Electronic Supporting information

Controlling Magnetism of $Au_{133}(TBBT)_{52}$ Nanoclusters at Single Electron Level and Implication for Nonmetal to Metal Transition

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Experimental

Chemicals. Tetrachloroauric(III) acid ($HAuCl_4 \cdot 3H_2O$, >99.99% metals basis, Aldrich), Tetraoctylammonium bromide (TOAB, ≥98%, Fluka), 2–Phenylethanethiol (PET, 99%, Acros Organics), Sodium borohydride ($NaBH_4$, Aldrich), 4–tert–butylbenzenethiol (TBBT, 97%, Alfa Aesar), H_2O_2 (33%, aquous). Solvents: Toluene (HPLC grade, ≥99.9%, Aldrich), Methanol (HPLC grade, ≥99.9%, Aldrich), Acetonitrile (HPLC grade, ≥99.9%, Aldrich), CH_2Cl_2 (HPLC grade, ≥99.9%, Aldrich). All chemicals were used as received.

Synthesis of $Au_{144}(PET)_{60}$. The synthesis of $Au_{144}(PET)_{60}$ is based on the two-step size-focusing method (Qian et al. *Nano Lett.* **2009**, *9*, 4083). Typically, $HAuCl_4 \cdot 3H_2O$ (0.10 g, 0.25 mmol, dissolved in 5 ml of water) was mixed with TOAB (0.16 g, 0.29 mmol, dissolved in 10 ml of toluene) in a 25 ml round–bottom flask and stirred vigorously. After 15 min, the yellow aqueous phase turned colorless while the colorless organic phase turned deep red due to the phase transfer of Au(III) salt from aqueous to toluene phase. The clear aqueous solution was removed by pipette. Then phenylethanethiol (105 μl, 0.3 mmol) was added to the toluene phase and the reaction solution was stirred for 30 min. The deep red color gradually changed to colorless due to the reduction of Au(III) to Au(I) and the formation of Au(I)-PET complex. Then $NaBH_4$ (0.1 g, 2.5 mmol) dissolved in 5 ml of H_2O was rapidly pour into the solution. After stirring overnight, the aqueous phase was removed and the toluene phase was dried by rotary evaporation. Methanol was added to the black oily residue and the resulted suspension was centrifuged at 3000 rpm for 5 min. The supernatant containing reaction byproduct was removed and the black precipitate containing mixture of $Au_x(PET)_y$ nanoclusters was washed with methanol for two more times. In the second step, the $Au_x(PET)_y$ nanoclusters was dissolved in 1 ml of toluene and 1ml of PET thiol. The solution was stirred and heated at 80 °C overnight. Then methanol was added and the mixture was centrifuged at 3000 rpm for 5 min to precipitate the $Au_{144}(PET)_{60}$ nanoclusters. The washing step was repeated two more times in order to remove excess of PET thiol. The typical yield was ~10 mg.

Synthesis of $[Au_{133}(TBBT)_{52}]^0$. The $Au_{133}(TBBT)_{52}$ was transformed from $Au_{144}(PET)_{60}$ based on the LEIST process (i.e. ligand–exchange induced size/structure transformation, Zeng et al. *Sci. Adv.* **2015**, *1*, e1500045). Typically, 10 mg of $Au_{144}(PET)_{60}$ nanoclusters was mixed with 1 ml of TBBT thiol and 1 ml of toluene. The reaction mixture was stirred and heated at 80 °C for four days. The transformation from Au_{144} to Au_{133} was usually completed within one day. Continue heating guaranteed that all the PET thiolates was completely replaced by TBBT thiolates on the surface of Au_{133} nanoclusters. The washing step was the same as described in $Au_{144}(PET)_{60}$. The typical yield of $Au_{133}(TBBT)_{52}$ was ~ 7 mg. The as synthesized $Au_{133}(TBBT)_{52}$ was found to be a mixture of $[Au_{133}(TBBT)_{52}]^+$ and $[Au_{133}(TBBT)_{52}]^0$. To obtain pure $[Au_{133}(TBBT)_{52}]^0$, single crystals was grown by diffusion of anti–solvent CH_3CN into the toluene solution of $Au_{133}(TBBT)_{52}$. After around a week, black needle crystals were formed and found to be pure $[Au_{133}(TBBT)_{52}]^0$, while the $[Au_{133}(TBBT)_{52}]^+$ was left in the supernatant.

Oxidation of $Au_{133}(TBBT)_{52}$. In a typical experiment to oxidize $[Au_{133}(TBBT)_{52}]^0$ to $[Au_{133}(TBBT)_{52}]^+$, ~ 5 mg of $[Au_{133}(TBBT)_{52}]^0$ was mixed with 500 µl of H_2O_2 (50 wt.%) in 5 ml of CH_2Cl_2. The reaction mixture was stirred for around 3 hours. The organic phase was rinsed with H_2O several times and dried.

Reduction of $Au_{133}(TBBT)_{52}$. In a typical experiment to reduce $[Au_{133}(TBBT)_{52}]^+$ to $[Au_{133}(TBBT)_{52}]^0$, ~ 5 mg of reduce $[Au_{133}(TBBT)_{52}]^+$ (dissolved in 5 ml of CH_2Cl_2) was mixed with 5 mg of $NaBH_4$ (dissolved in 1 ml of H_2O) and stirred for 1 hour. The organic phase was rinsed with H_2O several times and dried. Increasing the amount of $NaBH_4$ (e.g. 20 mg) and reaction time (e.g. 18 hours) did not further reduce $[Au_{133}(TBBT)_{52}]^0$ to $[Au_{133}(TBBT)_{52}]^-$, as evidenced by NMR characterizations.

EPR sample preparation and measurements. In a typical sample preparation, 6.7 mg of $[Au_{133}(TBBT)_{52}]^0$ (molar weight: 34790.83) was dissolved in 200 µl of CH_2Cl_2 and 200 µl of toluene in order to form clear glassy frozen solution at low temperature. The concentration of the $[Au_{133}(TBBT)_{52}]^0$ solution is 0.48 mM. X-band (9.6 GHz) and S-band (3.5 GHz) EPR spectra were recorded on a Bruker ELEXSYS spectrometer equipped with Oxford liquid helium cryostats. The quantification of all signals was measured relative to a CuEDTA spin standard prepared from a copper atomic absorption standard (Sigma-Aldrich). The microwave frequency was calibrated with a frequency counter, and the magnetic field was measured with a NMR gaussmeter. The sample temperature was calibrated against a calibrated cernox sensor (Lakeshore CX-1050) mounted inside an EPR tube. The quantitative simulations are least-squares fits of the experimental spectra generated with consideration of all intensity factors, which allows computation of simulated spectra for a specified sample concentration. Double integration of the $S = ½$ spectra gave the same spin concentration.

NMR measurements. NMR analysis was performed on a Bruker Avance 500 spectrometer operating at 500.13 MHz for ^1H and 125.77 MHz for ^{13}C. For data collection, ~5 mg of $Au_{133}(TBBT)_{52}$ nanoclusters were dissolved in $CDCl_3$.

Supporting figures and tables:

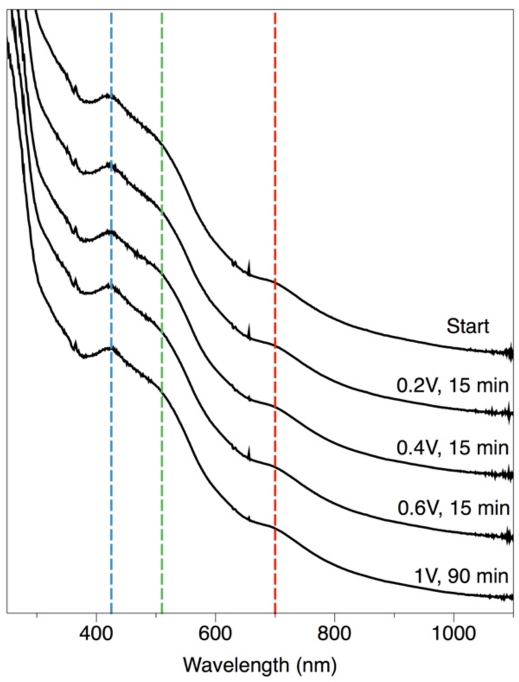

Figure S1. Electrochemical oxidation of $[Au_{133}(TBBT)_{52}]^0$.

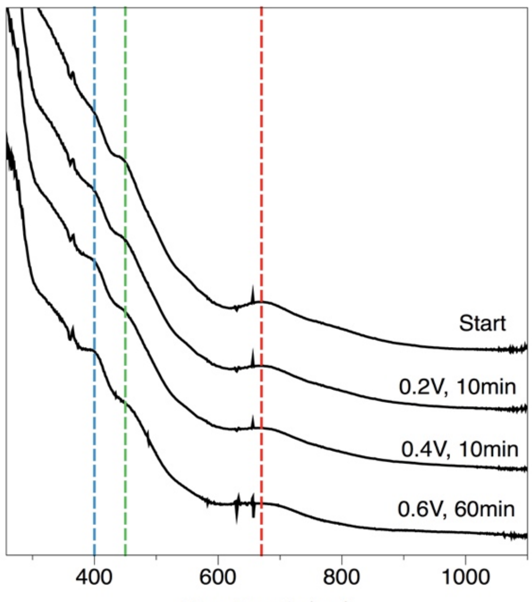

Figure S2. Electrochemical oxidation of $[Au_{25}(SC_2H_4Ph)_{18}]^-$.

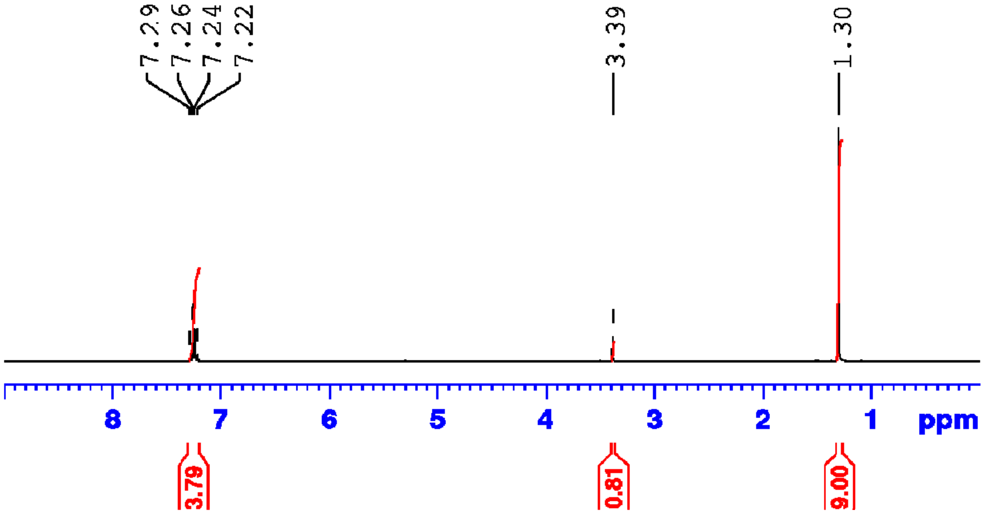

Figure S3. ^{1}H-NMR of free 4-tertbutylbenzenethiol (TBBT-H)

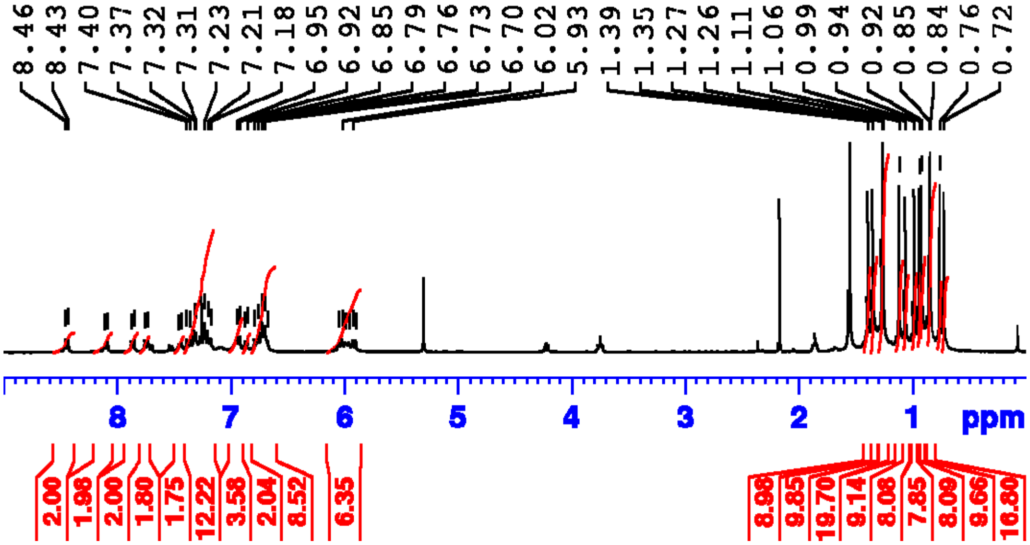

Figure S4. ^{1}H-NMR of $Au_{133}(TBBT)_{52}$ nanocluster.

Table S1. Identification and correlation of 13 groups of aromatic ^{1}H peaks in the NMR of $Au_{133}(TBBT)_{52}$ nanocluster. Ten groups can be clearly identified, while the other three groups may have broad signal.

1	8.46/8.43 & 7.23/7.20
2	8.11/8.09 & 7.76/7.73
3	7.88/7.85 & 6.72/6.70
4	7.46/7.44 & 7.23/7.20
5	7.40/7.37 & 6.79/6.76
6	7.31/7.30 & 7.23/7.21
7	7.20/7.18 & 5.99/5.96
8	6.95/6.92 & 6.05/6.02
9	6.79/6.75 & 5.93/5.90
10	6.88/6.85 & 6.70/6.68