(Supporting Information)

Electron Transfer between [Au₂₅(SC₂H₄Ph)₁₈]⁻TOA⁺ and Oxoammonium Cations

Zhao Liu,[†] Manzhou Zhu,^{*,†} Xiangming Meng,[†] Guoyong Xu,[†] and Rongchao Jin^{*,‡}

[†]Department of Chemistry, Anhui University, Hefei, Anhui 230039, P. R. China [‡]Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213, United States

1. Experimental section

Chemicals. 2,2,6,6-tetramethylpiperidinyl-oxy (TEMPO, 98%, Aldrich), tetrabutylammonium perchlorate (TBAP, \geq 98.0%, Aldrich), toluene (HPLC grade, \geq 99.9%, Aldrich), methylene chloride (HPLC grade, \geq 99.9%, Aldrich), acetonitrile (HPLC grade, \geq 99.9%, Aldrich). Reagents were purchased from commercial sources and used without further purification unless otherwise stated.

The synthesis of TEMPO⁺BF₄⁻ cation⁶¹ and growth of $[Au_{25}(SC_2H_4Ph)_{18}]$ ⁻TOA⁺ crystals⁵ were carried out following the previously reported procedures. The Au₂₅⁻ single crystals (redissolved in solvent) were used as the starting material for all the experiments in this work.

For the reaction of $[Au_{25}(SC_2H_4Ph)_{18}]$ TOA⁺ with TEMPO⁺BF₄, gold clusters (3 mg, ~0.38 mmol) were first dissolved in toluene, then different molar ratios of the acetonitrile solution of TEMPO⁺BF₄ was added using a syringe under ambient conditions. The solution was stirred or agitated, followed by characterization by UV-vis spectroscopy, ¹H NMR and ESR.

Cyclic voltammetric measurements (CV) were performed on an electrochemical workstation (CHI 660D) at a scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$ under ambient conditions. All potentials reported were measured relative to a AgCl/Ag reference. A platinum disk electrode and a platinum wire were used as the working electrode and the auxiliary electrode, respectively. The platinum disk electrode was polished with alumina before use. Prior to CV, 0.17 g of tetrabutylammonium perchlorate (TBAP) was added to the sample solution (final concentration of TBAP: 0.1 mol/L) and the CH₂Cl₂ solution was degassed at least for half an hour to remove oxygen dissolved in the solution.

UV-Vis absorption spectra of gold nanoclusters were recorded using a Hewlett-Packard (HP) 8453 diode array spectrophotometer.

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¹H NMR spectra were recorded with a Bruker AV400 NMR spectrometer.

Room temperature electron spin resonance (ESR) was conducted on JEOL JES-FA200 EPR spectrometer (300 K, 9048 MHz, X-band).



2. Supporting Figures:

Figure S1. UV-vis monitoring of the reaction of Au_{25} ⁻TOA⁺ (starting material, single crystals redissolved in solvent) with TEMPO⁺BF₄⁻. The inset indicates the volume of TEMPO⁺ solution added to the cluster solution, 40 uL of TEMPO⁺=1 equiv. per Au_{25}^{-} . Upon reaching 2 equiv. of TEMPO⁺, no further spectral changes were observed, indicating a complete reaction.



Figure S2. (H,H)-COSY of $Au_{25}(SC_2H_4Ph)_{18}$ -TOA⁺ in d-toluene.



Figure S3. ¹H NMR of phenyl groups of Au₂₅(SC₂H₄Ph)₁₈ in the redox process (conversion of anionic to neutral to cationic clusters).

Figure S4. (H,H)-COSY of the final product $Au_{25}(SC_2H_4Ph)_{18}^+BF_4^-$.

Figure S5. ¹H NMR of TEMPO⁺BF₄⁻.