LETTER

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Ordered anchored cavities at work: a new and rapid SPR-based method for the detection of trace amounts of Cs^+†

Giuseppe Arena,*[ac] Annalinda Contino,[a] Roberta D'Agata,[a] Carmelo Sgarlata[a] and Giuseppe Spoto*[abc]

[a] *Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6, 95125 Catania, Italy. E-mail: garena@unict.it; gspoto@unict.it*
[b] *Istituto di Biostrutture e Bioimmagini - Sezione di Catania, C.N.R., c/o Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy*
[c] *I.N.C.A., Analytical Research Unit, c/o Dipartimento di Scienze Chimiche, Università di Catania, Viale Andrea Doria 6, 95125 Catania, Italy*

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Fourier transform-surface plasmon resonance (FT-SPR) using Au(111) chips modified by a 1,3-alternate calix[4]arene-crown-6 derivative is proposed as a method to detect Cs^+ at the *ppb* level.

Calix[4]crown-6 derivatives have proved to be excellent sequestering agents for Cs^+ even in the contemporary presence in solution of massive amounts of other alkali metal ions.[1] This property has rendered this class of ligands good candidates for the selective detection/removal of Cs^+ from radioactive liquid waste. Within this framework, a variety of strategies based on *i*) the anchoring of such macrocyclic ligands onto silica-gel supports,[2] *ii*) their inclusion into polymeric membranes[3] and *iii*) the coating of microcantilevers with calix[4]crown based self-assembled monolayers[4] has so far been proposed for the detection/removal of Cs^+. However, there is still a pressing need for methods that lend themselves to the construction of multi-element sensing arrays for the *in situ* simultaneous determination of a wide variety of metal ions in trace amounts.

Here we report on the use of Au(111) Fourier transform-surface plasmon resonance (FT-SPR) chips modified by the 25,27-bis(propyloxy)-5,17-bis[3-(propylsulfanyl)propyl]calix[4]arene-crown-6 in the 1,3-alternate conformation (**CCS**) (see ESI†) as a method for the rapid detection of trace amounts of Cs^+. The method proposed is *i*) compatible with an array-based approach,[5] *ii*) amenable to modification and may be tailored to target the appropriate metal ion[6] and *iii*) simple and fast. An optimal response of the modified Au(111) chip requires a well-ordered **CCS** monolayer to be present on the surface. However, the use of such a method implies that three fundamental questions be answered in advance, *i.e. i*) is the FT-SPR response due the covalently linked rather than to a simply adsorbed receptor? *ii*) Is **CCS** orderly attached to the gold surface? *iii*) Is the FT-SPR response truly due to the modified surface?

X-Ray photoelectron spectroscopy (XPS) provides an answer to the first question. The study, carried out by minimizing the exposure time of the **CCS** monolayer to the monochromatized X-ray source,[7] demonstrated the absence of signals other than those coming from C, O, S and Au. The spectrum of the S 2p region clearly indicates the presence of two different contributing signals resulting from bound (S $2p_{3/2}$ binding energy of 161.5 eV) and unbound sulfur atoms (S $2p_{3/2}$ binding energy of 163.5 eV), respectively (Fig. 1);[8] the ratio between the area attributed to bound sulfur atoms and the S 2p total area leads to the conclusion that *ca.* 74% of the sulfur atoms are bound to the gold surface.[9]

To answer the second question the real chip was studied by polarization modulation infrared reflection–absorption spectroscopy (PM-IRRAS). Fig. 2(A) shows the CH stretching region (3150–2700 cm^{-1}) of the PM-IRRAS spectrum of the **CCS** modified gold surface. For the sake of comparison, Fig. 2(B) shows the FT-IR transmission spectrum of a **CCS** $CHCl_3$ solution, that depicts a representative PM-IRRAS spectrum for randomly oriented **CCS** molecules. The spectra show peaks attributed to the asymmetric (ν_{as}) and symmetric (ν_s) stretching vibration modes of the $-CH_2-$ and $-CH_3$ groups of the **CCS** receptor. The bands at 2933 cm^{-1} and 2874 cm^{-1}, attributed to CH_2 asymmetric and symmetric stretching vibration modes of $-O-CH_2-$ ether groups, respectively, are detected in the

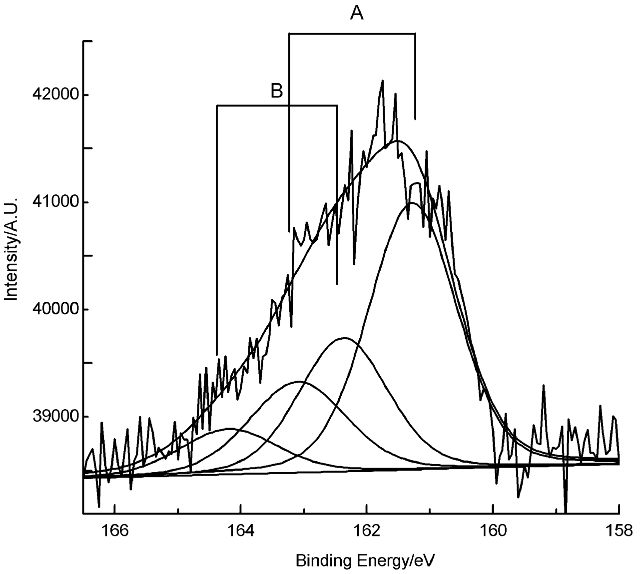

Fig. 1 Representative XP S 2p spectrum for **CCS** anchored onto Au(111) surfaces. The $S2p_{3/2}$–$S2p_{1/2}$ peaks were fitted using one S 2p doublet with a 2 : 1 area ratio and a splitting of 1.2 eV. The positions of the $S2p_{3/2}$–$S2p_{1/2}$ peaks assigned to bound (A) and unbound (B) sulfur containing species are shown. χ^2 for the fit shown in the figure was 1.59.

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† Electronic supplementary information (ESI) available: Procedure for the synthesis of **CCS**, ^1H NMR data. See http://dx.doi.org/10.1039/b511111k

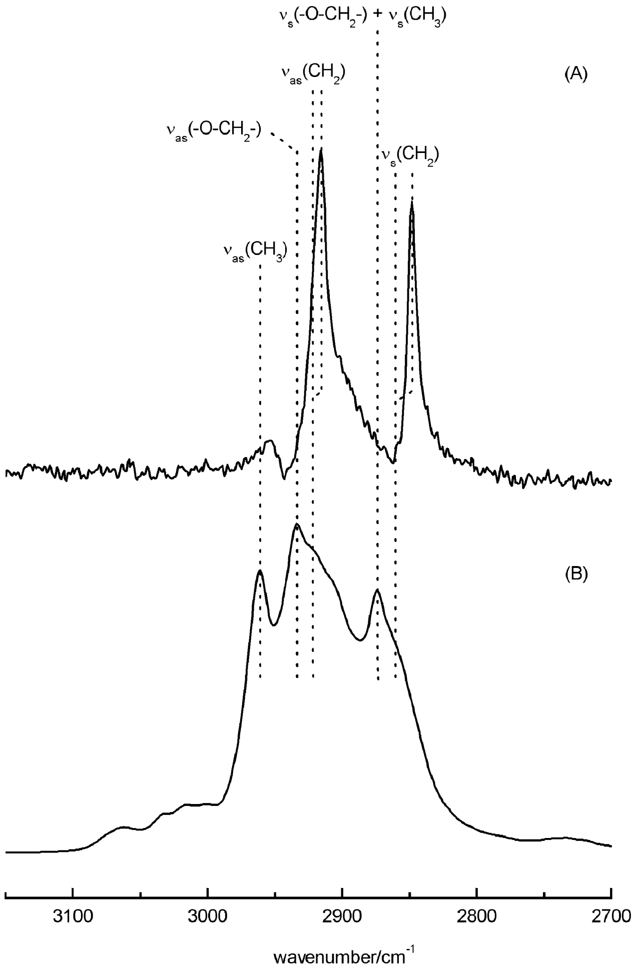

Fig. 2 (A) Representative PM-IRRAS spectrum of the monolayer formed by **CCS** on Au(111) in the 3150–2700 cm^{-1} spectral region. (B) The FT-IR transmission spectrum of **CCS** in solution is shown for comparison. Bands at 3016, 3034 and 3063 cm^{-1} are attributed to the aromatic C–H stretching vibration modes.

transmission spectrum only. The band at 2874 cm^{-1} partially overlaps with the signal attributed to the symmetric stretching mode of the –CH$_3$ groups. The 2915 cm^{-1} and 2848 cm^{-1} bands detected in the PM-IRRAS spectrum of the anchored **CCS** [Fig. 2(A)], which are assigned to the –CH$_2$– asymmetric and symmetric stretching mode, respectively, are indicative of a well-ordered, all-*trans* conformation of the alkyl chains present in the SAM formed by the **CCS** receptor[10] and differ in position from that obtained for the **CCS** solution (2922 cm^{-1} and 2856 cm^{-1}, respectively). Since no bands, generated by asymmetric and symmetric stretching vibration modes of the –O–CH$_2$– groups are detected in the PM-IRRAS spectrum, it may be concluded that the **CCS** molecule is oriented in such a way that causes the transition moments of the –O–CH$_2$– groups to have components parallel to the surface. This points toward an upward orientation of the crown moiety of **CCS** that favors the interaction with target species, such as Cs$^+$, present at the interface.

Fig. 3 shows two representative FT-SPR sensorgrams obtained when pumping a CsNO$_3$ 1 × 10^{-5} mol dm^{-3} ethanol solution over the bare gold surface [Fig. 3(A)] and a CsNO$_3$ 1 × 10^{-9} mol dm^{-3} ethanol solution over the **CCS** coated gold surface [Fig. 3(B)], respectively. Pure ethanol was pumped through before and after the injection of CsNO$_3$ solutions. Whilst the baseline goes virtually back to its initial position when the experiment is carried out with a bare gold surface [Fig. 3(A)], it shifts by 29 cm^{-1} when pumping pure ethanol over the **CCS** monolayer after the CsNO$_3$ solution [Fig. 3(B)], which answers the third question. The total standard deviation calculated for the overall shift is ±7%. 50 and 71 points were taken for the initial baseline and for the baseline obtained after pumping Cs$^+$, respectively. Such a shift clearly indicates that Cs$^+$ ions are interacting with the anchored **CCS** receptor and that such an interaction may be exploited to detect *ppb* of Cs$^+$.

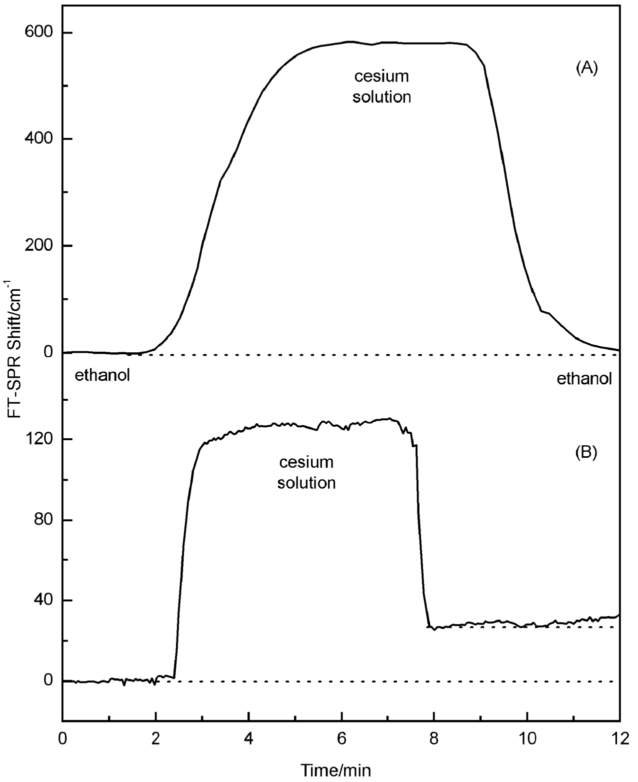

Fig. 3 FT-SPR representative sensorgrams obtained (A) when a CsNO$_3$ 1 × 10^{-5} mol dm^{-3} ethanol solution was pumped over a bare gold surface and (B) when a CsNO$_3$ 1 × 10^{-9} mol dm^{-3} ethanol solution was pumped over the **CCS** monolayer, respectively. The interaction between the Cs$^+$ ions and the **CCS** monolayer causes an FT-SPR shift of 29 cm^{-1}.

These results altogether show that *i*) **CCS** may be covalently attached to Au(111) with a relatively high degree of coverage, *ii*) **CCS** forms well ordered SAMs on the gold chip as shown by PM-IRRAS and *iii*) these SAMs may be conveniently exploited to determine trace amounts of Cs$^+$ (or other metal ions) by resorting to SPR-based techniques that have been shown to be compatible with an array-type approach.

Experimental

CCS 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$_2$SO$_4$ and 33% H$_2$O$_2$ 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.

X-Ray photoelectron spectra were obtained with a PHI5600 ESCA/SAM monochromator system using an Al K$_\alpha$ monochromatized source ($h\nu$ = 1486.6 eV). A filament current of 12 mA and an accelerating voltage of 15 kV (180 Watt) were maintained during analyses. The spectra were obtained at a 45° takeoff angle with a pass energy of 23.58 and 5.85 eV for the wide and narrow scans, respectively. The typical operating pressure was in the range 10^{-9}–10^{-10} Torr. The XPS spectrometer was calibrated using the Ag 3d region of an etched Ag sheet. The separation between Ag $3d_{3/2}$ (368.3 eV) and the Ag $3d_{1/2}$ was 6.00 eV. The energy resolution was 0.48 eV. The binding energy of the experimental spectra was calibrated on the basis of the most intense peak of the C 1s region at 284.5 eV. The curve fit of the experimental spectra was performed using XPSPeak 4.1 software. 80/20 Gaussian/Lorentzian functions (FWHM = 1.2 eV) and linear background subtractions were used to fit the XP S 2p regions. All XP values reported were obtained from the average of single acquisitions carried out on each one of three separate samples. No repeat measurements were carried out on the same sample to avoid artifacts generated by the X-ray induced decomposition of the organic overlayer. The typical sample exposure time to X-rays was in the range of 3–5 min, to minimize sample damage.

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 was 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 onto 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}.

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 an 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) onto 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).

Acknowledgements

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