Surface Ligand Networking Promotes Intersystem Crossing in the $Au_{18}(SR)_{14}$ Nanocluster

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Chemicals

Chemicals Tetrachloroauric (III) acid ($HAuCl_4 \cdot {}_3H_2O$, 99.99% metal basis, Aldrich), 2,4-dimethylbenzenethiol (DMBT, C_8H_9SH, 98 %, Aldrich), cyclohexanethiol (CHT, 97 %, Aldrich), sodium borohydride ($NaBH_4$, Aldrich), tetraoctylammonium bromide (TOAB, ≥98 %, Fluka), triethylamine (Et_3N, 99%), tetrahydrofuran (HPLC grade, ≥99.9%, Aldrich), toluene (HPLC grade, ≥99.9%, Aldrich), dichloromethane (DCM, ACS reagent, ≥99.5%, Aldrich), acetonitrile (HPLC grade, ≥99.9%, Aldrich), methanol (MeOH, HPLC grade, ≥99.9 %, Aldrich), ethanol (EtOH, HPLC grade, ≥99.9 %, Aldrich). All chemicals were used as received without further purification. Deionized water was prepared with a Barnstead NANOpure Diamond system (18.2 MΩ cm). Thin-layer chromatography (TLC) plates were purchased from iChromatography (silica gel, 250 μm).

Synthesis of $Au_{18}(DMBT)_{14}$

$Au_{18}(DMBT)_{14}$ was prepared following a published procedure.[1] Briefly, in a flask, $HAuCl_4 \cdot 3H_2O$ (78.99 mg, 0.2 mmol) and TOAB (136.7 mg, 0.25 mmol) were combined and dissolved with 28 mL of THF by continuous stirring. After 15 minutes, DMBT (138 μL) was added to the mixture while it was kept in an ice bath. Next, 70 μL of Et_3N was added all at once, and the stirring speed was decreased to 100 rpm. The mixture was stirred for 30 minutes. Then, a freshly prepared aqueous solution of $NaBH_4$ (47.5 mg, 1.25 mmol, in 2 mL solution) was added dropwise to the reaction mixture over a period of 5 minutes. The reaction was stirred for an additional 8 hours at 0 °C. After that, the solvent was removed by rotary evaporation, yielding a dark, oily substance. Methanol was used to precipitate the oily mixture, and the precipitate was washed with excess methanol. The black product obtained was further purified by thin-layer chromatography (TLC) using a hexane and dichloromethane mixture (1:1, v/v) as the developing solvent. The yield of $Au_{18}(DMBT)_{14}$ was about 5%, calculated based on gold atoms.

Synthesis of $Au_{18}(CHT)_{14}$

The synthesis of crude $Au_{18}(CHT)_{14}$ was carried out using a previous method[2] and purification was done by thin-layer chromatography (TLC). The mobile phase was a mixture of hexane and

dichloromethane in a 2:1 vol. ratio. The pure compound appeared as a grey band on the TLC plate, whereas the crude mixture also contained $Au_{28}(CHT)_{20}$, which appeared as an orange band.

Optical measurements

UV-Vis-NIR spectra were collected on a UV-3600 Plus UV-Vis-NIR spectrophotometer (Shimazu). Steady-state photoluminescence spectra were measured on a FLS-1000 spectrofluorometer (Edinburgh) with a wide-range photomultiplier tube (PMT-1700, 500 - 1700 nm) cooled to -80 °C by liquid nitrogen. The PL lifetimes were measured by time-correlated single photon counting (TCSPC) on the same instrument, with excitation at 450 nm (~100 ps pulsed laser). For r.t. measurement, the NCs were dissolved in toluene, while for cryogenic measurements, the NCs were dissolved in 2-MeTHF (clear "glass" formation at cryogenic temperatures).

A relative method was performed to determine the quantum yield of $Au_{18}(DMBT)_{14}$ and $Au_{18}(CHT)_{14}$ at room temperature using $Au_{25}(PET)_{18}^-$ (counterion: tetraoctylammonium) as the reference (QY = 1.0% in $CDCl_3$). The low temperature QY for $Au_{18}(DMBT)_{14}$ was determined by integrating the peak area and comparison with the peak area of $Au_{18}(DMBT)_{14}$ at room temperature after correcting the absorbance enhancement at low temperatures.

Transient absorption measurements were carried out using a broadband pump-probe setup, which is pumped by a commercial Ti:Sapphire laser (Coherent Astrella, 1 kHz) with an optical parametric amplifier (OPerA Solo, Light Conversion). For fs-TA measurements, the probe light is generated by focusing the fundamental pulse into a sapphire plate. The probe light is split into signal and reference beams. The pump-probe delay was controlled by a mechanical delay line. For ns-TA measurements, the probe light is generated with a fiber laser (Leukos), and the delay up to microseconds are controlled by an electronic delay configuration. The Au_{18} nanoclusters were excited at 400 nm, which is the same for both fs- and ns-TA measurements. TA measurements were performed in toluene and the optical density of the solutions was adjusted to ~0.3 OD (2 mm cuvette) at the excitation wavelength. The polarization of pump and probe pulse was set to magic angle (54.7°) to measure the isotropic signal.

Data fitting

The transient absorption spectra were analyzed using the publicly available program Glotaran based on the statistical fitting package TIMP.[3,4] A sequential model was adopted for the fs and ns TA data to give the evolution associated spectra (EAS).

Supporting figures from transient absorption measurements and data analysis:

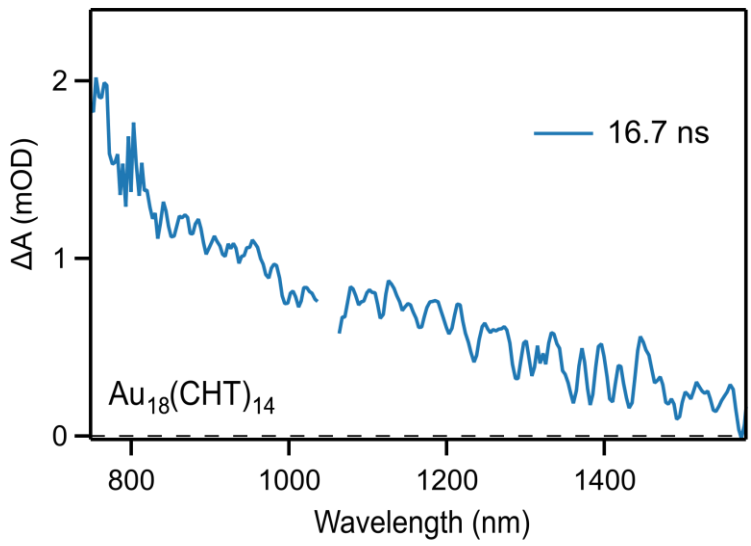

Figure S1. Global analysis of the ns-TA data of $Au_{18}(CHT)_{14}$.

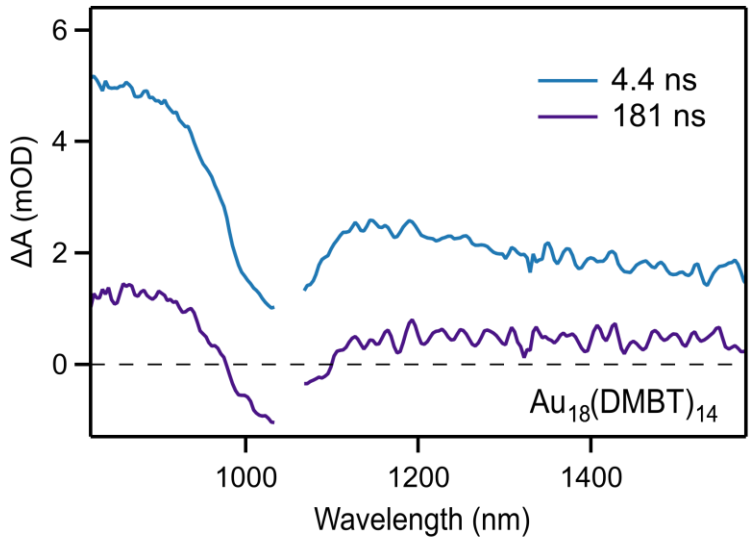

Figure S2. Global analysis of the ns-TA data of $Au_{18}(DMBT)_{14}$.

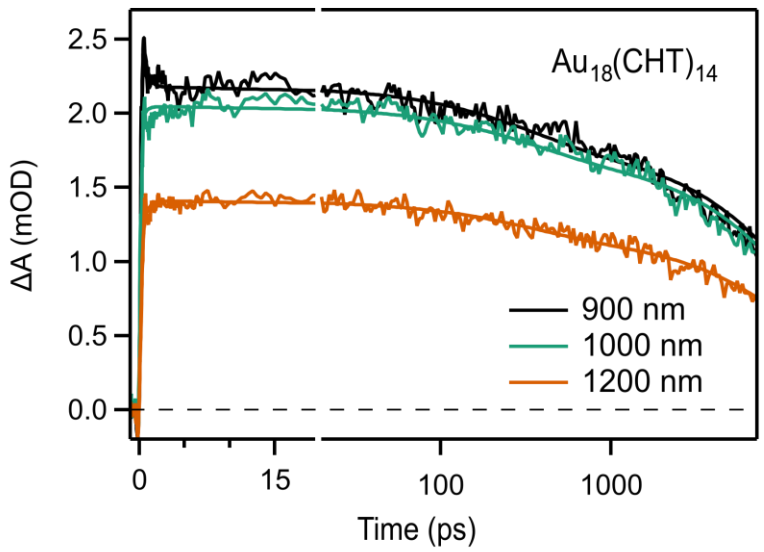

Figure S3. The kinetics of the fs-TA measurements of $Au_{18}(CHT)_{14}$ and global fitting.

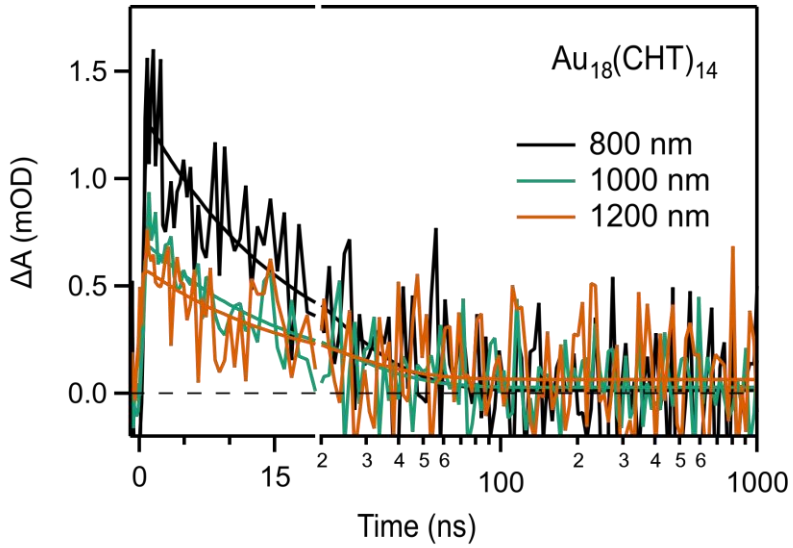

Figure S4. The kinetics of the ns-TA measurements of $Au_{18}(CHT)_{14}$ and global fitting.

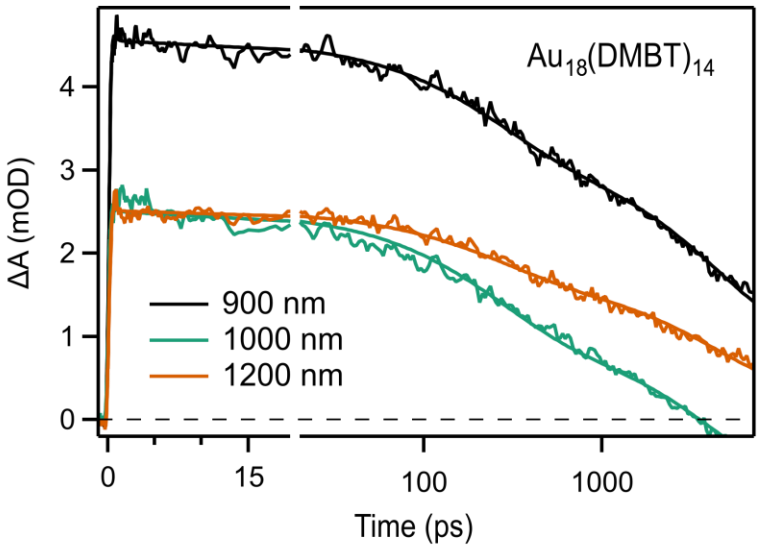

Figure S5. The kinetics of the fs-TA measurements of $Au_{18}(DMBT)_{14}$ and global fitting.

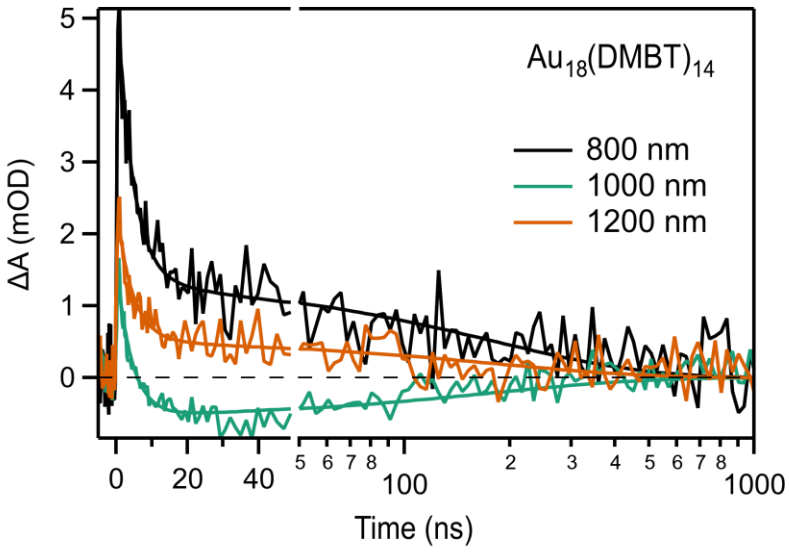

Figure S6. The kinetics of the ns-TA measurements of $Au_{18}(DMBT)_{14}$ and global fitting.

Temperature-dependent PL measurements:

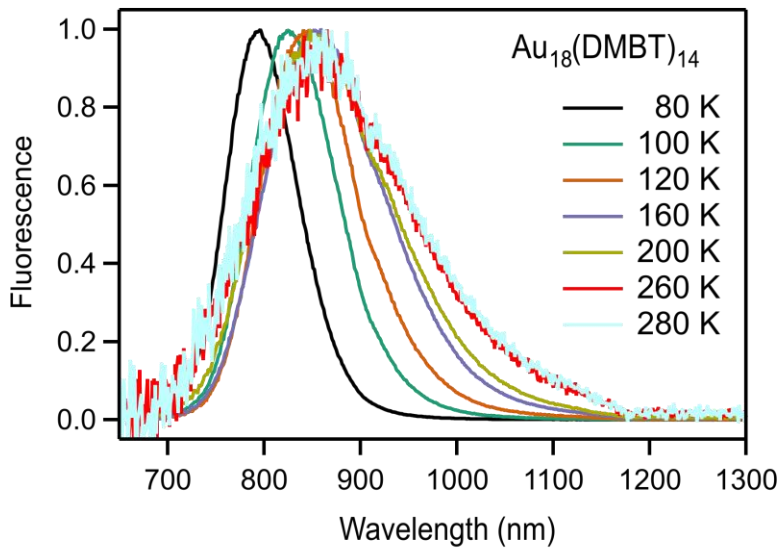

Figure S7. The normalized temperature-dependent PL spectra of $Au_{18}(DMBT)_{14}$.

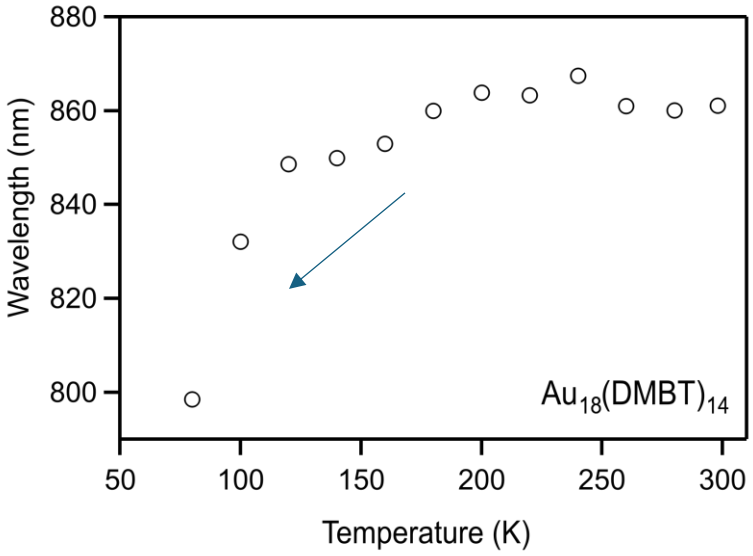

Figure S8. Temperature-dependent PL peak wavelength of $Au_{18}(DMBT)_{14}$.

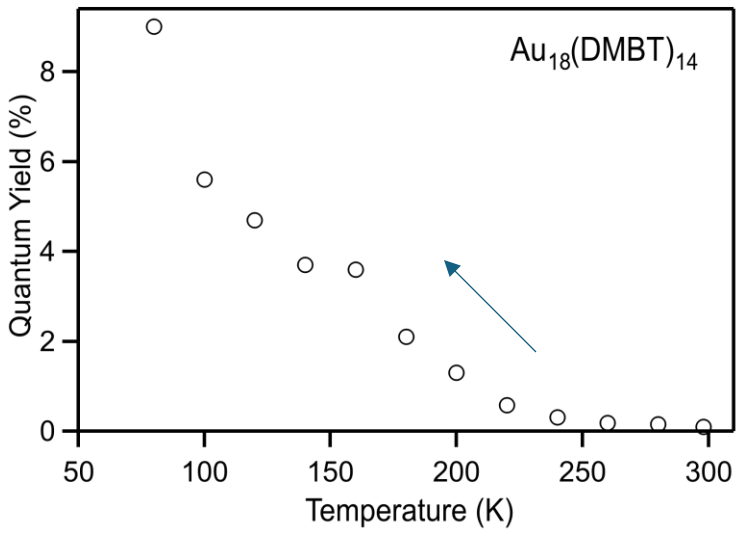

Figure S9. Temperature-dependent PLQY of $Au_{18}(DMBT)_{14}$.

References

1. Z. Liu, Y. Wang, W. Ji, X. Ma, C. G. Gianopoulos, S. Calderon, T. Ma, L. Luo, A. Mazumder, K. Kirschbaum, E. C. Dickey, L. A. Peteanu, D. Alfonso and R. Jin, *ACS Nano*, 2025, **19**, 9121–9131.
2. A. Das, C. Liu, H. Y. Byun, K. Nobusada, S. Zhao, N. Rosi and R. Jin, *Angew. Chem. Int. Ed.*, 2015, **54**, 3140–3144.
3. I. H. M. van Stokkum, D. S. Larsen and R. van Grondelle, *Biochim. Biophys. Acta - Bioenerg.*, 2004, **1657**, 82–104.
4. J. J. Snellenburg, S. P. Laptenok, R. Seger, K. M. Mullen and I. H. M. van Stokkum, *J. Stat. Soft.*, 2012, **49**, 1–22.