Supporting Information

Temperature-Dependent Absorption and Ultrafast Luminescence Dynamics of Bi-icosahedral Au$_{25}$ Clusters

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ESI-MS spectra were obtained using a Waters SYNAPT G1 HDMS mass spectrometer equipped with V and W-modes. The source temperature was kept at 100 Celsius and the source voltage is kept at 3.06 KV. The sampling cone voltage is kept at 20 V and extraction cone voltage is at 4 V. The sample was directly infused at 5 µL/min. The sample concentration was 10 µM in LCMS grade acetonitrile and ethanol solutions. For Au$_{25}$-sphere, measurements were carried out in dichloromethane while acetonitrile was used for bi-Au$_{25}$ clusters. Shown in Figure S1A is the ESI-MS of Au$_{25}$-sphere clusters. The m/z value of 7031 matches well with the isotopic mass of Au$_{25}$(SC$_6$H$_{13}$)$_{18}^-$ cluster.
**Figure S1.** ESI-MS of Au$_{25}$-sphere showing the molecular ion peak with a charge of -1.

Shown in Figure S2 is the ESI-MS Au$_{25}$-rod. Molecular ion peak of 4101 matches quite well with that of [Au$_{25}$(PPh$_3$)$_{10}$(C$_6$S)$_5$Cl$_2$]$^{2+}$.

**Figure S2.** ESI-MS of Au$_{25}$-rod showing the molecular ion peak with a charge of +2.