Mixed Dithiolate Durene-DT and Monothiolate Phenylethanethiolate Protected Au130 Nanoparticles with Discrete Core and Core-Ligand Energy States

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Introduction

- **Small gold nanoparticles stabilized by thiolates, often referred as monolayer protected clusters (MPC), have attracted extensive research interests due to their rich optical, electrochemical, and other physiochemical properties.**

- **Nanomaterials with desired physiochemical properties are needed for targeted applications. It is important to correlate the composition and structure of the nanoclusters with their properties for application design.**

- **Interfacial bonding structures are believed to play an important role in the properties of nanoclusters, in addition to the well-known quantum confinement factors such as shape and size/composition.**

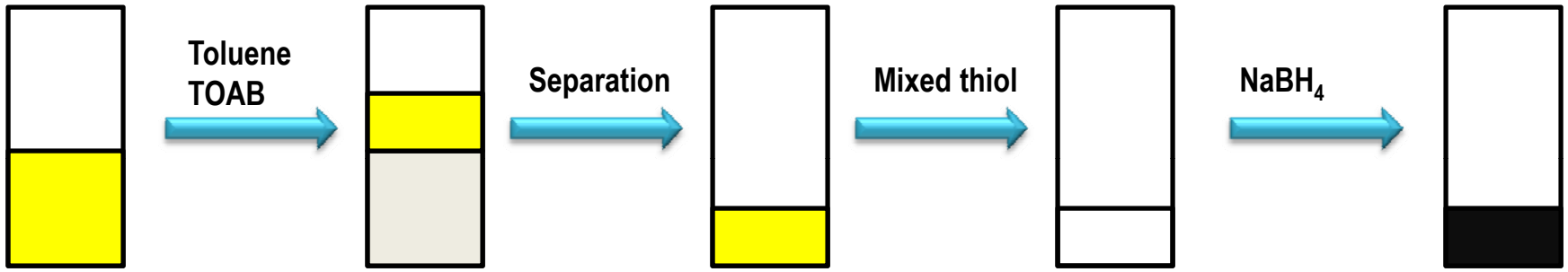
In this paper

- A new type of molecular gold nanocluster is created by employing mixed aromatic thiols, monothiol ligand phenylethanethiol (PhC2S) and dithiol ligand durene-α1, α2-dithiol (Durene-DT, a 1,4-dithiol).

- The impacts of dithiol molecular structure and dithiol/monothiol/Au ratio on the cluster formation and properties are studied.

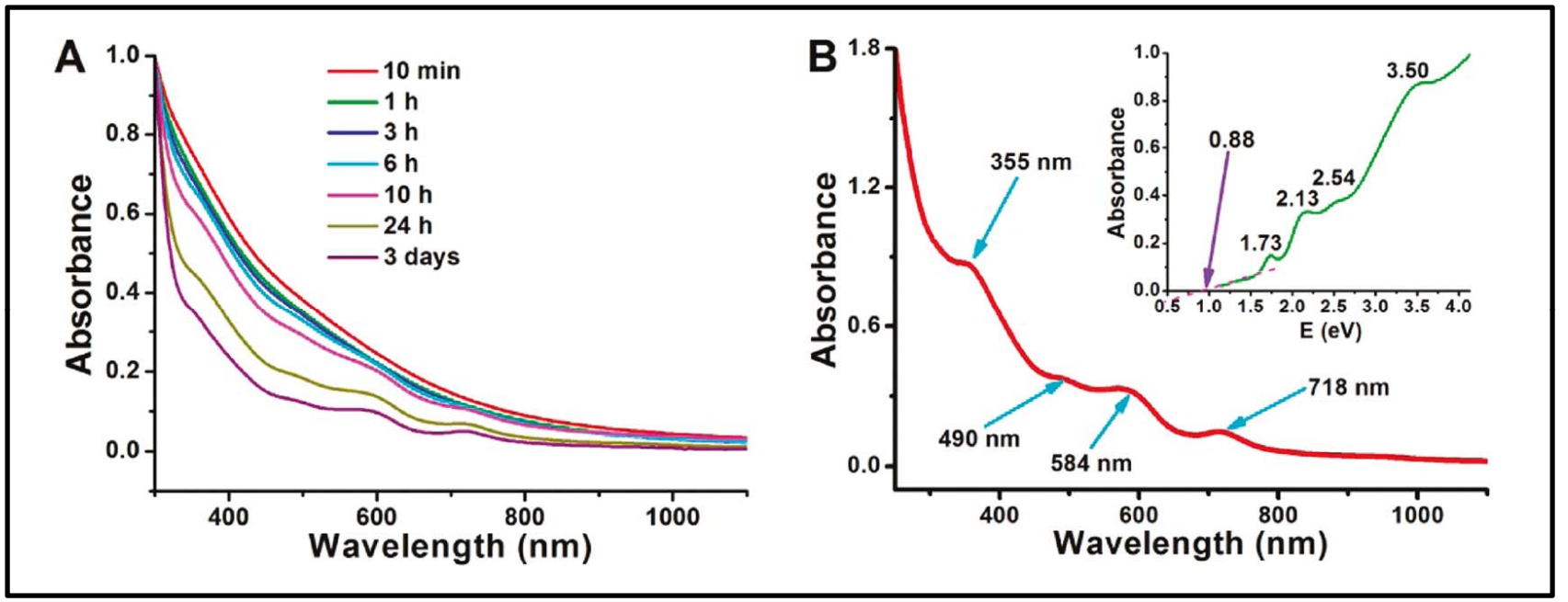
- The mixed thiolate clusters (MTCs) display discrete absorption bands and rich electrochemical properties. Near-IR luminescence is reported. The average composition is characterized as $Au_{130}(Durene\text{-}DT)_{29}(PhC_2S)_{22}$.

Experimental details



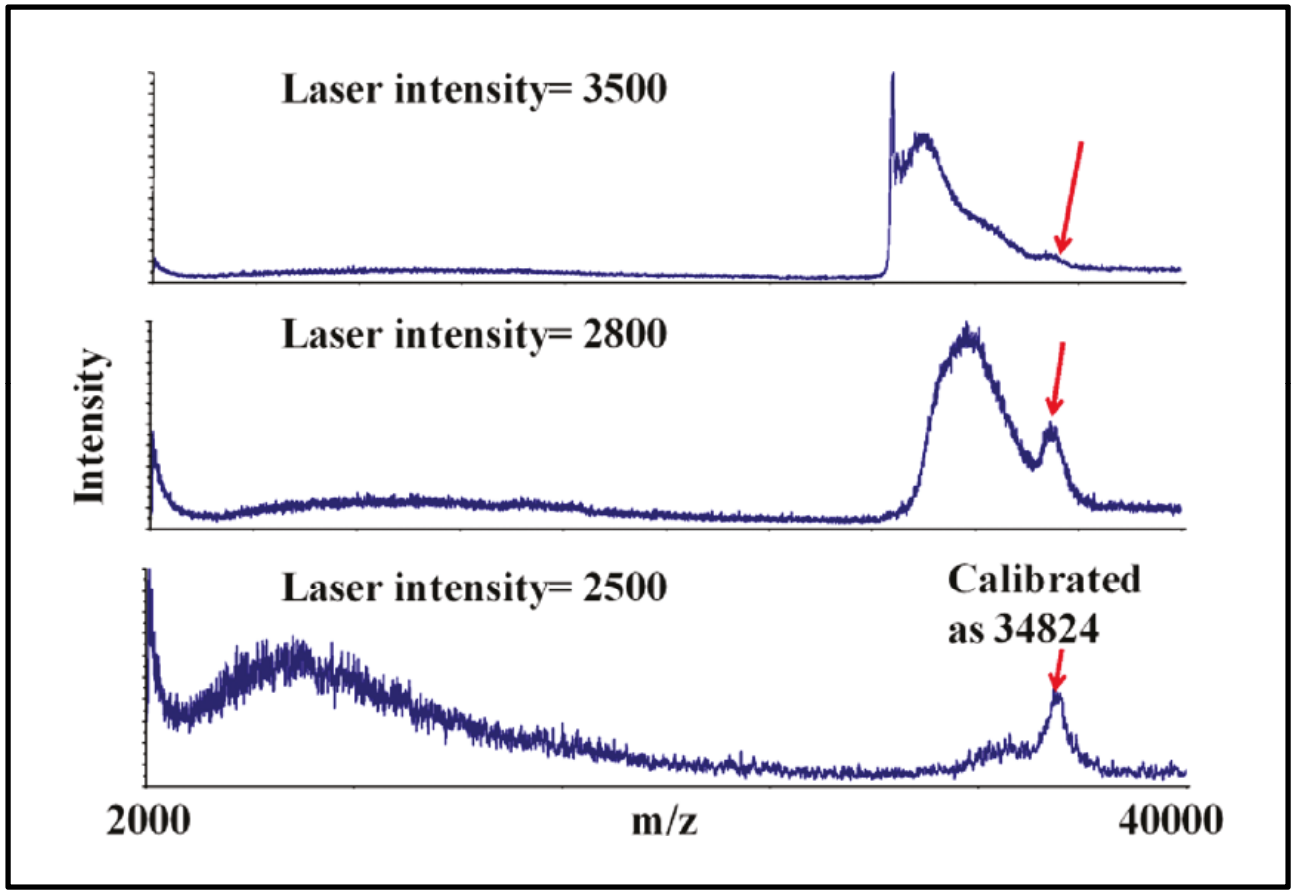
Gold solution Phase transferred Au-thiolate Au_{130} cluster

Results and discussion



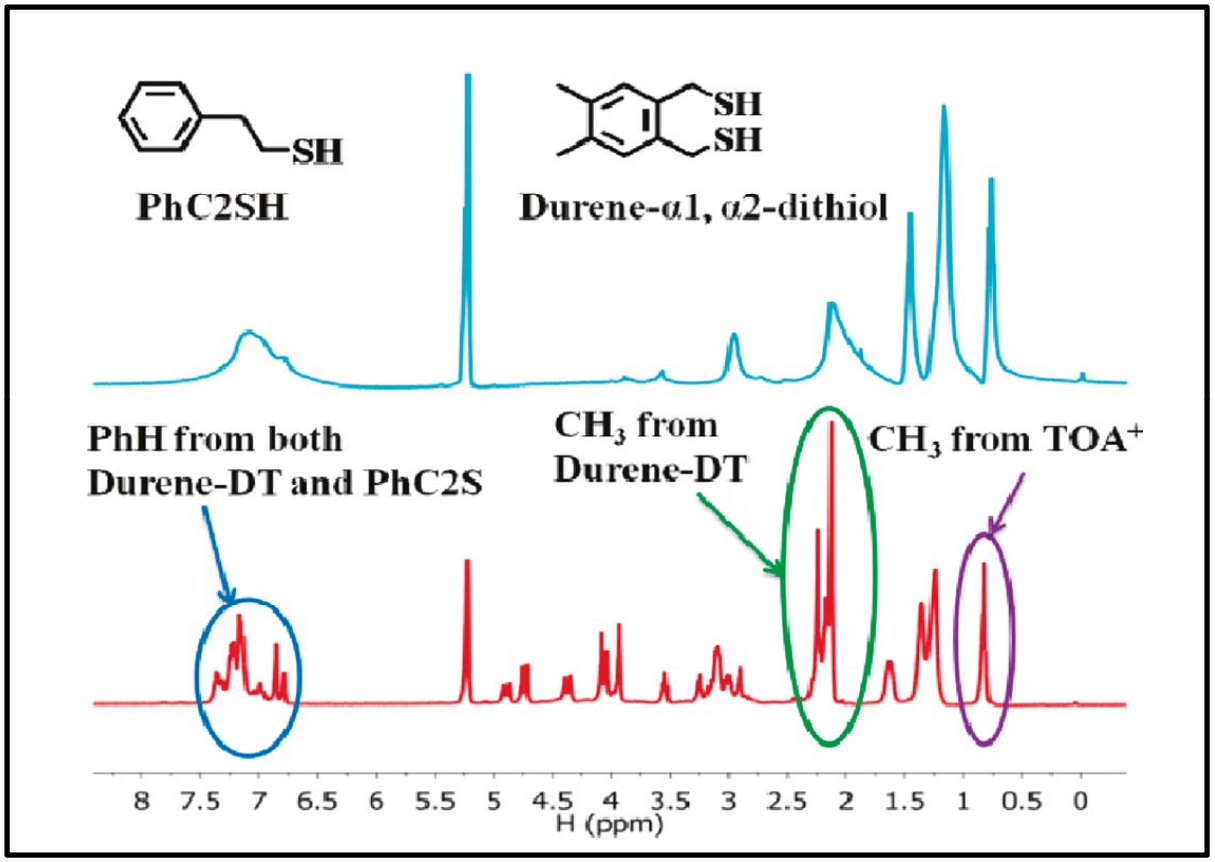
(A) The absorbance change during the reduction. An aliquot of the reaction mixture in toluene phase was diluted to proper absorbance range for each measurement. The spectra were normalized at 300 nm. (B) Absorbance spectrum of the purified product in methylene chloride. The spectrum plotted in energy axis is inserted.

Result and discussion



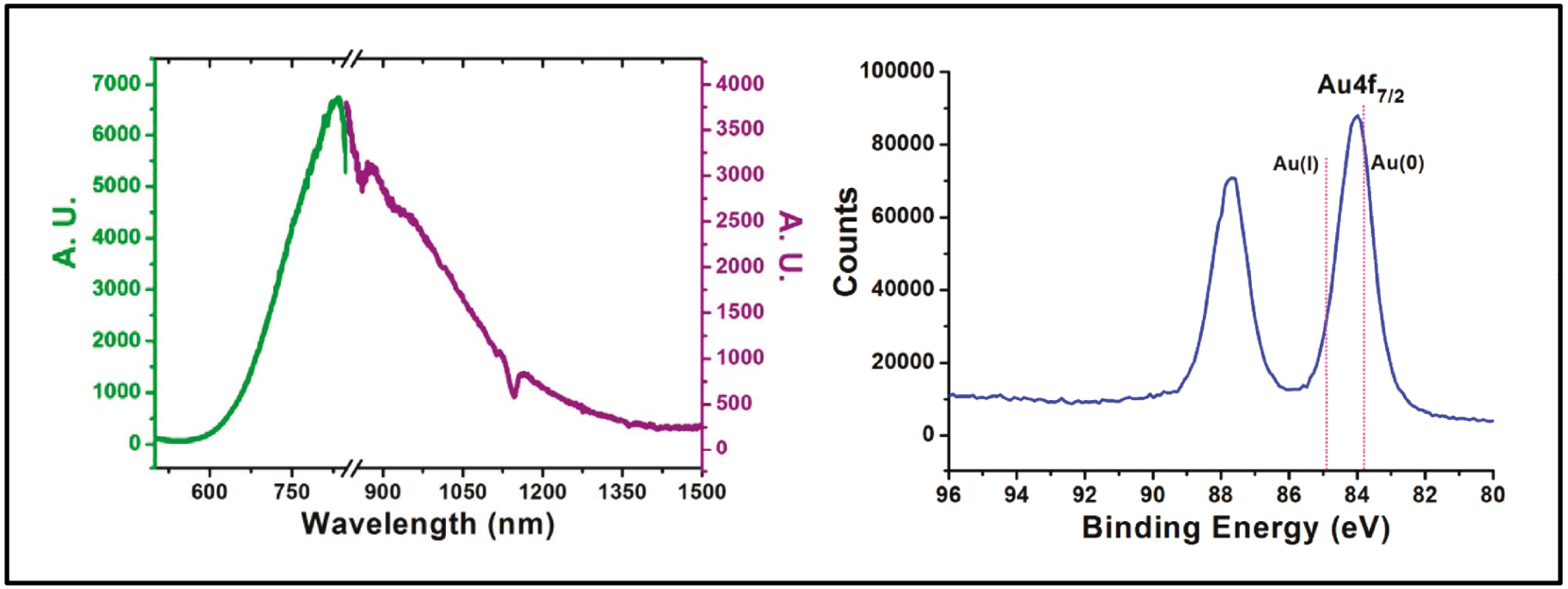
MALDI mass spectra of Au MTCs at different laser intensities. The spectra were collected under linear positive mode with DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyldidene]) as matrix. No discernible signal was detected above 40000.

Result and discussion



NMR spectra of (top) the purified MTCs and (bottom) the decomposed products. The purified MTCs (top panel) were decomposed in the same NMR tube without purification, from which the bottom spectrum was collected. The two spectra were aligned based on the sharp peak at 5.24 ppm withCD2Cl2 as solvent.

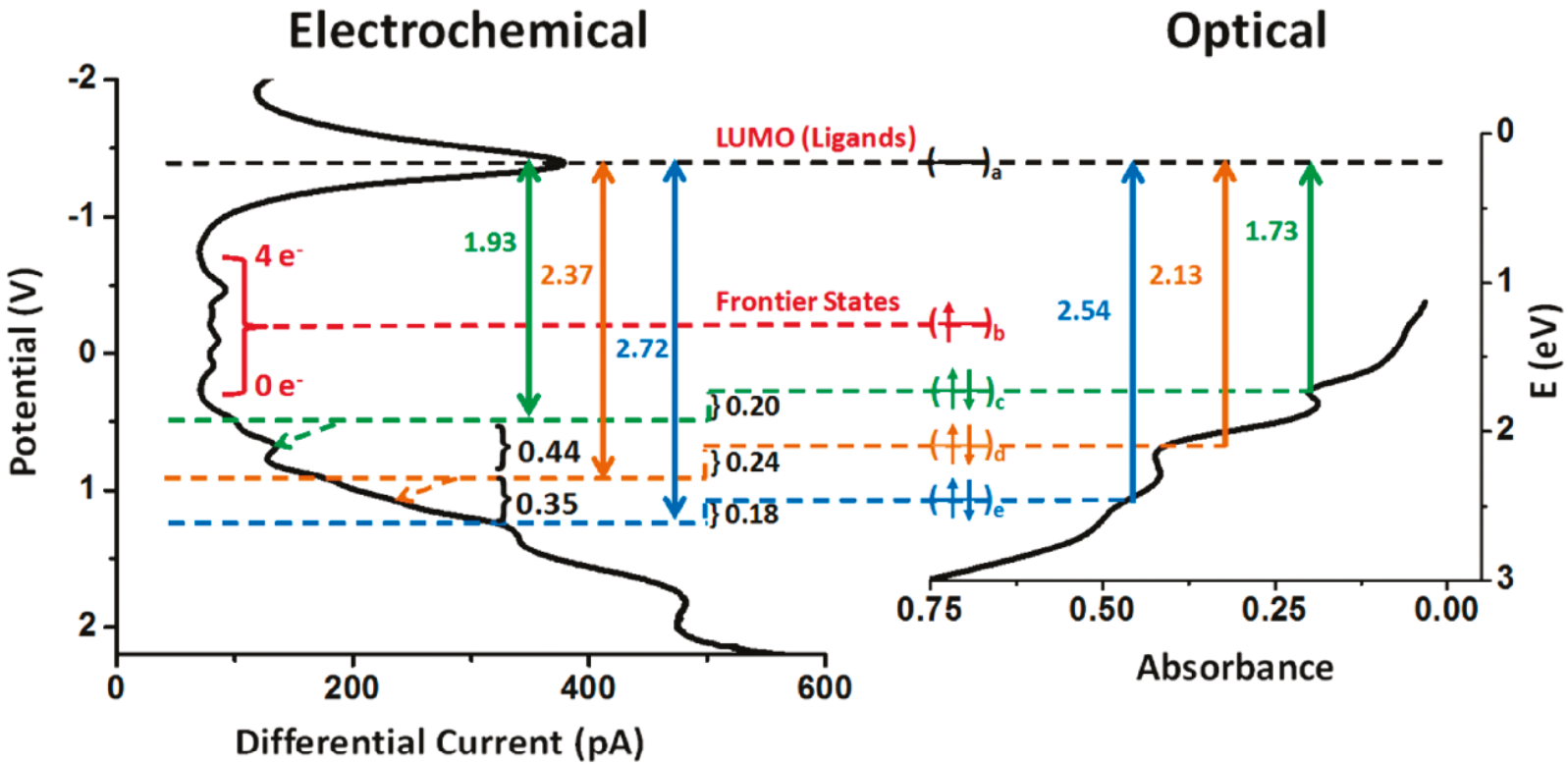
Result and discussion



Luminescence of dilute Au130 MTCs at room temperature in CH2Cl2, excited at 400 nm. The left and right emission spectra were collected by the visible (up to 850 nm) and near-IR detector (from 850 nm) separately.

Au XPS spectrum of the Au130 MTCs. Dash lines illustrate the previously reported Au (0) and Au(I)thiolate binding energies.

Result and discussion



Energy diagram that correlates optical and electrochemical features. The oxidation scan (left) and absorbance spectrum (right) are aligned based on the energy stated shown in the middle. The undetermined degeneracy of those states are denoted c, d, and e.

Summary and Conclusion

- Interesting energetics is observed from a new type of molecular gold cluster protected by mixed monothiol ligand and dithiol ligand.

- The average composition of the Au MTCs is determined as Au130(Durene-DT)29(PhC2S)22 at ± 1-2 resolution.

- An energy diagram has been proposed to correlate the optical and electrochemical energetics of this molecular nanocluster.


Happy New
Year