(Supporting Information)

Atomically Precise Large-Sized $Au_n(SR)_m$ Nanoclusters and Scaling Relationships between Size, Bandgap and Excited-State Lifetime

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1. Experimental

Chemicals

Tetrachloro Auric (III) acid ($HAuCl_4·3H_2O$, >99.99% metals basis, Aldrich), Tetraoctylammonium bromide (TOAB, ≥98%, Fluka), 2-Phenylethanethiol (PET, C_8H_9SH, 98%, Aldrich), Sodium borohydride ($NaBH_4$, Aldrich). Solvents: Methanol (MeOH, HPLC grade, ≥99.9%, Aldrich), Dichloromethane (DCM, ACS reagent, ≥99.5%, Aldrich). All chemicals were used without further purification. Nanopure water was prepared with a Barnstead NANO pure Diamond system.

Synthesis of Au_{100}

$Au_{100}(Napt)_{42}$ (Napt = 1-Naphthalenethiol) was prepared by a ligand-exchange reaction from polydispersed $Au_x(2,4\text{-DMBT})_y$ nanoclusters (2,4-DMBT = 2,4-dimethylbenzenethiol). The $Au_x(2,4\text{-DMBT})_y$ was formed by first phase transfer of $HAuCl_4·3H_2O$ into a toluene phase with TOAB (tetraoctylammonium bromide), then Napt reduction and further reduced by aqueous solution of $NaBH_4$. ~20 mg of $Au_x(2,4\text{-DMBT})_y$ was added into a 10 mL round-bottom flask with 1 mL toluene and 0.5 mL Napt. The reaction was allowed for overnight etching at 80 °C. Then, methanol was added, followed by centrifugation, and the precipitate was further washed three times with methanol. Separation of $Au_{100}(Napt)_{42}$ from other side products was done by thin-layer chromatography (TLC). Dichloromethane was used to extract the $Au_{100}(Napt)_{42}$, and the sample was dried by N_2 gas for further experiments.

Synthesis of Au_{102}

$Au_{102}(IPBT)_{44}$ was synthesized by a two-step size-focusing synthesis procedure. Briefly, a poly-dispersed $Au_x(IPBT)_y$ mixture was first obtained by the reactions of $HAuCl_4·3H_2O$ and 4-Isopropylbenzenethiol (IPBT) and then reduction by $NaBH_4$. Further etching of the poly-dispersed $Au_x(IPBT)_y$ was done in toluene with 0.5 mL IPBT at 80 °C. After washing with methanol, pure $Au_{102}(IPBT)_{44}$ was collected.

Mass spectrometry and optical absorption measurements

MALDI-MS was performed with a PerSeptive-Biosystems Voyager DE super-STR time-of-flight (TOF) mass spectrometer. Trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenyldidene] malononitrile (DCTB) was used as a matrix. ESI mass spectra were recorded using a Waters Q-TOF mass spectrometer equipped with Z-spray source. The source temperature was kept at 70 °C. The sample was directly infused into the chamber at 5 µL/min. The spray voltage was kept at 2.20 kV and the cone voltage at 60 V. The ESI sample was dissolved in CH_2Cl_2. UV-Vis-NIR spectra were collected on a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu).

Electrochemical analysis

Electrochemical measurements were performed in dry dichloromethane with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) using a CH Instruments (CHI 750C) potentiostat with Picoamp booster in a Faraday Cage. A three-electrode system was used in all the electrochemistry tests comprising a 0.2 mm radius Pt disk electrode, a Pt foil as counter electrode, and an Ag/AgCl wire as quasi-reference electrode. The solution was generally purged around 20 minutes with Ar prior to electrochemical measurements. The concentration of AuNCs is 0.5 mg/mL in DCM with 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the electrolyte. The potential scan rate in CV is 0.1 V/s. The pulse amplitude is 0.05 V, pulse width 0.05 s, pulse period 0.5 s, and step size 4 mV in DPV.

Femtosecond transient absorption spectroscopy

The pump beam was generated in a collinear optical parametric amplifier (Light conversion) pumped by the 805 nm output of an amplified Ti:sapphire laser (Coherent Astrella, 5 kHz). 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. The instrument response function was measured to be 100 fs. All the measurements were performed in diluted toluene solutions and the optical density was adjusted to ~0.3 OD at the excitation wavelength.

2. Supporting Figures

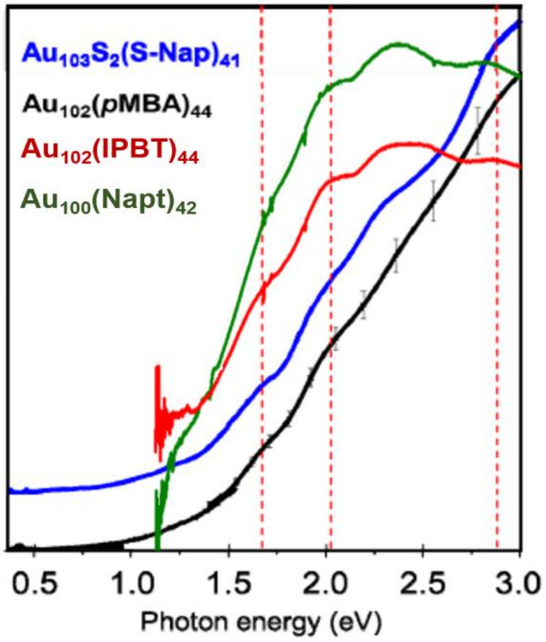

Figure S1. Comparison of the UV-Vis absorption spectra of $Au_{100}(Napt)_{42}$, $Au_{102}(IPBT)_{44}$, $Au_{103}S_2(S\text{-}Nap)_{41}$ and $Au_{102}(pMBA)_{44}$. The $Au_{102}(pMBA)_{44}$ and $Au_{103}S_2(S\text{-}Nap)_{41}$ are redrawn from refs.[s1,s2]

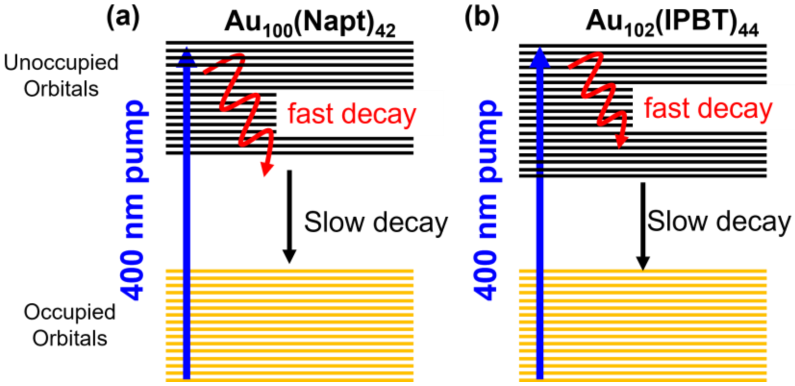

Figure S2. Excited state relaxation diagram of (a) $Au_{100}(Napt)_{42}$ and (b)$Au_{102}(IPBT)_{44}$. The fast relaxation comprises < 1 ps of internal conversion and a few ps of structural relaxation, whereas the slow process (hundreds of ps) is exciton recombination.

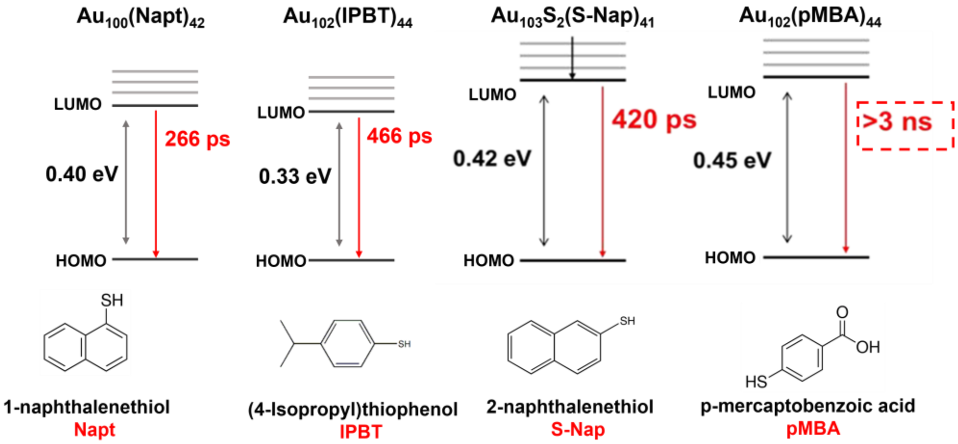

Figure S3. Excited-state lifetimes of the 58*e* series of NCs determined by fs-TA.

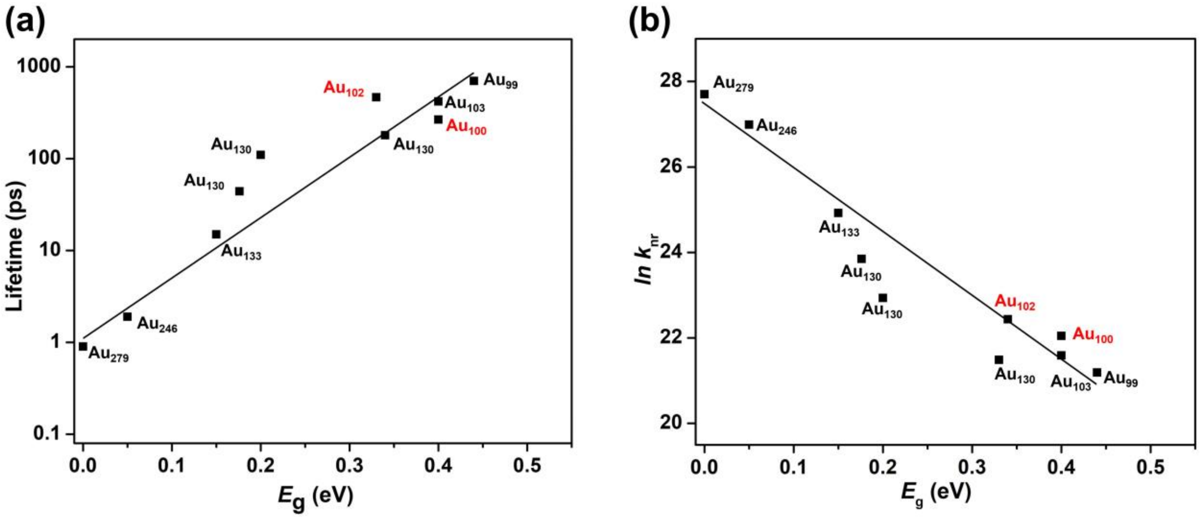

Figure S4. Scaling relationship between the excited-state lifetimes and the energy gaps of large-sized $Au_n(SR)_m$ NCs. (a) Lifetime vs E_g; (b) Logarithmic nonradiative relaxation rate $\ln k_{nr}$ vs E_g. Note: $Au_{100}(Napt)_{42}$ and $Au_{102}(IPBT)_{44}$ are from this work, and other data are collected from the previous reports.

Supporting references:

s1. Hulkko, E.; Lopez-Acevedo, O.; Koivisto, J.; Levi-Kalisman, Y.; Kornberg, R. D.; Pettersson, M.; Häkkinen, H. Electronic and Vibrational Signatures of the $Au_{102}(p\text{-}MBA)_{44}$ Cluster. *J. Am. Chem. Soc.* **2011**, 133, 3752−3755.

s2. Higaki, T.; Liu, C.; Zhou, M.; Luo, T. Y.; Rosi, N. L.; Jin, R. Tailoring the Structure of 58-Electron Gold Nanoclusters: $Au_{103}S_2(S\text{-}Nap)_{41}$ and Its Implications. *J. Am. Chem. Soc.* **2017**, 139, 9994−10001.