Supporting information

Quantized double layer charging of $Au_{130}(SR)_{50}$ Nanomolecules

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Table S1: Reproducibility table for the DPV of $Au_{130}(SR)_{50}$
Figure S1: Cyclic voltammogram for $Au_{130}(SR)_{50}$ nanomolecule
Figure S2: MALDI-MS and ESI-MS spectra of $Au_{130}(SR)_{50}$ showing different charge states.
Figure S3: UV-vis spectra of $Au_{130}(SR)_{50}$ with phenylethanethiol.

Methods

Chemicals: phenylethanemercaptan (SAFC, ≥ 99%), sodium borohydride (Acros, 99%), trans-2-[3[(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB matrix) (Fluka ≥ 99%) were purchased from Aldrich. Tetrahydrofuran (stablized) and other solvents like toluene, methanol , acetonitrile and acetone were used from fisher as received. Biorad-SX1 beads (Biorad) were used for the SEC.

Equipment: Electrochemical measurements were perfomed on a CHI 620 instrument using 10 mg of title compound in 6.5 mL of anhydrous 1,2-dichlorethane solution with 650 μM $BTPPATBF_{20}$ as supporting electrolyte under nitrogen atmosphere. UV-visible absorption spectra were recorded in toluene on a Shimadzu UV-1601 instrument. Matrix assisted laser desorption time-of-flight (MALDI TOF) mass spectra were collected on a Bruker Autoflex 1 mass spectrometer in linear postive mode using nitrogen laser (337 nm) with DCTB as a matrix. ESI-MS spectra were acquired on Waters SYNAPT HDMS instrument.

Experimental

Step 1: Synthesis of crude product

Using two phase Brust-Schiffrin method crude product was prepared. Briefly, 1:3 :: gold : thiol was used and reaction was performed in toluene. First, 0.1 g of $HAuCl_4.3H_2O$ in 10 mL distilled water was mixed with 0.16 g of Tetraoctlyammoniumbromide (TOABr) in 20 mL toluene. After 30 min of stirring the gold salt transferred to the organic phase evidenced by clear aqueous layer. The organic phase was separated and 105 μL of phenylethanethiol was added. After 1 h of thiol addition, 0.1 g $NaBH_4$ in 10 mL ice-cold water was added instantaneously to the reaction flask. Upon addition of reducing agent the reaction mixture turned dark in color indicating the formation of nanoparticles. The reaction was stopped after 3 h of $NaBH_4$ addition and processed. Then, clusters larger than 40 kDa were separated and etched at 80°C. The product from the etching was size separated by size exclusion chromatography.

Step 2: Separation by SEC

Size exclusion chromatrography was used for the isolation of $Au_{130}(SR)_{50}$ from the product obtained after thermochemical treatment. Biorad S-X1 beads were soaked in stabilized THF overnight and packed in the column.[1] The sample was dissolved in minimal amount of stabilized THF and loaded on to the column. Several fractions collected were analyzed by both MALDI-TOF mass spectrometry[2] and ESI-MS to check the presence of $Au_{130}(SR)_{50}$ in high purity.

Synthesis of $BTPPATBF_{20}$

The supporting electrolyte was synthesized according to the protocol published in the literature.[3,4] For the synthesis of the supporting electrolyte, Potassium teterakis (petafluorophenyl)borate was and Bis(triphenylphospharinylidene)ammonium chloride were mixed in 1:1 ratios in 1:2 Methanol : water. As soon as the salts were mixed, there was a precipitate observed in the flask. The precipitate was further separated by centrifugation. This $BTPPATBF_{20}$ salt was used as such for the electrochemical measurements after drying in the vacuum oven overnight at 40°C. During the preparation of the supporting electrolyte only HPLC grade solvents were used.

Electrochemical measurements:

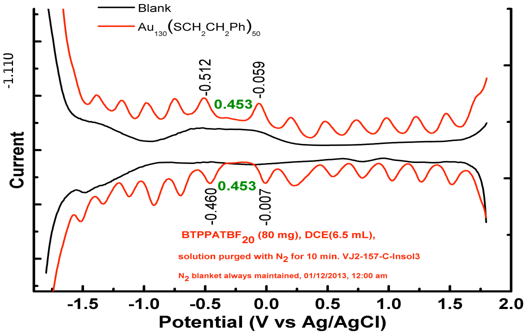
Electrochemical measurements were carried out in anhydrous 1,2-dichloroethane. The sample and the supporting electrolyte were dried in a vacuum oven overnight, prior to the measurements. The working electrode was polished using 0.03 micron buehler micropolish^{tm} alumina powder. All the electrodes were cleaned with anhydrous 1,2-dichloroethane and stored under nitrogen. The supporting electrolyte (650 µM) was dissolved in anhydrous dichloroethane and the blank runs were acquired before addition of the sample. The concentration of the nanomolecule used was 46 µM. The CV measurements were performed at 100 mV/s scan rate and DPV measurements were performed at scan rate of 4 mV/s, pulse height of 0.05 V, pulse width of 0.2 s and pulse period of 0.5 s. No ohmic-drop compensation was applied for voltammetric measurements. The solution was bubbled for 2 min in between the measurements.

Supporting table 1: Table showing the list of experiments in which QDL charging for $Au_{130}(SR)_{50}$ was observed.

#	Experiment name	Date of analysis	Solvent used	QDL charging
1	VJ3-18-A		$THF/TBAPF_6$	Observed
2	VJ3-19-A		$THF/TBAPF_6$	Observed
3	VJ3-28-A	01/11/2013	DCE/BTPPATBF20	Observed
4	VJ3-28-B	01/12/2013	DCE/BTPPATBF20	Observed
5	VJ3-30-C	01/15/2013	DCE/BTPPATBF20	Observed
6	VJ3-36-A	02/04/2013	DCE/BTPPATBF20	Observed
7	VJ3-36-B	02/05/2013	THF/BTPPATBF20	Observed

8	VJ3-37-A		DCE/BTPPATBF20	Observed
9	VJ3-37-B		DCM/BTPPATBF20	Observed
10	VJ3-42-B	02/20/2013	DCE/BTPPATBF20	Observed
11	VJ3-49-B	03/18/2013	DCE/BTPPATBF20	Observed
12	VJ3-69-A	04/22/2013	DCE/BTPPATBF20	Observed
13	VJ3-77-B	05/21/2013	DCE/BTPPATBF20	Observed

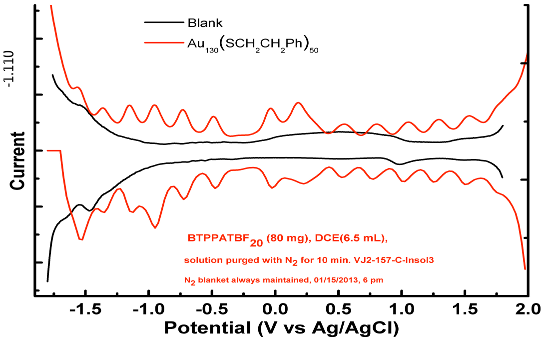
Few other DPV data for reproducibility



$BTPPATBF_{20}$ (80 mg), DCE(6.5 mL),

solution purged with N_2 for 10 min. VJ2-157-C-Insol3

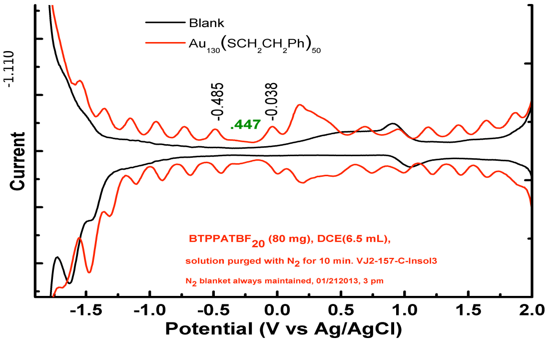
N_2 blanket always maintained, 01/12/2013, 12:00 am



$BTPPATBF_{20}$ (80 mg), DCE(6.5 mL),

solution purged with N_2 for 10 min. VJ2-157-C-Insol3

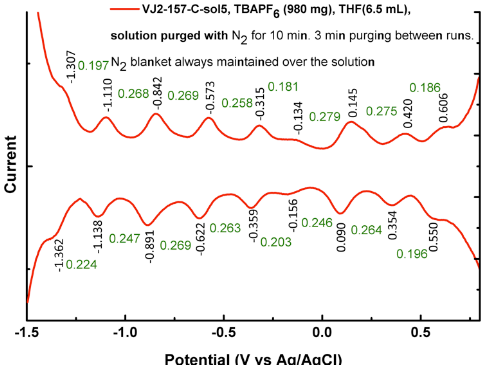
N_2 blanket always maintained, 01/15/2013, 6 pm



$BTPPATBF_{20}$ (80 mg), DCE(6.5 mL),

solution purged with N_2 for 10 min. VJ2-157-C-Insol3

N_2 blanket always maintained, 01/212013, 3 pm

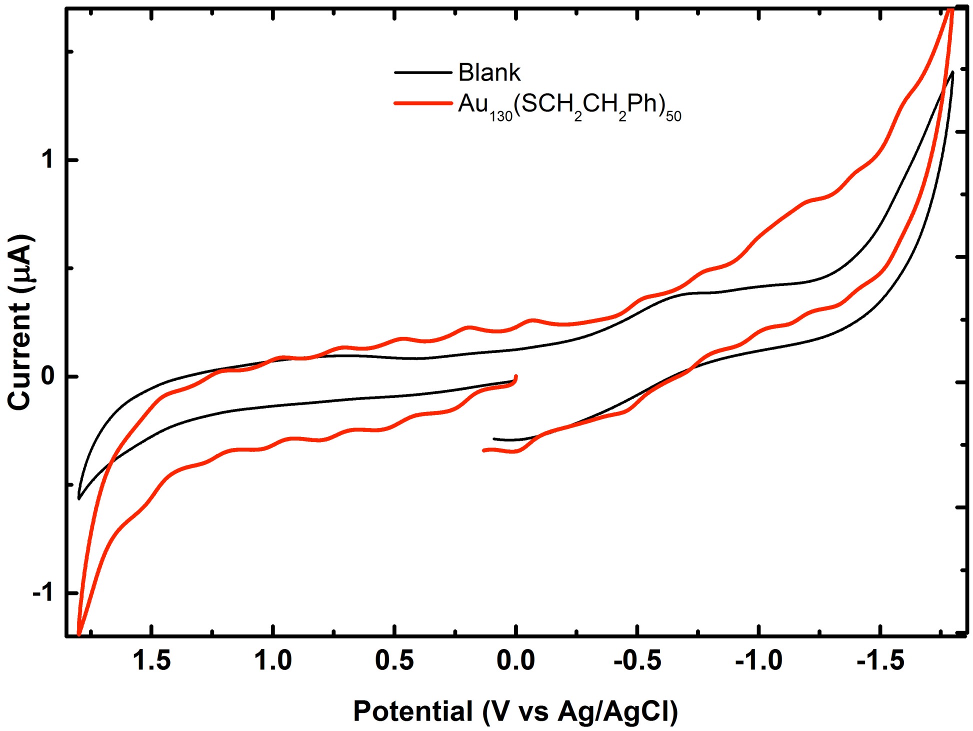


VJ2-157-C-sol5, $TBAPF_6$ (980 mg), THF(6.5 mL),

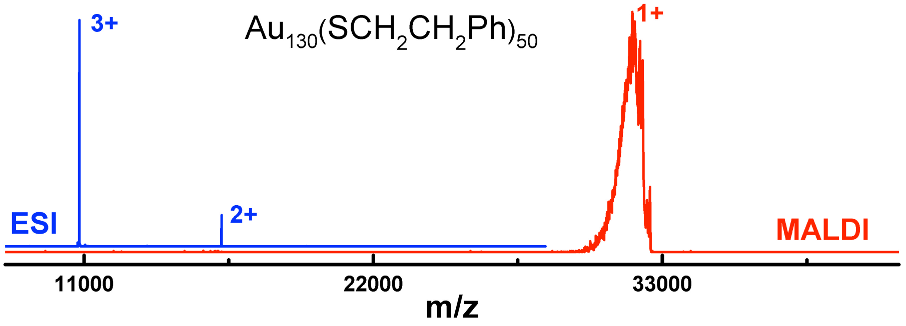
solution purged with N_2 for 10 min. 3 min purging between runs.

N_2 blanket always maintained over the solution

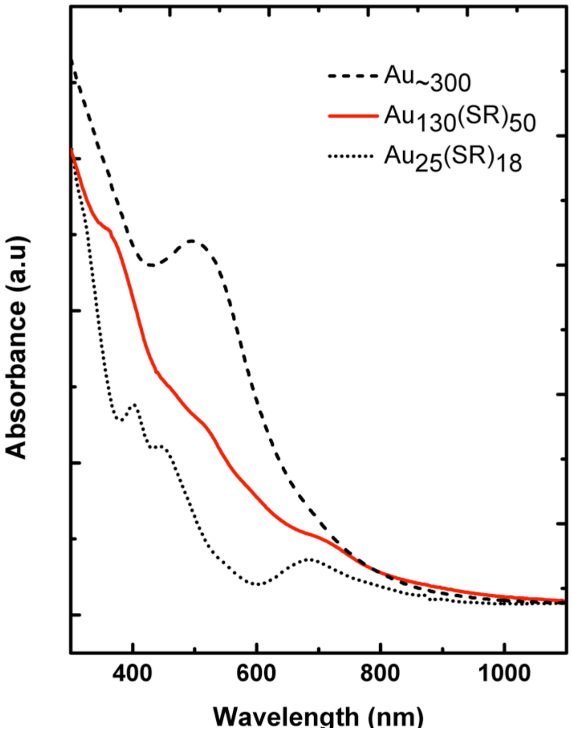
Supporting figure 1: Cyclic voltammetry (CV) of $Au_{130}(SR)_{50}$ nanomolecules in 1,2-dichloroethane in the presence of BTPPATBF20 supporting electrolyte. 1.5 mg/mL (46 μM) of gold nanomolecules and 8 mg/mL (650 μM) of supporting electrolyte was used for the voltammetry measurements.



Supporting figure 2: Postive ESI-MS (blue) and positive MALDI-MS (red) of $Au_{130}(SCH_2CH_2Ph)_{50}$ showing several charge states of the nanomolecule. No peaks corresponding to other nanomolecules were observed which confirms the high purity of the sample used for voltammetry measurements.



Supporting figure 3: UV-vis spectrum of $Au_{130}(SCH_2CH_2Ph)_{50}$ in comparison with $Au_{25}(SR)_{18}$ and 76 kDa faradaurate nanomolecule.



The HOMO-LUMO gap obtained from the electrochemistry experiments, does not agree with the optical absorption spectrum. The absorption onset is found to be around 1000 nm (~1.2 eV). For $Au_{144}(SCH_2CH_2Ph)_{60}$ absorbance data in the IR and NIR region has shown absorption onset around 0.2 eV.[5] Similar experiments need to be performed with $Au_{130}(SCH_2CH_2Ph)_{50}$ to further confirm the HOMO-LUMO gap from spectroscopy.

References

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