

## Electronic Supplementary Information

### **Isomerization-induced Enhancement of Luminescence in Au<sub>28</sub>(SR)<sub>20</sub> Nanoclusters**

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#### **1. Experimental**

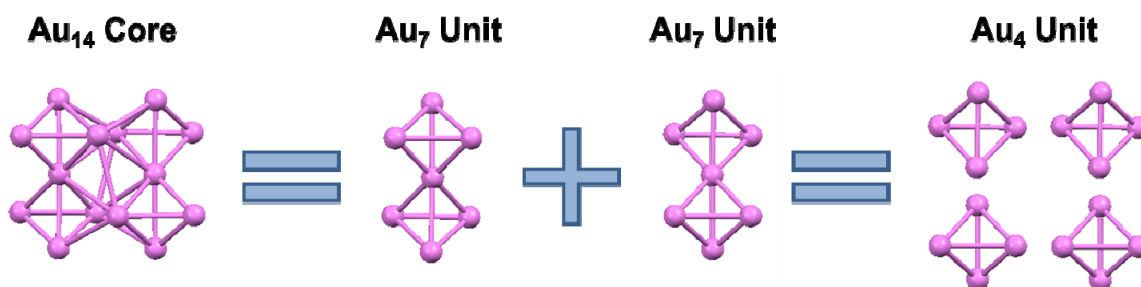
**Synthesis.** The Au<sub>28</sub>(TBBT)<sub>20</sub> and Au<sub>28</sub>(CHT)<sub>20</sub> nanoclusters were synthesized by literature approaches.<sup>42,51</sup> Briefly, Au<sub>28</sub>(TBBT)<sub>20</sub> was synthesized by reacting excess TBBT ligand with Au<sub>25</sub>(SR)<sub>18</sub> at 80 °C. The Au<sub>28</sub>(CHT)<sub>20</sub> nanocluster was synthesized by reacting Au<sub>28</sub>(TBBT)<sub>20</sub> nanoclusters with CHT thiol under thermal conditions (80 °C). We also prepared Au(I)-TBBT and Au(I)-SC<sub>6</sub>H<sub>11</sub> complexes to test whether these complexes are luminescent under the same excitation conditions as the nanoclusters. At r.t., 0.1 g of HAuCl<sub>4</sub> was dissolved in 10 ml of methanol, followed by addition of 210 μl of TBBT. The reaction mixture was stirred for 1 hr. The precipitate (Au<sup>I</sup>SR complexes) was collected and washed with methanol several times to remove the un-reacted thiol and other side products. The Au(I)-SC<sub>6</sub>H<sub>11</sub> complex was prepared by the same protocol except that TBBT was replaced with 1-cyclohexanethiol.

**Optical and PL measurements.** The UV-vis absorption spectra were recorded using a Hewlett-Packard (HP) 8543 diode array spectrophotometer. Fluorescence spectra were recorded on a Fluorolog-3 spectrofluorometer (HORIBA Jobin Yvon). Quantum yields (QY) were measured with dilute solutions of clusters using Au<sub>25</sub>(SG)<sub>18</sub> (QY=0.1%) as the reference. Fluorescence lifetimes were measured by a time-correlated single photon counting (TCSPC) technique; a pulsed LED source (376 nm, 1.1 ns) was used to excite the clusters. Both Au<sub>28</sub>(CHT)<sub>20</sub> and Au<sub>28</sub>(TBBT)<sub>20</sub> were dissolved in toluene.

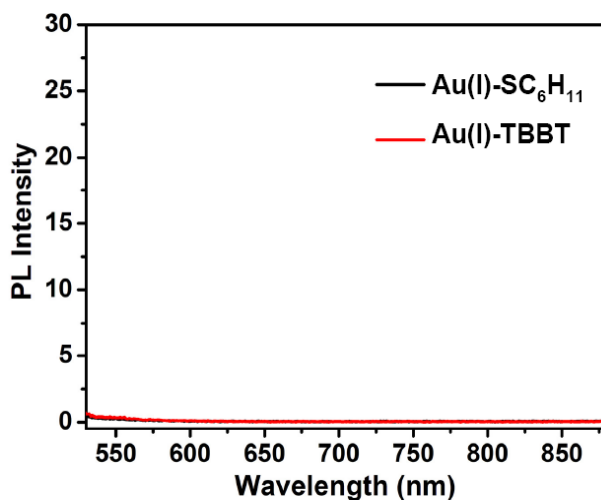
**Excited state dynamics measurements and data analysis.** Femtosecond (fs) TA spectroscopy was measured using a commercial Ti:Sapphire laser system (SpectraPhysics, 800 nm, 100 fs, 3.5 mJ, 1 kHz). The pump pulse was generated by a commercial optical parametric amplifier

(LightConversion). A small portion of the laser fundamental was focused into a sapphire plate to produce supercontinuum in the visible region, which overlapped in time and space with the pump. Multiwavelength transient spectra were recorded using dual spectrometers (signal and reference) equipped with array detectors whose data rates exceed the repetition rate of the laser (1 kHz). Solutions of both clusters in 2 mm path length cuvette were excited by the tunable output of the OPA (pump). Nanosecond (ns) transient absorption measurements were conducted using the same ultrafast pump pulses along with an electronically delayed supercontinuum light source with a sub-nanosecond pulse duration (EOS, Ultrafast Systems). Data analysis follows the methods reported previously.<sup>73</sup>

## 2. Supplementary Figure:



**Figure S1.** Structural dissection of the  $Au_{14}$  core via  $Au_4$  units.



**Figure S2.** PL spectra of Au(I)-SR complexes. No PL was observed under 370 nm excitation (the same condition as the NCs) or other wavelengths such as 410 and 450 nm.