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# Electronic Supplementary Information

# Preparation of Metal – SAM – Dendrimer – SAM – Metal Junctions by Supramolecular Metal Transfer Printing

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**Characterization of βCD SAMs on Au coated PDMS stamps**

Since the gold is coated on a PDMS stamp instead of silica, the conventional procedure for formation of a βCD SAM (*Langmuir*, **1998**, *14*, 6424 and *Chem. - Eur. J.* **2000**, *6*, 1176) was not useful. This is due to the properties of PDMS, which is oxidized by piranha and swells in chloroform. Regarding the use of piranha: cleaning the gold surface of the stamp may not be necessary, since the PDMS stamps are freshly coated by evaporation in a clean room. Direct immersion of the gold-coated stamps in the adsorbate solution should prevent the gold layer from fouling.

When pure ethanol is used for the βCD adsorbate solution instead of a chloroform/ethanol mixture, the βCD adsorbate does not dissolve at room temperature. Heating a suspension of 1 mg of adsorbate in 20 ml of ethanol to 60 °C yields a clear solution. βCD SAM formation from ethanol solution was investigated using glass-supported gold substrates. After 16 h of immersion, substrates were removed from the warm solution and repeatedly rinsed with ethanol and water. Cooling the solution first caused the βCD adsorbate to precipitate onto the substrate surface.

The βCD SAM was examined using contact-angle goniometry. The wettability of the substrate corresponds to the value of βCD SAM adsorbed from a chloroform/ethanol mixture (Table ESI 1). Heterogeneous electron transfer (HET) performed on the CD SAM did not give rise to any reduction or oxidation peaks, showing that the gold surface is well-protected from the redox couple by the adsorbed species. The values for the charge transfer resistance (RCT) and capacitance of the monolayer (CML) were found to be in the same order of magnitude as previously reported values. CML was found to be independent on the scanning rate. These results show that high quality βCD SAM can be obtained from ethanol solution. The βCD SAMs on the PDMS stamps were investigated by XPS. Characteristic elements (N, S) clearly indicated the presence of the βCD SAMs also on the Au coated PDMS stamp (Table ESI 2).

**Table ESI 1**: Comparison of monolayer characteristics obtained from contact-angle studies, EIS and cyclic voltammetry for monolayers prepared from ethanol and chloroform/ethanol solution. Values for the chloroform/ethanol solution were taken from *Langmuir*, **1998**, *14*, 6424 and *Chem. - Eur. J.* **2000**, *6*, 1176

| Solvent | $\theta_a$ / $\theta_r$ | RCT (kΩ) | CML (μF/cm$^2$) |
|---|---|---|---|
| Chloroform/Ethanol 2:1 | 55 / <20 | 45 | 2.6 |
| Ethanol | 55 / <20 | 35 | 4.3 |

**Table ESI 2**: Relative elemental composition of different substrates determined by XPS. Three different sites of each sample were measured, the average composition is reported here. The presence of gold was not accounted for. Percentages are calculated using 1s peaks for C,N and O and 2p peaks for Si and S.

| Substrate | C [%] | N [%] | O [%] | Si [%] | S [%] |
|---|---|---|---|---|---|
| PDMS-Au | 51.3 | 0.0 | 32.0 | 16.7 | 0.0 |
| PDMS-Au-βCD | 56.8 | 0.8 | 29.8 | 12.3 | 0.3 |
| Si-Au-βCD | 72.8 | 2.5 | 19.6 | 3.4 | 1.7 |