

Supplementary Material (ESI) for Chemical Communications
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ULTRATHIN MOLECULARLY IMPRINTED POLYMER SENSORS EMPLOYING ENHANCED TRANSMISSION SURFACE PLASMON RESONANCE SPECTROSCOPY**

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Supporting Material

Experimental

Gold nanoislands were deposited onto BK7 glass slides by evaporating gold shots at 10^{-7} mB in an Edwards AUTO 306 high vacuum evaporator. The temperature in the chamber was maintained below 40 °C. The deposition rate (0.0014-0.0028 nm/sec) and the nominal thickness (~4.0 nm) of the films were monitored, *in situ*, by a quartz crystal microbalance. The gold nanoislands were annealed overnight in a vacuum oven, at 1 torr and at 140°C.

Gold nanoparticles were prepared as described previously. Briefly, 200 mL of 0.01 % (w/v) HAuCl₄ was brought to boil, then 7 mL of 1% (w/v) aqueous trisodium citrate was added under vigorous stirring. The color changed into greyish-black then into wine-red within a few minutes. The dispersion was allowed to cool down and filtered through 0.2 µm pore size nylon bottle-top filter system. The 11.7±1.9 nm diameter gold nanoparticles had a surface plasmon absorbance at 518 nm.

A 3.0 ±0.6 nm thick layer of polyglycidylmethacrylate, PGMA, was deposited onto the annealed gold nanoislands by spin-coating from its 0.06 % solution in dehydrated methyl-ethyl-ketone (MEK) in a chamber with controlled humidity (less than 20 % relative humidity). PGMA was cross-linked by heating at 120 °C for 20 minutes in a vacuum oven (at 1 torr) and washed three times in dry MEK to remove the ungrafted polymer. This was followed by spin-coating a carboxyl group terminated poly(2-vinylpyridine), P2VP, $M_n = 39200$ g/mol, $M_w = 41500$ g/mol) film from its 0.5% solution in chloroform onto the cross-linked PGMA anchoring layer; and annealing for 8 h in a

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vacuum oven (at 1 torr) at 140°C. The epoxy groups of the PGMA anchoring layer reacted with the terminal carboxyl groups of the P2VP-COOH yielding a layer of tethered chains (polymer brushes) of P2VP (7.6±0.8 nm) as described elsewhere^[12]. Subsequent to washing by chloroform, ethanol and water, citrate capped gold nanoparticles (11.7±0.9 nm) were adsorbed onto the P2VP film. P2VP was then cross-linked by the immersing the entire sample into chloroform, containing 1 % 1,4-diiodobutane and 1 % cholesterol for 3 days at 65 °C. Finally, the sample was exposed again to the aqueous solution of gold nanoparticles for 12 hours, rinsed and dried.

The absorption spectra of samples were recorded on a single-beam, microprocessor controlled diode array spectrophotometer with collimating optics (Hewlett-Packard 8452A). The wavelength range and the resolution of the instrument was 190 to 820 nm (UV-Vis) and 2 nm, respectively.

A Multiskop null-ellipsometer (Optrel, Germany) equipped with a He-Ne laser ($\lambda = 633$ nm) was used for ellipsometric measurements. The angle of incidence of polarized light was set at 70°. Since gold nanoislands and gold nanoparticles are strong light scatterers, we used the null-ellipsometry to measure the thickness of the polymer layers prepared on a bare Si substrate. Heterogeneities and interface roughness were recognized as sources of incoherent scattering which cause measurement errors.^[13]

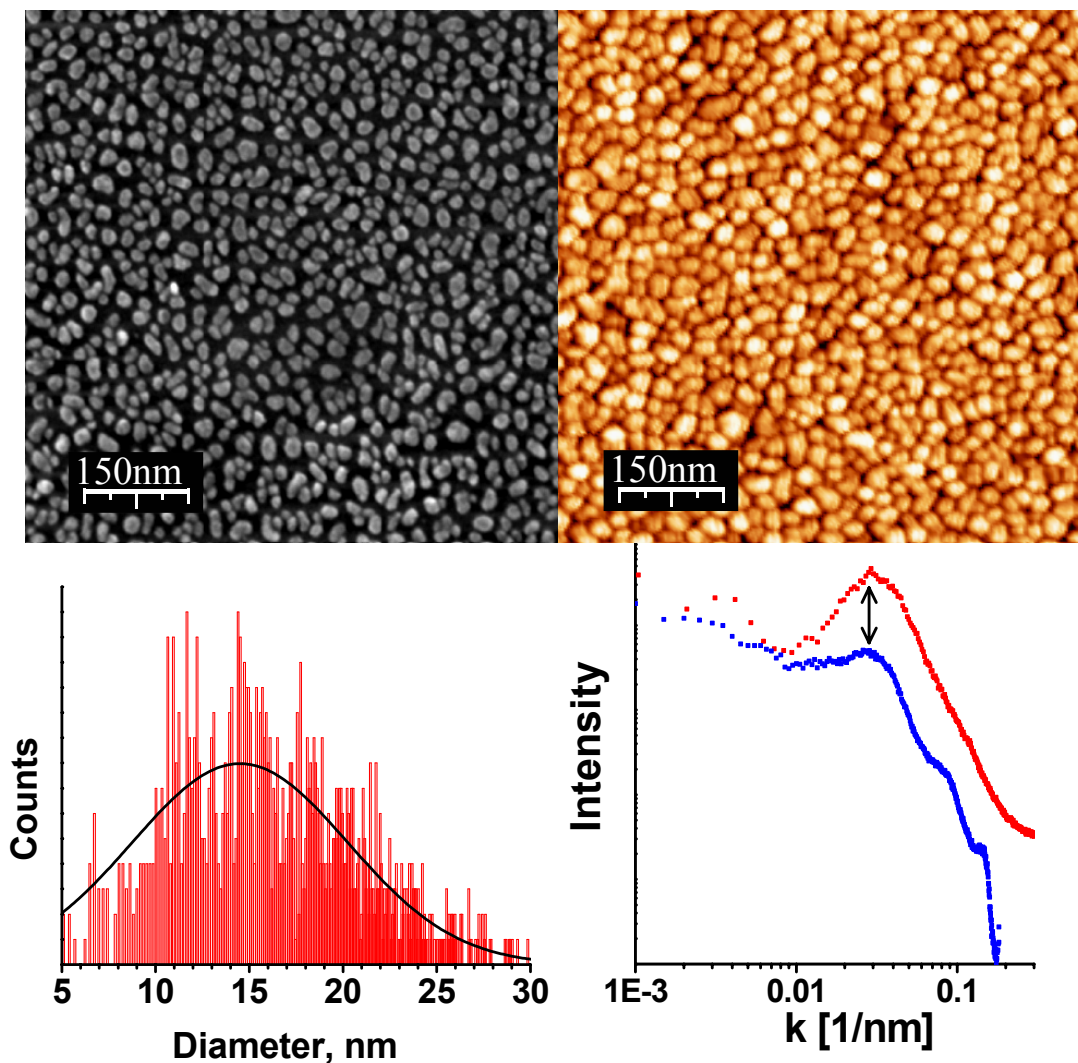
Atomic force microscopy (AFM) imaging of layer topography was performed using a Dimension 3100 Scanning Probe Microscope (Veeco Instruments, USA) in the tapping mode. We used AFM probes BS-Tap300 (BudgetSensors, Bulgaria) with the following characteristics: spring constant 40 N/m, resonant frequency 300 KHz, tip radius 20 nm nominal. AFM was employed to monitor the changes in the thickness of coating layers after each preparation step (See Supplementary Information).

Polarization Modulated Infrared Reflection Absorption Spectroscopy, PM-FTIRAS, was of the different preparations were taken as described previously.^[14,15,16]

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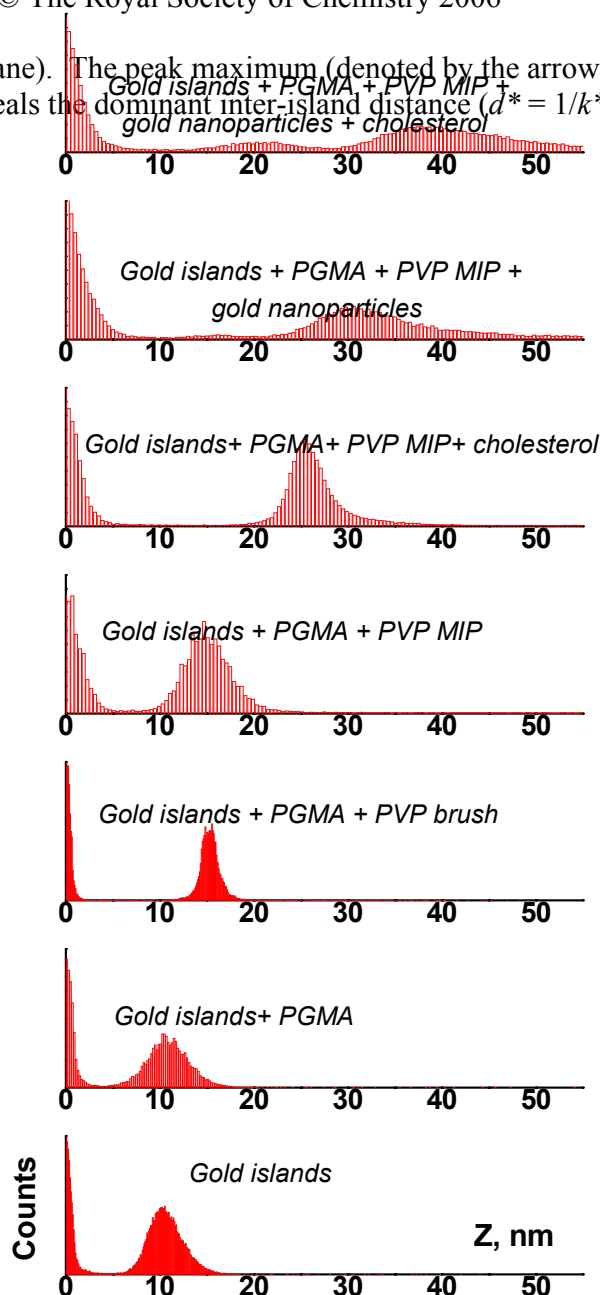


Supplementary Figure 1. Top: Scanning electron microscopic (left) and atomic force microscopic (right) images of typical gold nanoisland preparations. Bottom left: size histogram of gold islands with Gaussian fit (black curve: center at 14.5 nm, standard deviation is 5.8 nm), constructed subsequent to defining the perimeters in the SEM images. Bottom right: Calculated Power Spectral Density (PSD) of the SEM (top curve) and AFM (bottom curve) images to determine the dominant center-to-center inter-island distance. The one-dimensional PSD function is calculated on the base of two-dimensional Fast Fourier Transform (2D-FFT) of surface topography. It shows the occurrence probability of various spatial frequencies and is plotted as a function of wavevector, k ($k = 1/d$, where d is the distance between a pair of coordinates projected

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onto a surface plane). The peak maximum (denoted by the arrow, $k^* = 0.0285 \text{ nm}^{-1}$) on the PSD plot reveals the dominant inter-island distance ($d^* = 1/k^* = 35 \text{ nm}$).

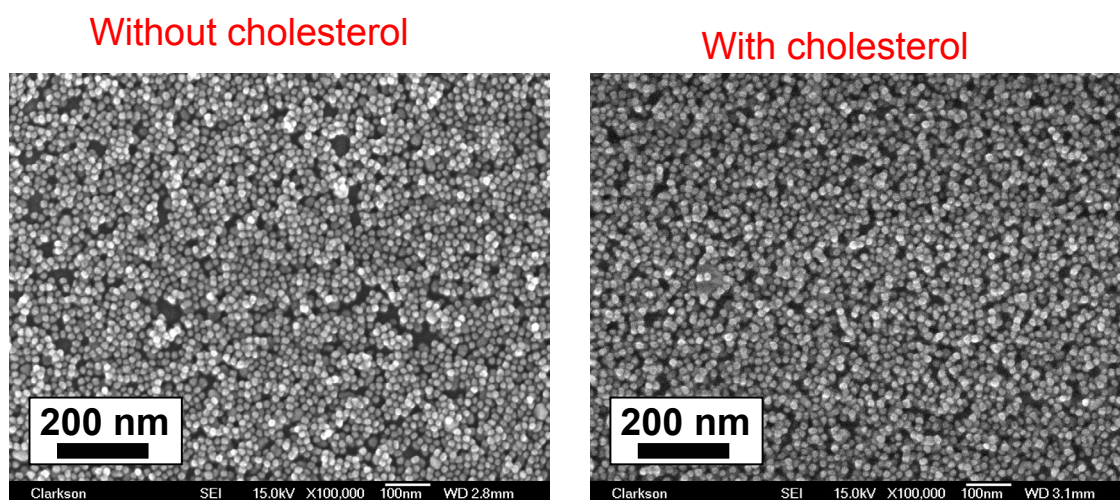


Supplementary Figure 2. The height histograms calculated from the AFM images of the layer scratches. The lower peaks with the maximum at $z = 0$ originate from a glass slide, while the upper peaks represent the layer surface.

AFM was employed to monitor the changes in the thickness of coating layers after each preparation step. For this, a layer was gently scratched by a steel needle and the topography of the scratch (width $\sim 40 \mu\text{m}$) was visualized by AFM (in the literature this measurement method is usually referred as AFM scratch test). It is worth noting that the

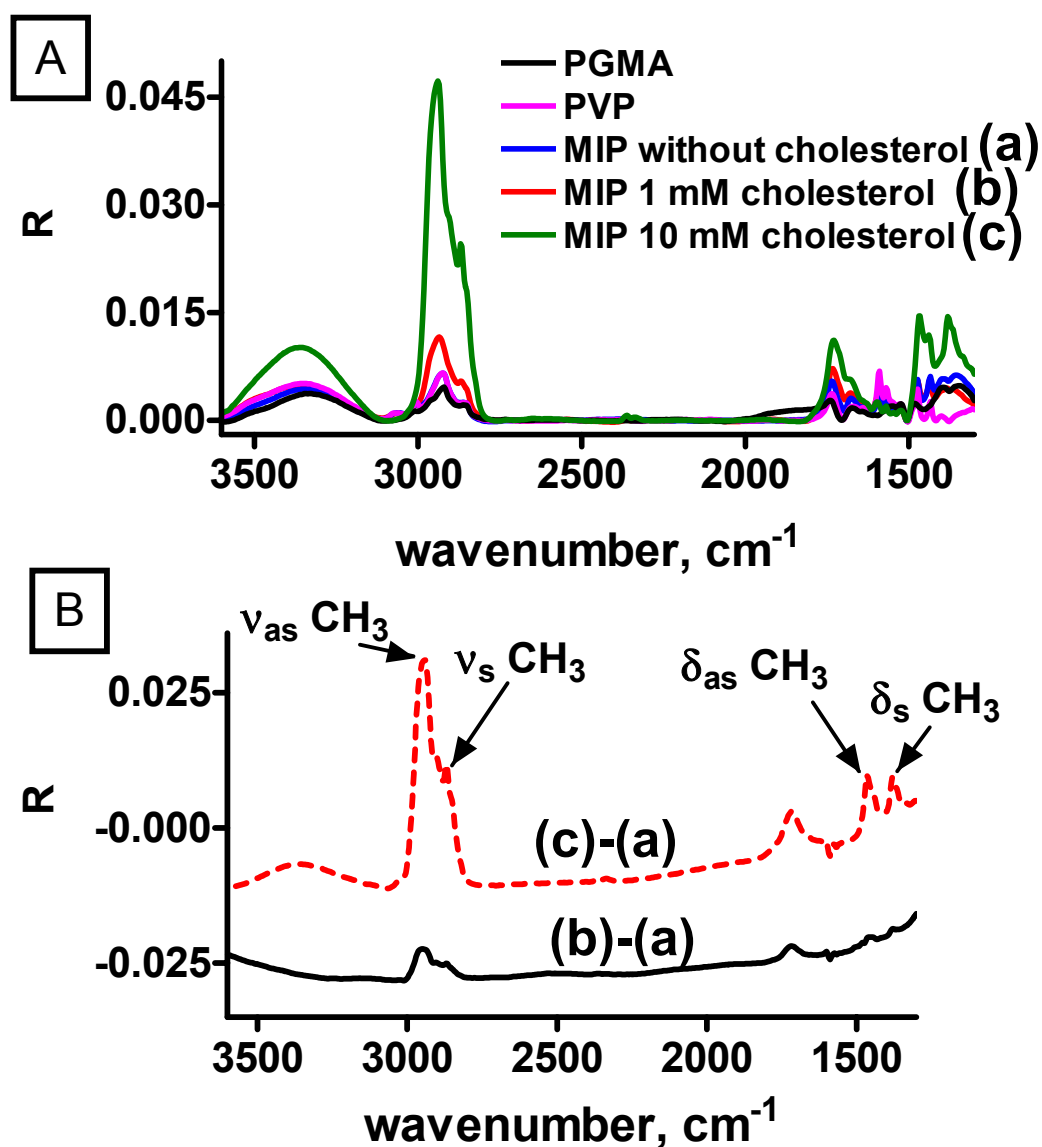
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surface of a glass slide was almost untouched by the scratching procedure, while polymer layers and gold islands were completely stripped off by the needle tip. The AFM images ($10 \times 2.5 \mu\text{m}^2$) were recorded in a way that the edge between the upper and lower terraces which represented respectively the layer and glass surfaces was in the middle of the images. We used the WSxM program (freeware from Nanotec Electronica, Spain) to remove any slope of the terraces on the AFM images and to calculate height histograms. All the height histogram showed bimodal distribution, where the peaks represented the layer and glass surfaces. The fitting of the peaks using the Gaussian function allowed us to determine the peak maxima and the standard deviation values. The difference between the maxima and the standard deviations were attributed to the layer thickness and the terrace roughness, respectively.



Supplementary Figure 3. Typical scanning electron microscopic images of the stratified molecularly imprinted sensors in the absence (left) and in the presence (right) of cholesterol. The layers consist of gold nanoislands, PGMA, PVP MIP and gold nanoparticles.

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Supplementary Figure 4. A: PM-FTIRRAS taken at different steps of the sample preparation (deposition of PGMA, deposition of the PVP, after crosslinking to form the MIP in the presence of cholesterol, washing out the cholesterol (a), and adding the cholesterol as an analyte at two different concentration (b and c). B: PM-FTIRRAS of cholesterol, obtained by subtracting the PM-FTIRRAS of that due to the empty MIP sensor (subsequent to having washed out the cholesterol from the MIP, prepared by

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cross-linking the PVP polymer in the presence of cholesterol) from samples which were exposed to 1.0 mM (solid line, b-a) and 10 mM (dashed line, c-a) solutions of cholesterol in chloroform.

Supplementary Table 1
Thickness of the Different Layers Determined by AFM Scratch Test and Ellipsometry

| Sequentially deposited layers ^a | | Total thickness, nm ^b | Layer thickness, nm | |
|--|------------------------|----------------------------------|--------------------------------|---------------------------|
| | | | AFM scratch test, ^c | Ellipsometry ^d |
| Gold nanoislands | | 10.1±1.7 | 10.1±1.7 | N/A |
| PGMA | | 11.6±2.1 | 1.5 | 3.0±0.6 |
| PVP brush (prior to cross linking) | | 15.4±0.8 | 3.8 | 7.6±0.8 |
| PVP MIP, imprinted with cholesterol, cross linked without gold nanoparticles | Cholesterol washed out | 16.4±2.4 | 4.8 | N/A |
| | Cholesterol readsorbed | 25.7±1.9 | 14.1 ^e | 15.6±1.9 |
| PVP MIP, imprinted with cholesterol, cross linked with gold nanoparticles | Cholesterol washed out | 31.0±4.1 | 14.6 | N/A |
| | Cholesterol readsorbed | 39.3±4.5 | 22.9 ^f | N/A |

^aSee Figure 1.

^bAs measured by AFM scratch test for the sequentially deposited layers as described in the Experimental section.

^cObtained by subtracting the thickness(es) of the previously deposited layers.

^dDetermined for polymers deposited on a silicon substrate (See Experimental)

^e9.3 nm due to the addition of cholesterol (ie., 14.1 nm - 4.8 nm = 9.3 nm).

^f8.3 nm due to the addition of cholesterol (ie., 22.9 nm - 14.6 nm = 8.3 nm).