(Supporting Information)

Understanding the Nascent Plasmons and Metallic Bonding in Atomically Precise Gold Nanoclusters

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Chemicals. Tetrachloroauric(III) acid (HAuCl$_4$·3H$_2$O, 99.99%, Aldrich), Phenylethanethiol (PET, PhCH$_2$CH$_2$SH, 99%, Aldrich), 4-tert-butylbenzenethiol (TBBT, C$_{10}$H$_{13}$SH, >97.0%, TCI), Sodium borohydride (NaBH$_4$, Aldrich), Toluene (HPLC grade, 99.9%, Aldrich), Methanol (HPLC grade, 99.9%, Aldrich) and Dichloromethane (HPLC grade, 99.9%, Aldrich) were used as received. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB, ≥99.0%, Sigma-Aldrich). Nanopure water was prepared with a Barnstead NANO pure Diamond system.

Synthesis of nanoclusters. The Au$_{144}$(PET)$_{60}$ and Au$_{333}$(PET)$_{79}$ were synthesized in a size-focusing methodology. Briefly, HAuCl$_4$·3H$_2$O was transferred into the toluene phase with TOAB (tetraoctylammonium bromide). Then phenylethyl thiol (PET for short) was added and turned the solution from deep red to colorless after one hour of stirring. Aqueous solution of NaBH$_4$ further reduced the Au precursors to poly-dispersed Au$_x$(PET)$_y$. After 1 h of reaction under vigorous stirring, the toluene phase was collected and dried by rotary evaporation. Then the product was washed by methanol three times. Then poly-dispersed Au$_x$(PET)$_y$ was dissolved in 1 mL of toluene and 1 mL of PET and heated to 80 ^{o}C for 2 days for size focusing. The etching gives rise to the two dominant species: Au$_{144}$ and Au$_{333}$, then both NCs were separated by thin-layer chromatography (TLC) in a mixed CH$_2$Cl$_2$/methanol (6:1, v/v) solvent. Au$_{279}$(TBBT)$_{84}$ was synthesized through ligand exchange-induced size transformation as follows. In a toluene solution of Au$_{333}$(PET)$_{79}$, 1 mL of TBBT thiol was added, and the mixture was etched at 80 ^{o}C for 2 days. Then, pure Au$_{279}$(TBBT)$_{84}$ was obtained by washing with methanol.

Preparation of nanocluster films. Preparation of polystyrene thin films of Au NCs follows a drop-cast method. The protocol was kept the same for all of the three Au NCs. First, 80 mg of polystyrene was dissolved in 1 mL of toluene to form a stock solution. Then, 20 μL of toluene solution of Au NCs (ca. 2 mg/mL) was added into 10 μL of the polystyrene solution. Finally, the mixture of Au NCs and polystyrene matrix was drop-cast onto a clean quartz plate, and the solvent was evaporated slowly at room temperature.

Characterization. MALDI-MS was performed with a PerSeptive-Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB) was used as a matrix. ESI mass spectra were recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 °C. The sample was directly infused into the chamber at 5 μL/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. The ESI sample was dissolved in CH$_2$Cl$_2$.

　　Room temperature optical spectra were measured on a HP 8453 spectrometer (190-1100 nm) or a UV-3600 Plus spectrophotometer (covering the UV-Vis-NIR 185-3300 nm range). Cryogenic optical absorption spectroscopic measurements were carried out on a home-built low temperature system, including a UV-3600 Plus spectrophotometer, an Optistat CF2 cryostat (Oxford Instruments), a Mercury Integrated Temperature Controller and several vacuum pumps. The sample plate was securely fixed on a

copper sample holder and placed in the cryostat which was filled with helium gas during the tests. Liquid helium was used as the cryogen to cool the system from room temperature (~300 K) to 2.5 K.
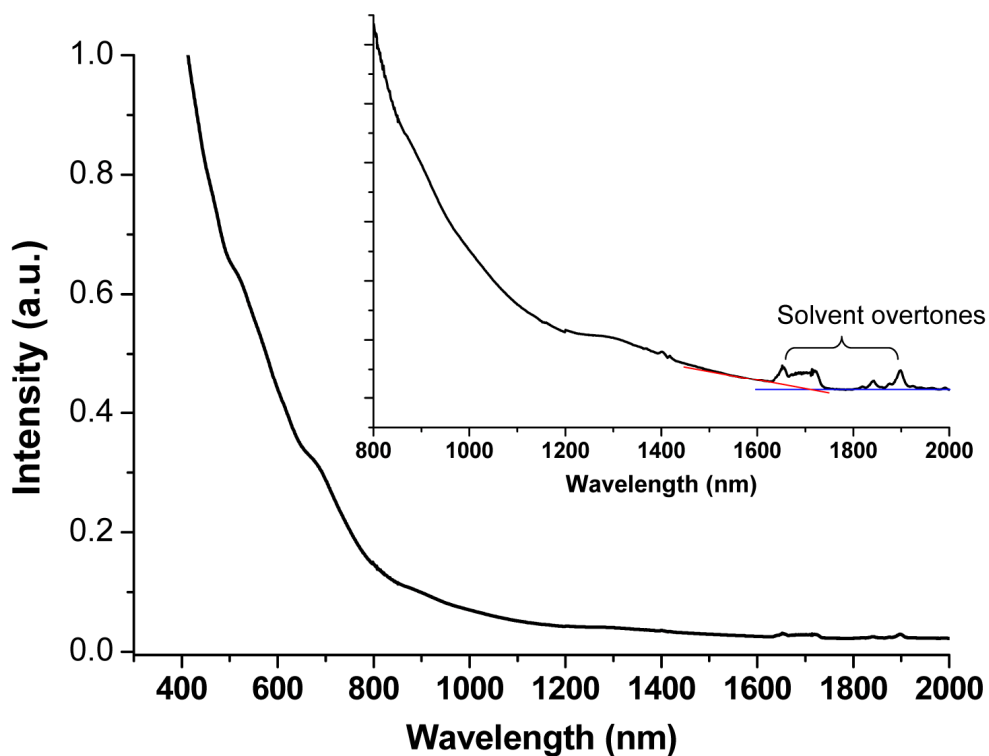

Figure S1. UV-Vis-NIR absorption spectrum of $Au_{144}(SR)_{60}$ in solution at r.t. Note that the absorbance onset wavelength (~1700 nm, or 0.72 eV) differs from the electrochemically determined HOMO-LUMO of 0.17 eV.