# **Supporting Information**

# Intensive Near-Infrared Emitting Au7Cu10 Nanoclusters for Both

# **Energy and Electron Harvesting**

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## **S1. Materials and Methods**

## 1. Chemical

All reagents and solvents were commercially available and used as received without further purification. Tetrachloro-auric(III) acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O,  $\geq$ 99.99% metals basis, Energy Chemical), cuprous chloride (CuCl<sub>2</sub>,  $\geq$ 98.8% metals basis, Alfa Aesar), 1-adamantanethiol (HSC<sub>10</sub>H<sub>15</sub>, 98%, Alfa Aesar), disphenyl-2-pyrldylphosphine (PPh<sub>2</sub>Py,  $\geq$ 98%, TCI), sodium borohydride (NaBH<sub>4</sub>,  $\geq$ 98%, Energy Chemical), sodium hexafluoroantimonate (NaSbF<sub>6</sub>,  $\geq$ 98%, Aldrich), tetrahydrofuran (C<sub>4</sub>H<sub>8</sub>O, HPLC, Aladdin), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, HPLC, Aladdin), *n*-hexane ( $\geq$ 98%, Aladdin), and nanopure water, methanol ( $\geq$ 99.5%, Sinopharm), perylene ( $\geq$ 98%, Macklin), methyl viologen ( $\geq$ 99%, Aladdin), tetrabutylammonium hexafluorophosphate ( $\geq$ 99%, Aladdin).

To confirm the stability of the  $Au_7Cu_{10}$  of with the addition of Pery and  $MV^{2+}$ , we performed the ESI-MS as shown in Figure S15, which show that the ESI-MS has no change compared to the pure  $Au_7Cu_{10}$  (Figure 1B).

# 2. Synthesis of Au<sub>7</sub>Cu<sub>10</sub> nanoclusters

This Au-Cu nanocluster was directly synthesized by a one-pot method. Briefly, 80 mg HAuCl<sub>4</sub>·3H<sub>2</sub>O and 50 mg cuprous chloride were dissolved in 13 mL tetrahydrofuran under vigorous stirring. Then, 100 mg 1-adamantanethiol (1-Adm) was added into the solution directly, and the color of the mixture changes from yellow to dark green, indicating the formation of Au(I)/Cu(I)-SR complex. After 30 min, 130 mg disphenyl-2-pyrldylphosphine was added into the solution directly, and the color of the color of the mixture changes from dark green to light orange. 15 min later, 50 mg NaBH<sub>4</sub> dissolved in 5 ml ice water was added into the above solution, and the color of the solution turned to black. After 16 h, the reaction solution was mixed with the methanol solution of NaSbF<sub>6</sub> (15 mg), in which the organic phase was evaporated and the aqueous phase was removed by centrifugation. Finally, the black precipitation was washed several times with dichloromethane/n-hexane to remove the redundant ligands and by-products. The crude products were recrystallized in dichloromethane /*n*-hexane at 4 °C. After 5-7 days, some black block-shaped crystals were obtained. The resulting black block crystals were collected, and one piece of high-quality crystal was chosen for SC-XRD analysis, which are the pure [Au<sub>7</sub>Cu<sub>10</sub>(1-Adm)<sub>3</sub>(PPh<sub>2</sub>Py)<sub>6</sub>Cl<sub>3</sub>](SbF<sub>6</sub>)<sub>3</sub> nanoclusters.

### 3. Theoretical Calculations

In this work, all of the theoretical calculations were performed with the Gaussian  $16^1$  and ORCA 5.0.3 package.<sup>2</sup> The 1-Adm ligands and benzene ring in the **Au**<sub>7</sub>**Cu**<sub>10</sub> nanocluster are replaced by -SCH<sub>3</sub> groups and -CH<sub>3</sub>. The present ligand simplification is reasonable because the relevant excited states do not involve 1-adamantanethiol and benzene ring ligands. The experimental

absorption spectra are very well reproduced by the present model, indicating that it is reasonable to replace 1-adamantanethiol ligands and benzene ring with SCH<sub>3</sub> and CH<sub>3</sub>. The geometries of the ground state (S<sub>0</sub>) and the first excited triplet state (T<sub>1</sub>) of **Au<sub>7</sub>Cu<sub>10</sub>** were optimized using DFT/UDFT at the hybrid functional PBE1PBE<sup>3</sup> with the Def2TZVP basis set.<sup>4</sup> Au uses the viable core potentials with 19 valence electrons including scalar relativistic corrections, the rest of the atoms use all-electron basis set. Structural optimizations were done within the D3 dispersion correction.<sup>5</sup> Vibrational frequencies were then calculated based on their optimized structures S<sub>0</sub> to verify the minimum energy geometry. Time-dependent DFT calculations of the UV-vis absorption spectra and the charge difference densities (CDDs) were done at optimized geometries using PBE1PBE/Def2TZVP. The electron–hole distributions were carried out on the Multiwfn program based on the output from Gaussian calculations.<sup>6</sup>

The spin-orbit coupling (SOC) matrix elements between singlet and triplet states were evaluated to rationalize the ISC mechanism using ORCA program. The SOC matrix elements from Tn to S<sub>1</sub> are obtained by RI-SOMX(1X) method using scalar relativistic all-electron calculations with Douglas-Kroll-Hess Hamiltonian of 2nd order (DKH2) at TD-PBE0 level.<sup>7-8</sup> SARC-DKH-TZVP are used for Au atoms and DKH-def2-TVZP basis sets are used for the remaining atoms (C, H, Cu, P, N and S).<sup>8</sup> The solvent effect of DCM is considered using the Conductor-like Polarizable Continuum (C-PCM).<sup>9</sup> Resolution of identity approximation for Coulomb integrals (RIJ) and chain of spheres algorithm for exchange ones (COSX) with corresponding auxiliary basis and grid settings are used to speed up the computations.<sup>10-11</sup>

#### 4. Steady-State Spectral Measurements

All the steady-state spectral measurements were performed at room temperature. The absorption spectra in different solvents were measured using a UV-Vis spectrophotometer (Cary 60, Agilent). The steady-state emission spectra were obtained using fluorescence spectrometer (cary eclipse, Agilent). The quantum yields were acquired on a Quantaurus QY Plus UV-NIR absolute photoluminescence quantum yield spectrometer (C13534, HAMAMATSU, Japan) with excitation at 400 nm. The emission lifetimes ( $\tau$ ) were measured on a time-correlated single photo counting spectrometer (FluoTime 300, PicoQuant, Germany), samples were excited at 375 nm picosecond laser (PDL 820, PicoQuant diode laser), and the instrument response function was about 200 ps.

For the time-resolved emission measurements shown in Figure 1D, a 375 nm excitation was used for two reasons: (1) it was the only available laser for the PicoQuant spectrometer, and (2) as demonstrated in Figure S1,  $Au_7Cu_{10}$  has a single emission origin because the excitation spectra at different emission wavelength both show same spectra profiles, meaning that the emission lifetime remains the same regardless of the excitation wavelength. In contrast, for the

emission measurements of the  $Au_7Cu_{10}$ /Pery system in THF (Figure 2C), a 600 nm excitation was used to selectively excite  $Au_7Cu_{10}$  NCs while avoiding interference from excitation scattering in the detection of Pery emission. Using 375 nm excitation in this system would excite both  $Au_7Cu_{10}$  and Pery simultaneously, leading to unreliable results. Although different excitation wavelengths were used in these measurements, the results remain reliable.

### 5. Electrochemical Measurements

Differential pulse voltammetry (DPV) measurements were made by using a CHI-620E potentiostat with a one-compartment electrochemical cell. All measurements were carried out at a scan rate of 50 mV·s<sup>-1</sup> in the DCM containing 0.1 M of Bu<sub>4</sub>NClO<sub>4</sub> as the supporting electrolyte. A disk platinum electrode with a diameter of 2.0 mm was used as the working electrode. The electrode was polished prior to use with 0.05 mm alumina and rinsed thoroughly with water and acetone. The counter electrode was a large area platinum wire coil. All the potentials are referenced to an Ag/AgCl electrode in saturated aqueous KCl without regard for the liquid junction potential. The electrolyte solution was in a nitrogen atmosphere during the entire experimental procedure.

### 6. Time-Resolved Transient Absorption Spectroscopy Measurements

The fs-TA spectra were measured using a home-built femtosecond pump-probe set-up. Briefly, a regenerative amplified femtosecond Ti:sapphire laser beam with pulse duration of ~35 fs, centered at 800 nm, repetition rate of 1000 Hz, and pulse energy of 7 mJ was directed on to a beam splitter to generate the pump and the probe beams (Coherent Astrella-Tunalbe-USP, USA). The pump beam used in this investigation was produced by an optical parametric amplifier (TOPAS-C, Coherent) and focused into the sample cell (1 mm quartz cuvette). The probe beam was delayed with a computer-controlled optical delay line and then focused on a thin sappire plate to generate the white light supercontinuum which split into two beams by using a broadband 50/50 beam splitter as the signal and reference beams (450 - 780 nm). The white light and the pump beam were overlapped into the sample and the linear polarizations were set at the magic angle (54.7°) in order to record the isotropic response. No degradation was observed throughout the experiment that was checked by absorption spectra. Data analysis was performed with the global analysis using R-package TIMP and Glotaran software. The nanosecond transient absorption spectra were measured by a commercial spectrometer (Nano100, Time-Tech Spectra). The generation of the pump beam is the same as that in fs-TA. The probe beam was generated from a supercontinuum laser (LEUKOS-DISCO, French) with the spectral region from 400 to 950 nm, the repetition rate is 2 kHz, pulsewidth is 700 ps-1 ns.

# **S2.** Supplementary Data

# 1. Spectroscopy Data



Figure S1. Excitation spectra of Au<sub>7</sub>Cu<sub>10</sub> at different emission wavelengths.



**Figure S2.** (A) Absorption spectra of the sensitizers and emitters in diluted THF solutions  $(\lambda pump = 630 \text{ nm})$ . (B) Absorption and fluorescence spectrum of Pery in THF.



Figure S3. Photoluminescence (PL) decay curves of Au<sub>7</sub>Cu<sub>10</sub> with Pery (0-6.6 mM) in THF.



Figure S4. A. Time-wavelength two-dimensional transient absorption color maps of  $Au_7Cu_{10}$ . B. Nanosecond transient absorption spectra of  $Au_7Cu_{10}$ . C. Nanosecond transient absorption spectra of  $Au_7Cu_{10}$  with Pery. D. Global analysis results EADSs derived from Ns-TA of  $Au_7Cu_{10}$  with Pery.



Figure S5. TA dynamics probed at 488 nm of  $Au_7Cu_{10}$  solutions containing different concentrations of Pery after laser excitation at 630 nm.

#### 2. Estimation of Diffusion-Limited Rate Constant (k<sub>d</sub>)

The diffusion-limited rate constants ( $k_d$ ) between the alloy nanoclusters (NC) and annihilator (AN) in THF were calculated by following equation:

$$k_d = 4\pi N_A (R_{NC} + R_{AN}) \left(\frac{k_B T}{6\pi \eta R_{NC}} + \frac{k_B T}{6\pi \eta R_{AN}}\right)$$
S1

where  $N_A$  is the Avogadro number,  $k_B$  is the Boltzmann constant, T is the temperature,  $\eta$  is the viscosity of THF (4.9×10<sup>-7</sup>J • dm<sup>-3</sup> • s), R is the radius (R<sub>NC</sub>=8.52 Å; R<sub>AN</sub>=4.44 Å).



Figure S6. Spin density distribution of the lowest triplet state of Au<sub>7</sub>Cu<sub>10</sub>.



**Figure S7.** (A) ns-TA transient absorption color maps of  $Au_7Cu_{10}$  ( $\lambda_{pump} = 360$  nm). (B) fs-TA transient absorption color maps of  $Au_7Cu_{10}$  ( $\lambda_{pump} = 360$  nm). (C) ns-TA transient absorption color maps of  $Au_7Cu_{10}$  ( $\lambda_{pump} = 630$  nm). (D) fs-TA transient absorption color maps of  $Au_7Cu_{10}$  ( $\lambda_{pump} = 630$  nm). (E) Comparison of spectra at different delay times (1 ps vs 500 ns). (F) The 500 nm kinetic trace of  $Au_7Cu_{10}$  in THF at excitation 360 nm.



Figure S8. (A) Experimental absorption spectra (black lines) and TD-DFT simulated absorption spectra (red lines) of  $Au_7Cu_{10}$ ; (B) Kohn–Sham orbitals of  $Au_7Cu_{10}$ .

As shown in Figure S8, the experimental spectral profiles and peak positions of Au<sub>7</sub>Cu<sub>10</sub> are well reproduced by TD-DFT calculations, with the simulated edge absorption peak of Au<sub>7</sub>Cu<sub>10</sub> being at 2.081 eV (~0.1 eV deviated from experiment). This peak is almost entirely (96%) contributed by the HOMO→LUMO transitions. The T<sub>1</sub> transition is also almost entirely (98%) contributed by the HOMO→LUMO transitions, the T<sub>2</sub> transition (96%) and T<sub>3</sub> transition (96%) are contributed by the HOMO-1→LUMO transitions and HOMO-2→LUMO transitions, respectively.



**Figure S9**. The electrons and holes distribution and CDDs between  $S_1 / T_{1-3}$  and  $S_0$  states of  $Au_7Cu_{10}$ . Note that the up/down, front/back, left/right represents the distribution position of the isosurface within the nanoclusters.

# 3. Evaluation of TTA-UC Quantum Yield ( $\Phi_{UC}$ ) via Relative Method

Photon upconversion measurements were performed using 663 nm semiconductor laser as excitation source and a commercial fiber-optic spectrometer (ULS2048-2-USB2, AvaSpec, the spectral resolution 1.2 nm) for detection of upconverted fluorescence. For upconversion measurement, the system was calibrated using methylene blue dissolved in ethanol as an emission standard (PLQY = 4 %). The relative TTA-UC yield ( $\Phi_{UC}$ ) was calculated using the following equation:

$$\Phi_{\rm UC} = 2 \times \Phi_{std} \times \frac{A_{std}}{A_{sam}} \times \frac{I_{sam}}{I_{std}} \times \left(\frac{n_{sam}}{n_{std}}\right)^2$$

where  $\Phi_{std}$  represents the known fluorescence quantum yield of the standard sample, A and F are the absorbance intensity at the excitation wavelength ( $\lambda_{ex}$ ) and the PL integrated intensity of the emitter, respectively, and n is the refractive index of the solvent used for the standard and the samples. "std" and "sam" represent standard and samples, respectively. Notably, the equation is multiplied by a factor of 2 in order for the maximum quantum yield to be unity.

# 4. Correcting Photon Upconversion Quantum Yields to Account for Reabsorption of Emitter

For photon upconversion measurements, a high emitter concentration can lead to a strong reabsorption of upconverted light by emitter molecules in solution (inner filter effect), thereby leading to an underestimate of the UCQY if one was to simply integrate the intensity of emission bands recorded in an experiment. Therefore, corrections for self-absorption losses of Pery were applied during the calculation of upconversion quantum yield.

We present an example of this reabsorption correction that follow a procedure outlined by Olesund et al.<sup>12</sup> Figure S2 shows the fluorescence spectrum of perylene (1 $\mu$ M) in a low-concentration THF solution measured at 385 nm excitation wherein negligible reabsorption of emitted light occurs. In these low concentration solutions, the shape of their emission spectra does not change with the concentration of the emitter suggesting that negligible reabsorption in these low concentration reference solutions. Emission spectra measured from upconversion samples were then normalized to these low-concentration reference spectra by matching spectra along their long-wavelength band.<sup>13</sup> This allowed us to compute the ratio of the emitter, which was then used to scale measured UCQYs to account for the reabsorption of emitted light. Taking into account the inner filter effect, UCQY of Au<sub>7</sub>Cu<sub>10</sub>: Pery systems were calculated to adopt maximum values of 18.4%, following add the different concentration of Pery.



**Figure S10.** Comparison of the fluorescence spectrum of Pery in THF (1  $\mu$ M, red dashed line, $\lambda_{ex} = 385$  nm), UC emission spectra observed with I<sub>ex</sub> = 4000 mW·cm<sup>-2</sup> (3 mM perylene as emitter black solid line,  $\lambda_{ex} = 663$  nm).

# 5. Dependence of TTA-UC Emission on Excitation Intensity and Threshold Excitation Intensity

For photon upconversion measurements, the excitation density threshold is an important parameter that characterizes the performance of the upconversion system. Bimolecular TTA process has two regimes. This is because that the dominant deactivation channels of triplet excitons at different concentrations are different. At low triplet density, before encountering another one, most of triplets will decay with monomolecular form. So, the up-converted fluorescence is proportional to the square of the excitation, namely  $I_{up} \propto I_{ex}^2$ . At sufficiently high triplet density, every excited emitter can undergo triplet fusion with an excited spin-triplet partner before their triplet excitations decay to the ground state. In this regime, the rate of recombination of the monomolecular triplet state is a constant. Photon upconversion with its maximum quantum efficiency because only decay processes intrinsic to each participating triplet species compete with upconversion process. Hence up-converted fluorescence to a linear dependence that is independent of triplet concentration, namely  $I_{up} \propto I_{ex}$ . In double log plot, a slope of 2 and 1 can be obtained for up-converted fluorescence and the inflection point is called excitation density threshold. This relation can be used to identify the occurrence of TTA.



Figure S11. Fluorescence decays of the Pery.

#### 6. Thermodynamics of Charge Transfer.

To theoretically elucidate the charge separation process of  $Au_7Cu_{10}$  in triplet excited state and  $MV^{2+}$ , the thermodynamic driving forces are calculated from Rehm-Weller equation<sup>14</sup>, in which the free energy change is used to estimate the putative photo-induced electron transfer process and the energy level of the ET state.

$$\Delta G_{CS} = e(E_{OX} - E_{RED}) - E_{0,0} + \Delta G_S \tag{1}$$

$$\Delta G_S = W + S = -\frac{e^2}{4\pi\varepsilon_0\varepsilon_s R_{CC}} - \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{R_A + R_D}\right) \left(\frac{1}{\varepsilon_{REF}} - \frac{1}{\varepsilon_S}\right) \tag{2}$$

where  $E_{OX}$  and  $E_{RED}$  are the half-wave potential for oxidation of the Au<sub>7</sub>Cu<sub>10</sub> and reduction of the MV<sup>2+</sup>;  $\Delta G_S$  is the static Coulombic energy that consists of two parts, S is corrects for the interactions of the formed radical ions with the solvent environment and W accounts for the interactions between the generated radical ions.  $E_{0,0}$  is the 0-0 energies of the triplet state of the Au<sub>7</sub>Cu<sub>10</sub>.

The redox potentials of the  $Au_7Cu_{10}$  (*vs* Ag/AgCl) have been determined by differential pulse voltammetry in anhydrous dichloromethane. For the  $Au_7Cu_{10}$ , the first oxidation potential *E*ox is 0.74 V (see Figure S12), which is converted relative to SHE by the following formula: E (vs SHE) = E (Au<sub>7</sub>Cu<sub>10</sub> vs Ag/AgCl) – E (Fc vs Ag/AgCl) + E (Fc vs SHE).



Figure S12. Differential pulse voltammetry of  $Au_7Cu_{10}$  clusters and ferrocene at room temperature (in DCM).

The calculated results are summarized in Table S1. It is found that the CS process is favored in MeOH for the Au<sub>7</sub>Cu<sub>10</sub> as evidenced by negative  $\Delta G_{\text{ET}}$ , confirming that the charge transfer from nanocluster to MV<sup>2+</sup> is an exergonic process and thermodynamically allowed.

**Table S1.** Driving forces  $\Delta G_{CS}$  of CS process for Au<sub>7</sub>Cu<sub>10</sub> and MV<sup>2+</sup> in MeOH.

$E_{OX}(V)^{a}$	$E_{\text{RED}}(V)^{b}$	R <sub>CC</sub> (Å) <sup>c</sup>	$R_D  (\text{\AA})^d$	$R_A(\text{\AA})^d$	$\Delta G_{\rm ET}({ m eV})$
0.69	-0.45	11.1	8.52	4.44	-0.98

<sup>a</sup>The data of E (Fc vs SHE) is 0.49 V. <sup>15</sup>

<sup>b</sup>The  $E_{\text{RED}} = E (MV^{2+}/MV^{+} vs \text{ SHE})$  is -0.45 V.

 ${}^{c}R_{CC}$  is center-to-center separation distance. Here the distance is between the cluster center and the counter ion in the crystal structure.  ${}^{d}R_{D}$  is the radius of the **Au<sub>7</sub>Cu<sub>10</sub>** and R<sub>A</sub> is the radius of the MV<sup>2+</sup>, which are both determined by optimized geometric molecular structure.

e, electron charge;  $\epsilon_S$ , static dielectric constant of the solvent ( $\epsilon_{MeOH=}$  32.6);  $\epsilon_0$  (= 5.526 × 10<sup>-3</sup> e V<sup>-1</sup> Å<sup>-1</sup>), permittivity of free space;  $\epsilon_{REF}$ , the dielectric constant of the reference solvent (DCM: 9.1) used in electrochemistry.



Figure S13. Fs-TA spectra of Au<sub>7</sub>Cu<sub>10</sub> in MeOH. The pump laser wavelength is 400 nm.



Figure S14. The pump laser wavelength is 400 nm. (A) Time–wavelength two dimensional sub-ns transient absorption color maps of  $Au_7Cu_{10}$ . (B) The 500 and 600 nm kinetic traces of  $Au_7Cu_{10}$  (C) Time–wavelength two dimensional sub-ns transient absorption color maps of  $Au_7Cu_{10}$  in presence of  $MV^{2+}$ . (D) The 500 and 600 nm kinetic traces of  $Au_7Cu_{10}$  in presence of  $MV^{2+}$ .

# 7. Stability Verification

To confirm the stability of the  $Au_7Cu_{10}$  of with the addition of Pery and  $MV^{2+}$ , we performed the ESI-MS as shown in Figure S15, which show that the ESI-MS has no change compared to the pure  $Au_7Cu_{10}$  (Figure 1B).



Figure S15. The ESI-MS of Au<sub>7</sub>Cu<sub>10</sub> with addition of (A) Pery and (B) MV<sup>2+</sup>.

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