Supplementary Information: Nanometer Control in Plasmonic Systems Through Discrete Layer-By-Layer Macrocycle-Cation Deposition

Steven J. Barrow,[†,‡,⊥] Aniello Palma,[†,¶,⊥] Bart de Nijs,[§] Rohit Chikkaraddy,[§]

Richard W. Bowman,[§,‖] Jeremy J. Baumberg,[§] and Oren A. Scherman[∗,†]

[†]*Melville Laboratory for Polymer Synthesis, Department of Chemistry, University of Cambridge, CB2 1EW, UK*

[‡]*Current address: School of Applied Chemistry and Environmental Science, RMIT University, Melbourne, 3000, Australia*

[¶]*Current address: School of Physical Sciences, Ingram Building, University of Kent, Canterbury, Kent, CT2 7NH, UK*

[§]*Nanophotonics Centre, Cavendish Laboratory, University of Cambridge, CB3 0HE, UK*

[‖]*Current address: Department of Physics, University of Bath, BA2 7AY, UK*

[⊥]*Contributed equally to this work*

E-mail: oas23@cam.ac.uk

Experimental Methods

Chemicals and Sample Preparation

Chemicals: $FeCl_3 \cdot 6\,H_2O$ was purchased from Breckland Scientific Supplies and used as received. Gold nanoparticles (80 nm diameter) were purchased from BBI Solutions and used as received. CB[7] was synthesised according to literature procedures.[1]

CB[7]-Fe^{3+} crystal growth CB[7] (25 mg, 22 /mumol, 1 eq.) was dissolved in deionized water (2.0 mL) and treated with $FeCl_3 \cdot 6\,H_2O$ (3 mg, 11 μmol, 0.5 eq). The reaction was heated to reflux over night. The solvent was removed and the crude mixture was recrystallized via slow evaporation of a solvent mixture of water-DMF (90:10).

Substrate Preparation: For gold substrates, silicon wafers are coated using electron-beam-evaporation of a 70 nm thick gold layer on a 5 nm chrome adhesive layer. The surface roughness of the film is minimised by choosing a slow evaporation rate of 0.1 A s^{-1}.

Layer-By-Layer Deposition Method: Prepared gold substrates were immersed in a 1 mM aqueous solution of CB[7] for 30 min, then rinsed with Millipore water and dried gently with N_2. Fe^{3+} was then deposited by immersing the CB[7] coated gold substrate in an aqueous solution of 1 mM $FeCl_3 \cdot 6\,H_2O$ for 1 hr, then rinsed with Millipore water and dried gently with N_2. These steps were alternated to build up the desired structure thickness.

Instrumentation

QCM crystals of frequency 8 MHz (AT-cut) were purchased from IJ Cambria Scientific Ltd. with 1000 $\mathring{A}$ gold electrodes mounded on 100 $\mathring{A}$ Titanium, (working surface diameter of 5 mm). The crystal frequency was monitored through a vector network analyser (DG8SAQ USB-Controlled VNWA 3E, SDR-Kits) and data was recorded at 1.37 s intervals. Aqueous solutions of CB[7] and $FeCl_3$ were prepared using Millipore water. A flow rate of 50 μM per minute was maintained with a syringe pump. Contact angle measurements were performed on a KSV CAM 200 goniometer.

Normalising Plasmon Resonance Spectroscopy

To demonstrate what effect the change in spacing and refractive index has on the plasmonic scattering of the NPoM geometries with the deposition of CB-Fe layers dark-field scattering spectra from individual NPoM geometries were collected using an Olympus BX51 optical microscope with an MPlanFLN 100x/0.80 dark-field objective. The microscope was fibre-coupled with a 50 μm VIS/NIR optical fibre to an Ocean Optics QE65pro spectrometer. To collect large data sets of Au NPoM scattering spectra, in-house particle tracking software was used. This software identifies particles based on a scattering intensity threshold and combined with a Prior Scientific xyz-motorized stage iteratively scans 9 spectral intensities in a 0.36 μm^2 map adjusting the xy-position accordingly to centre the collection spot on the Au NPoM. To correct for chromatic aberration 25 spectra were collected over a focal range of 5.5 μm and the highest intensity (i.e. focus point for that wavelength) was determined by fitting a Gaussian over the focal range at each wavelength, eliminating focus effects on the spectra.

The resulting spectra were then isolated by fitting a multi Gaussian fit between 500 nm and 900 nm sorted the largest mode by wavelength in bin sizes of 5.7 nm, averaging the result. If more than one peak was found in a given spectrum between 600 nm and 900 nm exceeding half the amplitude of the coupled mode (between 600 and 900 nm), the spectrum was considered to have a double-peaked coupled plasmon mode and was sorted out thereby minimizing the influence of non-spherical nanoparticles on the analysis. Finally, to eliminate collection angle dependent chromatic aberration in dark-field microscopy, collection efficiency as a function of angle was determined by scanning across a 100 μm diameter glass capillary providing a reference to compensate for infra-red collection drop-off at higher angles. Corrected spectra were then normalised on the transverse mode (at 533 nm), and compared to FDTD simulations for an 80 nm nanoparticle on a gold surface with a spacer of varying thickness and refractive index, See ref. for more details[2].
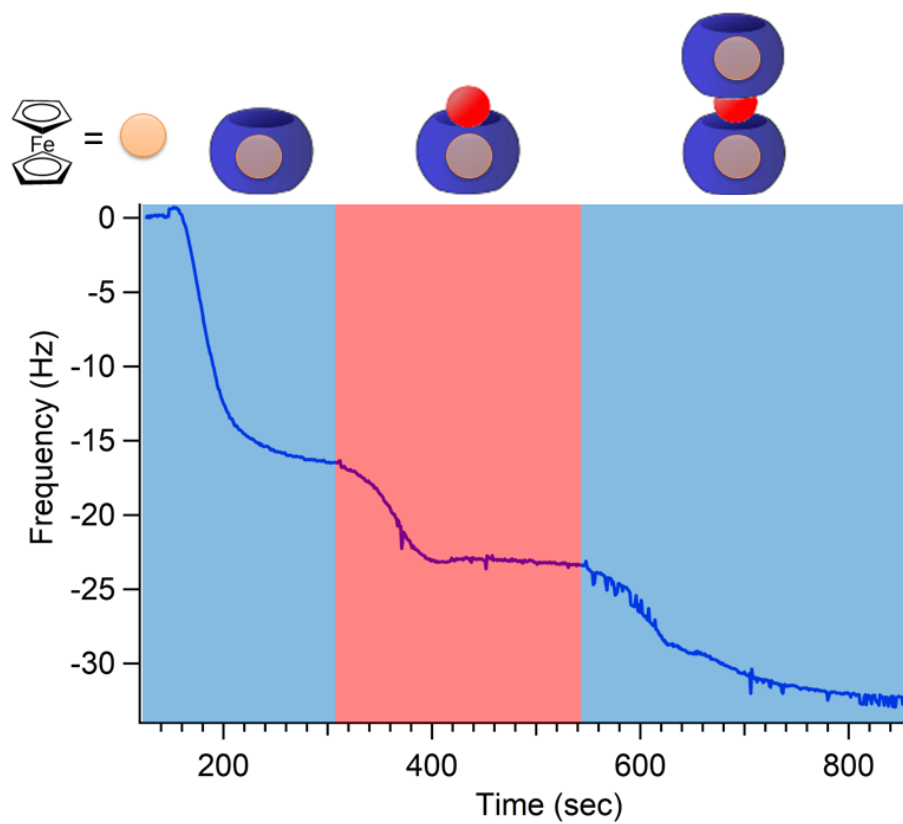
Figure 1: Quartz Crystal Microbalance data demonstrating the layer-by-layer build up of CB[7]⊂ferrocene-Fe^{3+} nano-layers.

References

(1) Day, A.; Arnold, A. P.; Blanch, R. J.; Snushall, B. Controlling Factors in the Synthesis of Cucurbituril and Its Homologues. *J. Org. Chem.* **2001**, *66*, 8094–8100.

(2) de Nijs, B.; Bowman, R. W.; Herrmann, L. O.; Benz, F.; Barrow, S. J.; Mertens, J.; Sigle, D. O.; Chikkaraddy, R.; Eiden, A.; Ferrari, A.; Scherman, O. A.; Baumberg, J. J. Unfolding the Contents of Sub-nm Plasmonic Gaps using Normalising Plasmon Resonance Spectroscopy. *Faraday Discuss.* **2015**, *178*, 185–193.