsed with pure dry dichloromethane, dried with an N<sub>2</sub> stream and submitted to XPS, AFM, FESEM and electrochemistry measurements.

**XPS measurements:** XPS measurements were performed using a modified Omicron NanoTechnology MXPS system with a monochromatic Xray source (Omicron XM-1000) and an Omicron EA-127 energy analyser. The experimental conditions adopted were excitation by  $Al_{K\alpha}$  photons ( $h\nu = 1486.7 \text{ eV}$ ), which were generated operating the anode at 14–

8004 -

15 kV, 10-20 mA. No charging of the samples was experienced during measurements. All the photoionisation regions were acquired using an analyser pass energy of 20 eV, except the survey scan, which was recorded at a 50 eV pass energy. A take-off angle of 11° with respect to the sample surface normal was adopted. The measurements were performed at room temperature and the base pressure in the analyser chamber was about  $2 \times 10^{-9}$  mbar during the spectral detection. The binding energy (BE) of the Si 2p<sub>3/2</sub> bulk component at 99.7 eV was used as an internal standard reference for the BE scale (accuracy of  $\pm 0.1$  eV). All measurements were conducted in the least possible time after sample preparation. No sizeable sign of degradation upon extended acquisition times under the X-rays was observed. The effects on quantitative analysis possibly due to photoelectron diffraction at preferential directions of electron collection were minimised by always mounting the Si(100) wafers with the same orientation with respect to the analyser axis.<sup>[36,37]</sup> After subtraction of a Shirley background, the experimental spectra were theoretically reconstructed by fitting the peaks to symmetric Voigt functions. XPS atomic ratios ( $\pm 10\%$  associated error) between relevant core lines were estimated from experimentally determined area ratios corrected for the corresponding Scofield cross sections<sup>[38]</sup> and for a square-root dependence of the kinetic energies of the photoelectrons.

AFM and FESEM measurements: The morphology of the hybrid assemblies obtained after deposition of NPs with a mean core diameter of 5 nm was investigated under ultra-high vacuum (UHV) conditions by a needle-sensor atomic force microscope (VT-AFM, Omicron NanoTechnology), which was attached to a UHV chamber in which XPS measurements were also run (see below). The silicon nitride micro-fabricated tip had a nominal curvature radius of <10 nm and a resonance frequency of 997.500 kHz. The values of average z-height and of root-mean-square (rms) roughness (defined as the standard deviation from the average zheight values) were determined by Scala Pro software (Omicron Nano-Technology) and WSxM software. A Veeco Multimode atomic force microscope equipped with a Nanoscope III controller was used for morphology characterisation on ambient air of the same sample. All images were collected using the tapping mode and a silicon tip. The drive frequency was 260 kHz, the drive amplitude was about 180 mV, the voltage was 1 V and the scan rate was 0.5-1 Hz. The same system was studied also with a FESEM instrument (Auriga Zeiss) equipped with an EDS probe. Metallization of samples was not required.

Electrochemical measurements: After monolayer formation, ohmic contact was made to the back of the derivatised silicon samples by scratching the Si surface, rubbing it with Ga-In eutectic and attaching a copper contact to it. The electrode setup was obtained by pressing the Si crystal against an O ring, sealing a small aperture in the polytetrafluoroethylene (PTFE) cell, thereby exactly defining the electrode area  $(0.3 \text{ cm}^2)$ . The electrochemical properties of the supramolecular assemblies covalently bound to n-Si(100) surfaces were explored by cyclic voltammetry in 0.1 M NBu<sub>4</sub>ClO<sub>4</sub> (tetrabutylammonium perchlorate, or TBAP) in dry CH<sub>3</sub>CN. All electrochemical measurements were performed after thoroughly purging the solution with nitrogen and using an Autolab electrochemical analyser (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<sub>3</sub>/0.1 M TBAP in CH<sub>3</sub>CN, separated from the main solution by a porous fritted glass plus agar plug, served as a reference electrode. All potentials reported here use this as reference. Cyclic voltammograms were acquired at a 0.8 Vs<sup>-1</sup> scan rate under illumination with a low-intensity halogen lamp. CV waves were smoothed with a Savitzky-Golaybased algorithm to eliminate electrical noise that hampered the recognition of voltammogram features.

### Acknowledgements

The authors thank Università La Sapienza and the Centro di Ricerca per le Nanotecnologie applicate all'Ingegneria della Sapienza (CNIS) in Rome, Italy, for access to the AFM and FESEM facilities of the SNN Lab. They also thank Centro Interdipartimentale di Misure—G. Casnati in Parma, Italy, for the NMR spectroscopic measurements.

# **FULL PAPER**

- [1] Z. Liu, C. Lee, V. Narayanan, G. Pei, E. C. Kan, *IEEE Trans. Electron Devices* **2002**, *49*, 1606–1613.
- [2] N. Liu, S. Mukherjee, K. Bao, Y. Li, L. V. Brown, P. Nordlander, N. J. Halas, ACS Nano 2012, 6, 5482–5488.
- [3] J. A. Fan, C. Wu, K. Bao, J. Bao, R. Bardhan, N. J. Halas, V. N. Manoharan, P. Nordlander, G. Shvets, F. Capasso, *Science* 2010, 328, 1135–1138.
- [4] S. A. Maier, P. G. Kik, H. A. Atwater, S. Meltzer, E. Harel, B. E. Koel, A. A. G. Requicha, *Nat. Mater.* 2003, *2*, 229–232.
- [5] Functionalization of Semiconductor Surfaces (Eds.: F. Tao, S. L. Bernasek), Wiley, Hoboken (NJ), 2012.
- [6] B. K. Teo, X. H. Sun, Chem. Rev. 2007, 107, 1454–1532 and references therein.
- [7] J. M. Buriak, *Chem. Rev.* **2002**, *102*, 1271–1308 and references therein.
- [8] B. Fabre, D. D. M. Wayner, Langmuir 2003, 19, 7145-7146.
- [9] B. J. Eves, Q.-Y. Sun, G. P. Lopinski, H. Zuilhof, J. Am. Chem. Soc. 2004, 126, 14318–14319.
- [10] F. Cattaruzza, A. Llanes-Pallas, A. G. Marrani, E. A. Dalchiele, F. Decker, R. Zanoni, M. Prato, D. Bonifazi, *J. Mater. Chem.* 2008, 18, 1570–1581.
- [11] A. Aurora, F. Cattaruzza, C. Coluzza, C. Della Volpe, G. Di Santo, A. Flamini, C. Mangano, S. Morpurgo, P. Pallavicini, R. Zanoni, *Chem. Eur. J.* 2007, *13*, 1240–1250.
- [12] E. Biavardi, M. Favazza, A. Motta, I. L. Fragalà, C. Massera, L. Prodi, M. Montalti, M. Melegari, G. G. Condorelli, E. Dalcanale, J. Am. Chem. Soc. 2009, 131, 7447–7455.
- [13] F. Tancini, D. Genovese, M. Montalti, L. Cristofolini, L. Nasi, L. Prodi, E. Dalcanale, J. Am. Chem. Soc. 2010, 132, 4781–4789.
- [14] A. Boccia, V. Lanzilotto, R. Zanoni, L. Pescatori, A. Arduini, A. Secchi, Phys. Chem. Chem. Phys. 2011, 13, 4444–4451.
- [15] M. Frasconi, F. Mazzei, Langmuir 2012, 28, 3322-3331.
- [16] B. Rybtchinski, ACS Nano 2011, 5, 6791-6818.
- [17] X. Y. Ling, D. N. Reinhoudt, J. Huskens, Chem. Mater. 2008, 20, 3574–3578.
- [18] F. Ciesa, A. Plech, C. Mattioli, L. Pescatori, A. Arduini, A. Pochini, F. Rossi, A. Secchi, J. Phys. Chem. C 2010, 114, 13601–13607.
- [19] A. Boccia, V. Lanzilotto, V. Di Castro, R. Zanoni, L. Pescatori, A. Arduini, A. Secchi, *Phys. Chem. Chem. Phys.* 2011, 13, 4452–4462.
- [20] A. Arduini, R. Bussolati, A. Credi, A. Pochini, A. Secchi, S. Silvi, M. Venturi, *Tetrahedron* 2008, 64, 8279–8286.
- [21] A. Arduini, R. Bussolati, A. Credi, G. Faimani, S. Garaudee, A. Pochini, A. Secchi, M. Semeraro, S. Silvi, M. Venturi, *Chem. Eur. J.* 2009, 15, 3230–3242.
- [22] A. G. Marrani, E. A. Dalchiele, R. Zanoni, F. Decker, F. Cattaruzza, D. Bonifazi, M. Prato, *Electrochim. Acta* 2008, *53*, 3903–3909.
- [23] M. Cossi, M. F. Iozzi, A. G. Marrani, T. Lavecchia, P. Galloni, R. Zanoni, F. Decker, J. Phys. Chem. B 2006, 110, 22961–22965.
- [24] F. Decker, F. Cattaruzza, C. Coluzza, A. Flamini, A. G. Marrani, R. Zanoni, E. A. Dalchiele, J. Phys. Chem. B 2006, 110, 7374–7379.
- [25] J. Terry, R. Mo, C. Wigren, R. Cao, G. Mount, P. Pianetta, M. R. Linford, C. E. D. Chidsey, *Nucl. Instrum. Methods Phys. Res. Sect. B* 1997, 133, 94–101.
- [26] A. Credi, S. Dumas, S. Silvi, M. Venturi, A. Arduini, A. Pochini, A. Secchi, J. Org. Chem. 2004, 69, 5881–5887.
- [27] T. R. Tshikhudo, D. Demuru, Z. X. Wang, M. Brust, A. Secchi, A. Arduini, A. Pochini, Angew. Chem. 2005, 117, 2973–2976; Angew. Chem. Int. Ed. 2005, 44, 2913–2916.
- [28] The C/N and Au/Si ratios are not as accurate as the small 1 nm AuNPs since in this case the thickness of the assembled layer (> 5 nm) is larger than the photoelectron escape depth.
- [29] E. Laviron, J. Electroanal. Chem. 1979, 101, 19-28.
- [30] A. G. Marrani, F. Cattaruzza, F. Decker, P. Galloni, R. Zanoni, *Electrochim. Acta* 2010, 5, 5733–5740.
- [31] J. J. González, R. Ferdani, E. Albertini, J. M. Blasco, A. Arduini, A. Pochini, P. Prados, J. De Mendoza, *Chem. Eur. J.* 2000, 6, 73–80.
- [32] R. Métivier, I. Leray, B. Lebea, B. Valeur, J. Mater. Chem. 2005, 15, 2965–2973.

www.chemeurj.org

## CHEMISTRY

- [33] R. Laudien, I. Yoshida, T. Nagamura, J. Chem. Soc. Perkin Trans. 2 2002, 1772–1777.
- [34] L. Pescatori, A. Boccia, F. Ciesa, F. Rossi, V. Grillo, A. Arduini, A. Pochini, R. Zanoni, A. Secchi, *Chem. Eur. J.* 2010, 16, 11089–11099.
- [35] B. Gadenne, I. Yildiz, M. Amelia, F. Ciesa, A. Secchi, A. Arduini, A. Credi, F. M. Raymo, J. Mater. Chem. 2008, 18, 2022–2027.
- [36] M. P. Seah, S. J. Spencer, Surf. Interface Anal. 2002, 33, 640-652.

[37] M. P. Seah, S. J. Spencer, Surf. Interface Anal. 2003, 35, 515-524.

[38] J. H. Scofield, J. Electron Spectrosc. Relat. Phenom. 1976, 8, 129– 137.

> Received: December 4, 2012 Revised: March 13, 2013 Published online: April 18, 2013

8006 -