**Supplementary Information**

**Synthesis of Au clusters-redox centre hybrids by diazonium chemistry employing double layer charged nanoparticles.**

Humaira Razzaq, # † Rumana Qureshi,† Laura Cabo-Fernandez# and David J. Schiffrin#\* #Chemistry Department, University of Liverpool, L69 7ZD, United Kingdom.

†Chemistry Department, Quaid-i-Azam University, Islamabad. 45320, Pakistan.

**SI 1. Experimental details**

HAuCl4·3H2O (ACS, 99.99 %, metal basis, Au 49.5% min) and tetraoctylammonium bromide (TOABr) were purchased from Alfa-Aesar (98+%). Sodium borohydride, NaBH4, (98 %), 1-hexanethiol (99 %), tetrabutylammonium hexafluorophosphate (TBAPF6, electrochemical grade, 99.9%) and tetrabutyl ammonium chloride (TBACl, electrochemical grade, 99.9%) were purchased from Sigma Aldrich and were used as received. Acetonitrile and toluene were of the highest purity grade commercially available (HPLC, CHROMASOLV, 99.9%); absolute ethanol and acetone were of analytical grade. H2SO4 (99.999%) was purchased from Sigma–Aldrich. Aqueous solutions were prepared with Milli-Q water (Millipore, 18.2 MΩ).The tetrafluoroborate salt of the anthraquinone diazonium compound, anthraquinone-1-diazonium tetrafluoroborate (referred in the paper as AQ-), was synthesised from 1-amino anthraquinone (Acros, 98%) by Dr. Jerzy Paprotny, of Liverpool University, following standard diazotisation methods.

For the electrochemical measurements, the working electrode was polished on microcloth pads (Buehler GmbH, Germany) using alumina suspensions of 1 and 0.05 m diameter (Buehler GmbH, Germany), sonicated in Milli-Q water and cleaned electrochemically in 0.1 M H2SO4 by cycling between -0.35 V and 1.5 V at 4 V/s (100 scans) and then between 0.4 and 1.4 V at 100 mV/s until the CV becomes stable (approximately 12 times).[J. M. Abad, M. Gass, A. Bleloch, D. J. Schiffrin, J. Am. Chem. Soc. 131 (2009) 10229-10236] All experiments were carried out at room temperature (21 ± 1) oC.

UV/Vis measurements for cluster solutions in toluene were made with a Perkin Elmer UV/Lambda 25 spectrometer using 1 cm path length quartz cuvettes. Infrared spectra were obtained with a JASCO spectrometer (FT/IR-4200 type A). Particles were imaged with a JEM 3010 TEM microscope with an accelerating voltage of 300 kV. The samples were prepared from dilute toluene solutions of the clusters; a drop of this solution was deposited on copper TEM grids coated with a Lacey carbon film (Agar Scientific, 300 mesh) and the solvent left to evaporate in air. Elemental composition was determined by Inductively Coupled Plasma analysis using a Spectro Ciros CCD spectrometer.

**SI-2 UV-vis spectrum of the diazonium salt of the anthraquinone compound employed**



**Figure SI-1.** UV-Vis spectra of 33 μM 1-AQN2+BF4- in toluene

**SI-3 Elemental composition of C6-Au**

**Table SI-1**. Analysis of C6-Au nanoparticles **(Sample 4)**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Element | % Exp. | % Calc | Elemental Ratio | Molar ratio- experimental | Molar ratio- calculated |
| C | 11.23 | 11.30 | C/H | 0.49 | 0.46 |
| H | 1.91 | 2.06 | C/S | 5.33 | 6 |
| S | 5.65 | 5.03 | C/Au | 2.26 | 2.27 |
| Au | 81.15 | 81.61 | Au/S | 2.35 | 2.64 |

The elemental composition was calculated considering a Au140[S(CH2)5CH3]53 (M.W = 33,788 gmol-1) cluster.

**SI-4 Collection of DPV results for the different preparation conditions investigated**

**Table SI-2 Sample identification**

|  |  |  |
| --- | --- | --- |
| **Sample No** | **Thiol reaction time/min** | **NaBH4 reduction time/min** |
| **1** | 30 | 15 |
| **2** | 45 | 15 |
| **3** | 60 | 15 |
| **4** | 30 | 30 |
| **5** | 180 | 25 |
| **6** | 360 | 30 |













**Figure SI-2**. Collection of all the DPV data for different preparation conditions used for the synthesis of C6-Au particles. Identification of the samples is given in Tables 1 and SI-2. Steps amplitude: (1) 5; (2) 10; (3) 20 and (4) 50 mV.

**SI-5 Calculation of the viscosity of the Tol:AN 2:1 solvent mixture employed**

The data reported in J. H. Dymond, M. A. Awan, N. F. Glen, and J. D. Isdale, *Int. J. Thermophys.* 1991, **12**, 433-447, was employed. To calculate the viscosity at 21oC, the results for XTol = 0.5 at different temperatures were fitted to:

with

A = 997.43

B = -11.046

The mole fraction of toluene in a Tol:AN 2:1 by volume mixture is XTol = 0.495. The small correction between XTol 0.5 and 0.495 was calculated employing the mole fractions given in the paper by Dymond and using a linear relationship between viscosity and mole fraction, a factor of 0.9997 was found for correcting the calculated viscosity at 21oC for XTol = 0.495.