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Self-assembling, patterning and SPR imaging of a 1,3 alternate bis(dipyridyl)calix[4]arene derivative–Cu^{2+} complex immobilized on to Au(111) surfaces†

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The electrochemically switchable Cu^{2+} complex of a 1,3 alternate bis(dipyridyl)calix[4]arene derivative forms self-assembled monolayers on Au(111) surfaces. The receptor is patterned on the surface by using microcontact printing procedures and the resulting surface is imaged *via* SPR.

The experience so far accumulated in the field of molecular devices has demonstrated that the ability to switch a molecular property is of relevance to the design and development of new nanodevices.[1,2] Metal complexes have been shown to act as switches, which can be operated through external inputs.[3] The anchoring of new metal complexes showing switchable properties on to solid supports is thus a fundamental step toward incorporating a molecular switch into a solid-state device.

Here we report on the characterization of a Au(111) surface modified with an electrochemically switchable Cu^{2+} complex of 25,27-bis(1-propyloxy)-26,28-bis(2,2′-dipyridyl-6-methoxy)calix-[4]arene in the 1,3 alternate conformation (**CBP**).[4,5] The [Cu(**CBP**)]$^{2+}$ complex has been already shown to undergo a quasi-reversible one-electron redox process in CH_3CN solution.[5] This process is characterized by a difference between the cathodic and anodic peak potential (ΔE_p = 110 mV; sweep rate: 100 mV s^{-1}; reference electrode: silver/silver nitrate; background electrolyte: 0.1 mol dm^{-3} tetrabutylammonium perchlorate)[5] that, although larger than the theoretical value, is well below the value (180 mV) that is considered a limit value for a reversible process;[6] both the anodic over cathodic peak current ratio (i_{pa}/i_{pc} = 0.9), close to unity, and the linearity of i_p *vs.* the square root of the sweep rate (R = 0.998)[5] further indicate that [Cu(**CBP**)]$^{2+}$ may be quasi-reversibly reduced.

Two dialkyl sulfide moieties were introduced into **CBP** to yield a receptor (25,27-bis[12-(thiododecyl)undecyloxy]-26,28-bis(2,2′-dipyridyl-6-methoxy)calix[4]arene 1,3 alternate, **CBPS**) (see ESI†) that would easily self-assemble on to Au(111) surfaces.[7] Fourier transform–surface plasmon resonance (FT-SPR) was employed to check whether the immobilized receptor was still able to complex Cu^{2+}.[8] Fig. 1 shows two representative sensorgrams obtained when pumping a $Cu(ClO_4)_2$ 1×10^{-4} mol dm^{-3} ethanol solution over the bare gold surface and the **CBPS** self-assembled monolayer, respectively. In the experiments pure ethanol was pumped before and after the $Cu(ClO_4)_2$ solution. Whilst the baseline goes back virtually to its initial position when the experiment is carried out with a bare gold surface (Fig. 1a), it shifts by some 60 cm^{-1}, corresponding to a change in the refractive index of $\Delta n = 3.6 \times 10^{-4}$,[9] when pumping pure ethanol over the **CBPS** monolayer after the $Cu(ClO_4)_2$ solution (Fig. 1b). This results from the interaction of Cu^{2+} ions with the anchored **CBPS** receptor. It is noteworthy that non-specific interactions between the $Cu(ClO_4)_2$ and the bare gold surface do not cause significant changes in the FT-SPR response (Fig. 1a).

The modified surface was studied by using polarization modulation infrared reflection–absorption spectroscopy (PM-IRRAS).[11] Fig. 2b and 2c show the CH stretching region (3000–2800 cm^{-1}) of the PM-IRRAS spectra of the **CBPS** modified Au(111) surface and of the same surface after a 60 minute immersion into $Cu(ClO_4)_2$ 0.001 mol dm^{-3} ethanol solution, respectively. The IR transmission spectrum of the **CBPS** solution is also shown for comparison (Fig. 2a). All the spectra show peaks attributed to the asymmetric and symmetric stretching vibration modes of the –CH_2– and –CH_3 groups of the **CBPS** receptor. The 2918 cm^{-1} and 2849 cm^{-1} bands detected in the PM-IRRAS spectrum of the anchored **CBPS** (Fig. 2b), which are assigned to the –CH_2– asymmetric (ν_{as}) and symmetric (ν_s) stretching mode, respectively, are indicative of a well-ordered, all-*trans* conformation of the alkyl chains present in the SAM formed by the **CBPS** receptor.[12] The changes induced by Cu^{2+} interaction with the **CBPS** monolayer are reflected by the shifts detected by PM-IRRAS. The bands at ν_{as} = 2927 cm^{-1} and at ν_s = 2856 cm^{-1}, assigned to the –CH_2– stretching modes of the Cu^{2+} complex of the **CBPS** monolayer (Fig. 2c) are indicative of a liquid-like, less-ordered conformation of the alkyl moieties.[12] Such conclusions are also supported by the position of the IR transmission peaks of the **CBPS** in $CHCl_3$ solution. The bands assigned to the –CH_2– stretching modes in solution (ν_{as} = 2926 cm^{-1}, ν_s = 2855 cm^{-1}) are virtually superimposable with those observed in the PM-IRRAS spectrum of the Cu^{2+} complex of the **CBPS** monolayer and well agree with the expected position for the –CH_2– stretching bands of liquid-like (less-ordered) alkyl chains.[12]

The above reported results confirm that **CBPS** forms well ordered SAMs on Au(111) surfaces. SAMs anchored on to solid surfaces are still able to complex Cu^{2+} ions even though the complexation increases the disorder of the SAMs.

In view of the fact that electrochemically switchable metal ion complexes anchored on to solid surfaces can find practical

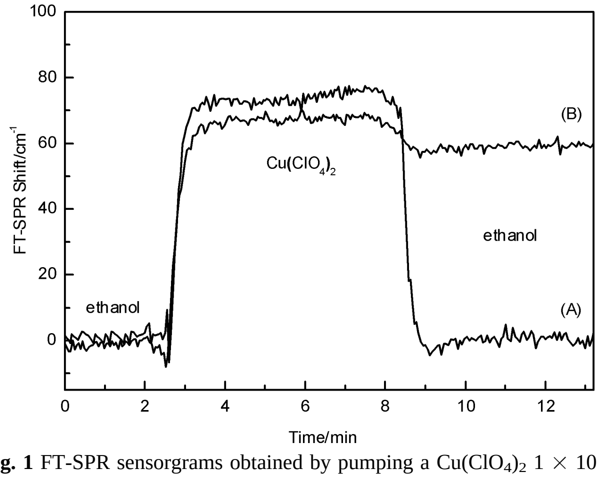

Fig. 1 FT-SPR sensorgrams obtained by pumping a $Cu(ClO_4)_2$ 1×10^{-4} mol dm^{-3} ethanol solution over a bare gold surface (A) and the **CBPS** monolayer (B).

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† Electronic supplementary information (ESI) available: procedures for the synthesis of **CBPS**, ^{1}H NMR data. See http://www.rsc.org/suppdata/cc/b4/b408326c/

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applications only if a spatial control of their distribution on to the surface is achieved, we patterned gold surfaces by depositing our systems. Microcontact printing (μCP) of SAMs has been proposed as a method for patterning organic molecules on to solid supports at scales >1 μm.[13] This procedure was used to pattern the **CBPS** receptor on to Au(111) surfaces.[14] The patterned surfaces were imaged by using SPR imaging.[15] A representative SPR image of the **CBPS** patterned Au(111) surface is shown in Fig. 3. SPR results show that **CBPS** may be patterned on to the surface in an ordered manner with relative ease and speed.

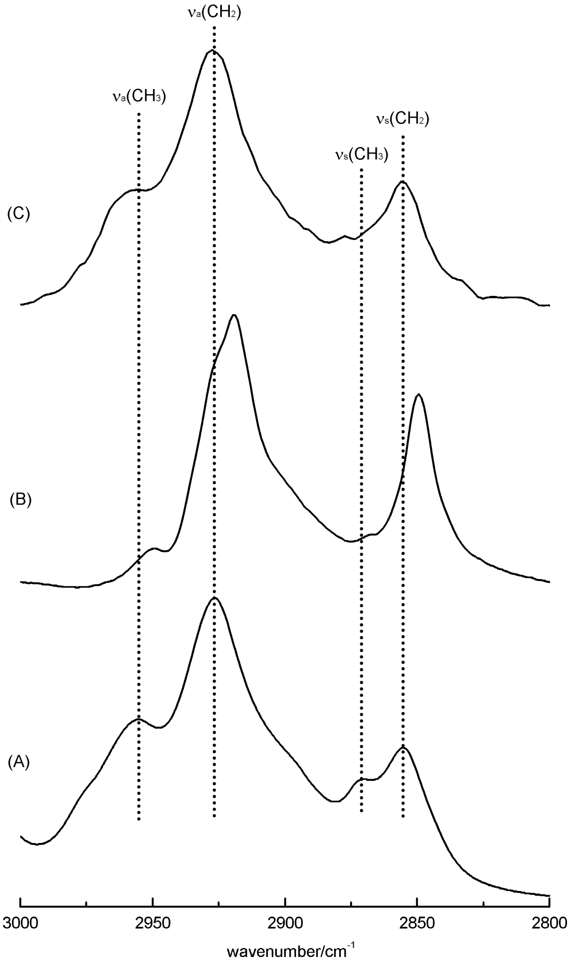

Fig. 2 PM-IRRAS spectra of the monolayer formed from **CBPS** on gold (B) and of the same monolayer after Cu^{2+} ion complexation (C) in the 3000–2800 cm^{-1} spectral region. The IR transmission spectrum of the **CBPS** in solution (A) is shown for comparison.

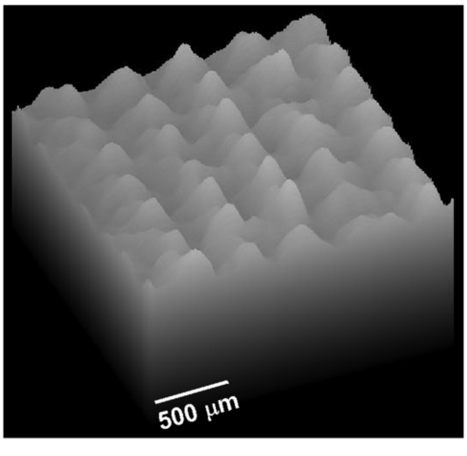

Fig. 3 Representative SPR image of the **CBPS** patterned gold surface.

In conclusion we have shown that the **CBPS** receptor, whose parent (**CBP**) compound can be reversibly reduced in solution, forms well-ordered SAMs on Au(111) surfaces. **CBPS** is still able to complex Cu^{2+} ions, thus providing a system that can be electrically operated; to this end, studies are under way to check whether the Cu^{2+} complex of the **CBPS** still works within a real microelectronic device. In addition, we have shown that the **CBPS** system may be patterned on to a gold surface by μCP procedures and that the patterned surface may be imaged by SPR much faster than it is usually accomplished *via* other surface-sensitive imaging techniques.

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Notes and references

1 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003.

2 *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.

3 (*a*) V. Amendola, L. Fabbrizzi, M. Licchelli, C. Mangano, P. Pallavicini, L. Parodi and A. Poggi, *Coord. Chem. Rev.*, 1999, **190–192**, 649; (*b*) S. Sortino, S. Petralia, S. Conoci and S. Di Bella, *J. Am. Chem. Soc.*, 125, **2003**, 1122.

4 G. Arena, A. Contino, E. Longo, D. Sciotto, C. Sgarlata and G. Spoto, *Tetrahedron Lett.*, 2003, **44**, 5415.

5 R. P. Bonomo, personal communication.

6 A. M. Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York, 1980.

7 **CBPS** monolayers were prepared by immersing the gold substrates in a 10^{-2} mol dm^{-3} ethanol–chloroform (3 : 1, v/v) solution of the receptor for at least 48 h at 60 °C. The samples were then removed from the solution and rinsed with large amounts of ethanol and chloroform. All glassware used in monolayer preparation was cleaned in piranha solutions (concentrated H_2SO_4 and 33% H_2O_2 in a 3 : 1 v/v ratio) and rinsed with copious amounts of high-purity water (Milli-Q Element Ultrapure Water) before use. **Warning**: piranha solutions should be handled with caution as they can detonate unexpectedly.

8 FT-SPR experiments were carried out by using an FT-SPR 100 (GWC Instruments, WI) apparatus. The light beam from an external port of a Nexus 870 FT-IR spectrometer (Nicolet, WI), equipped with a Quartz-Halogen source and a XT-KBr beam splitter, was used as the near-IR source of the FT-SPR. Gold substrates (GWC Instruments, WI) were obtained by thermally evaporating a gold layer (450 Å) on to SF-10 glass slides. Chromium (50 Å) was used as the adhesion layer. Gold substrates were brought into optical contact with the SF-10 equilateral prism present in the FT-SPR by using a refractive index matching fluid (Cargille Laboratories).

9 The FT-SPR sensor response was converted into refractive index changes by using 10 independent sucrose aqueous calibrating solutions whose concentration ranged from 0 to 17%. The refractive indexes of the sucrose solutions were obtained from the literature (ref. 10).

10 *Handbook of Chemistry and Physics*, 71st edn., ed. D. R. Lide, CRC Press, Boston, 1990.

11 PM-IRRAS experiments were conducted on a Nicolet Nexus 870, equipped with a PM-IRRAS external unit. The polarization was achieved by using a wire-grid polarizer and modulated by using a 50 kHz ZnSe photoelastic modulator (PEM-90, Hinds Instruments, OR). The IR beam was collected by a BaF_2 lens and focused on to an MCT detector, after reflection at grazing angle (83°) from the gold surface. The signal was demodulated by a Synchronous Sampling Demodulator (GWC Instruments, WI) to measure the differential intensity of p- and s-polarized IR radiations. The reported normalized differential reflectance spectra results from the average of 1000 spectra collected with a resolution of 2 cm^{-1}.

12 M. D. Porter, T. B. Bright, D. L. Allara and C. E. D. Chidsey, *J. Am. Chem. Soc.*, 1987, **109**, 3559.

13 (*a*) Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 550; (*b*) Y. Xia, J. A. Rogers, K. E. Paul and G. M. Whitesides, *Chem. Rev.*, 1999, **99**, 1823.

14 Polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning, MI) stamps were created from patterns (masters) having 200 μm × 200 μm squares. The stamp was "inked" with a 0.01 mol dm^{-3} 3 : 1 (v/v) ethanol–chloroform solution of **CBPS**. Organic microstructures were generated by bringing the stamp into contact with a clean Au substrate.

15 SPR imaging experiments were carried out by using a SPRimager (GWC Instruments, WI) apparatus. SPR images were acquired using the V++ software (Digital Optic, New Zealand) and analyzed by using the Scion Image Beta 4.02 (Scion Corp., MD) software package.