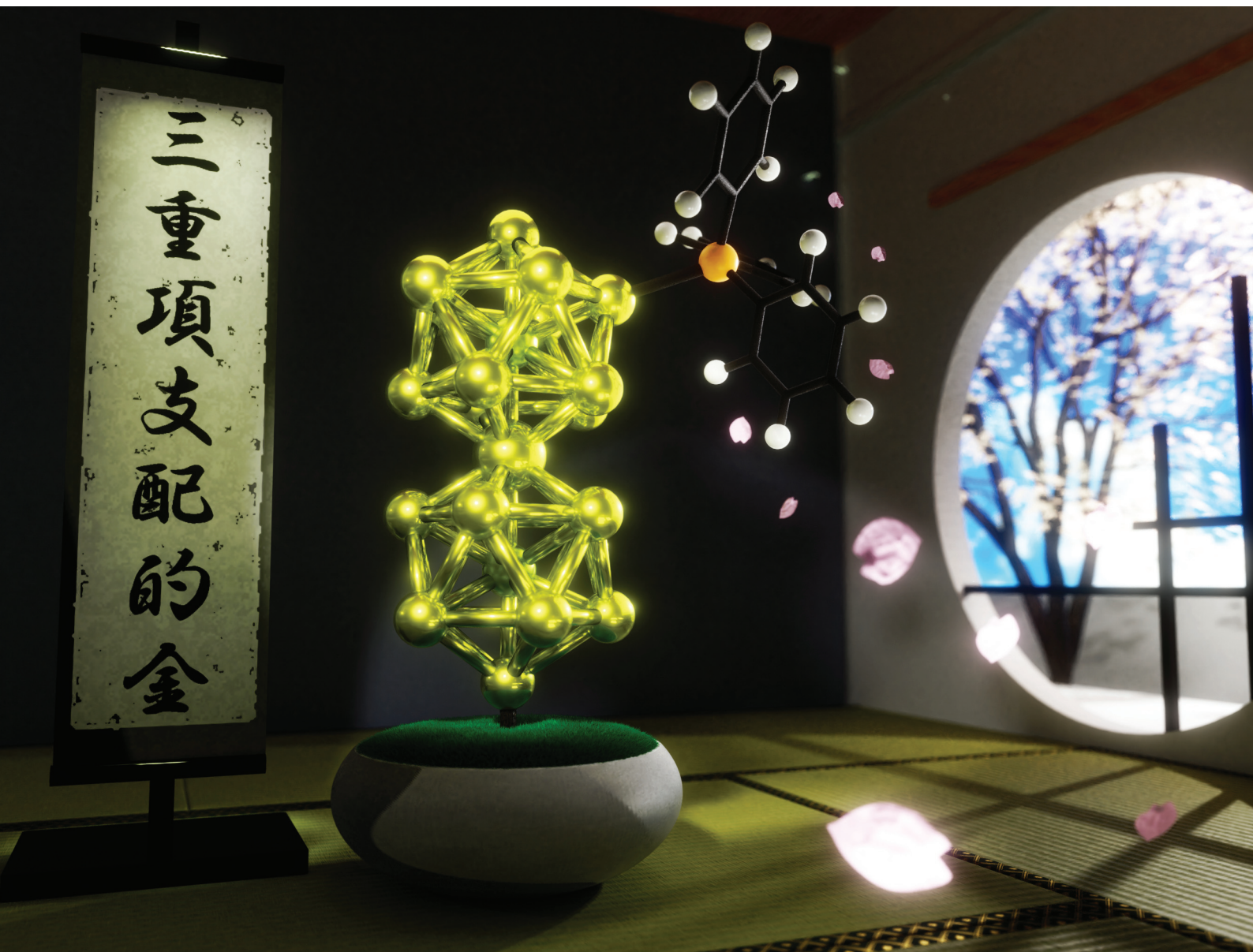


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## Evidence for triplet-state-dominated luminescence in biicosahedral superatomic molecular Au<sub>25</sub> clusters†

Masaaki Mitsui, \* Yuki Wada, Ryoto Kishii, Daichi Arima and Yoshiki Niihori

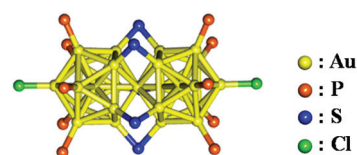
In photoluminescence (PL) quenching and triplet fusion upconversion experiments with fluorescent organic-molecule quenchers, it was revealed that a rod-shaped, phosphine- and thiolate-protected biicosahedral Au<sub>25</sub> cluster (a representative di-superatomic molecule) exhibits only phosphorescence, not fluorescence, at room temperature with an intersystem crossing quantum yield of almost 100%. By virtue of these photophysical properties, this cluster can be used as a triplet sensitizer that undergoes direct singlet–triplet transitions in the near-infrared (NIR) region (730–900 nm), inducing photon upconversion from NIR to visible light.

Metal clusters of specific compositions and sizes often exhibit a peculiarly high stability and chemical robustness. As is well-known, these properties originate from geometrical and electronic factors.<sup>1</sup> The electronic factor is qualitatively explained by using the Jellium model,<sup>2</sup> which assumes that the valence electrons in a metal cluster are confined to a uniformly positive potential formed by constituent metal cations. This model predicts the existence of superatomic orbitals (1S, 1P, 1D, 2S...), discrete orbitals with similarities to atomic orbitals. Like noble gas atoms, clusters with closed-shell electron configurations of superatomic orbitals (the total number of valence electrons: 2, 8, 18...) are electronically stable. Therefore, metal clusters can be regarded as “superatoms” with electronic structures similar to those of normal atoms. The emerging creation of functional materials from superatom building blocks has recently gathered much attention.<sup>3–7</sup>

The most representative di-superatomic molecule is the rod-shaped, phosphine- and thiolate-protected gold cluster [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> (henceforth abbreviated as Au<sub>25</sub>-rod; PPh<sub>3</sub> = triphenylphosphine) formed by two icosahedral Au<sub>13</sub><sup>5+</sup>(8e<sup>−</sup>) superatoms sharing a single vertex Au atom. As shown in Scheme 1, the Au<sub>25</sub>-rod possesses an Au<sub>25</sub><sup>9+</sup>(16e<sup>−</sup>)

core. The crystal structure of this biicosahedral gold cluster was first reported by Tsukuda and co-workers.<sup>8</sup> Since then, the structural,<sup>8–11</sup> electronic,<sup>8–12</sup> catalytic,<sup>13–15</sup> photophysical,<sup>16–19</sup> and photoluminescence (PL)<sup>18,20–22</sup> properties of the Au<sub>25</sub>-rod have been widely reported. The PL of the Au<sub>25</sub>-rod has been dramatically enhanced by alloying with doping of Ag atoms.<sup>23</sup> Previous reports have suggested that the PL emission from the Au<sub>25</sub>-rod is fluorescence.<sup>18,23</sup> However, this suggestion has not been backed by clear experimental evidence and requires further investigation. In addition, the PL quantum yield ( $\Phi_{\text{PL}}$ ) of the Au<sub>25</sub>-rod was thought to be as small as 0.1%,<sup>23</sup> but the study reporting this conclusion was limited to the short-wavelength region (700–800 nm) of near-infrared (NIR) PL (700–1200 nm). More recently, the  $\Phi_{\text{PL}}$  value was determined as ~8% over almost the entire NIR emission signal.<sup>22</sup> Motivated by these facts, we investigated the PL properties of the Au<sub>25</sub>-rod cluster in more detail. In PL quenching and triplet fusion upconversion (TF-UC) experiments, we confirmed that the observed room-temperature PL of the Au<sub>25</sub>-rod clusters actually originates from phosphorescence from the excited triplet state. The excited cluster exhibits no discernible fluorescence emission at room temperature and is exclusively deactivated by an intersystem crossing (ISC) process.

Fig. 1a shows the electrospray ionization mass spectrum of [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(PET)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup> (PET = 2-phenylethanethiolate; counterion: SbF<sub>6</sub><sup>−</sup>) synthesized in this study. The synthesis method was based on a previously reported method for the preparation of ultra-pure Au<sub>25</sub>-rod samples (see the ESI† for details).<sup>12</sup> The strong signal at *m/z* = 4151.5 well matched the expected mass

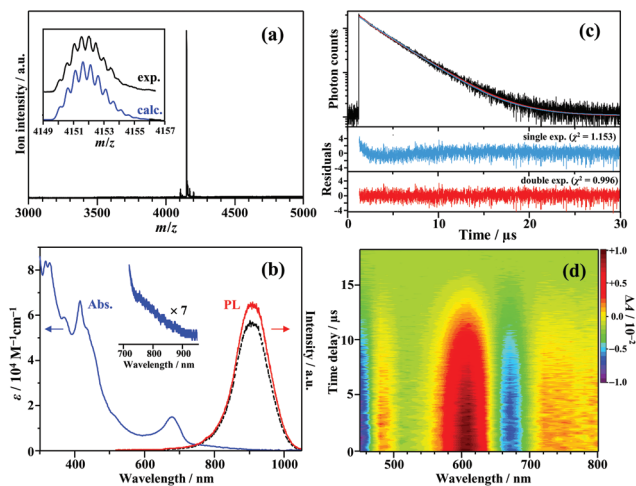


**Scheme 1** Crystal structure of [Au<sub>25</sub>(PPh<sub>3</sub>)<sub>10</sub>(SR)<sub>5</sub>Cl<sub>2</sub>]<sup>2+</sup>.<sup>8</sup>

Department of Chemistry, College of Science, Rikkyo University, 3-34-1,

Nishiikebukuro, Toshima-ku, Tokyo 171-8501, Japan. E-mail: mitsui@rikkyo.ac.jp

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**Fig. 1** (a) Positive-ion electrospray ionization mass spectrum of  $[\text{Au}_{25}(\text{PPh}_3)_{10}(\text{PET})_5\text{Cl}_2]^{2+}$  ( $\text{Au}_{25}$ -rod). (b) UV-vis absorption and PL spectra ( $\lambda_{\text{ex}} = 640$  nm) of the  $\text{Au}_{25}$ -rod ( $13 \mu\text{M}$ ) measured under deaerated conditions (the solid line) and aerated conditions (the dashed line). A magnified view of the absorption tail is also shown. (c) PL decay curve of the  $\text{Au}_{25}$ -rod ( $13 \mu\text{M}$ ) in deaerated THF ( $\lambda_{\text{ex}} = 634$  nm), obtained by monitoring the  $\lambda \geq 750$  nm region, along with the single (red) and double (blue) exponential fitting curves. Bottom panels show the corresponding residuals and  $\chi^2$  values. (d) Color plot of the transient absorption spectra of the  $\text{Au}_{25}$ -rod ( $50 \mu\text{M}$ ) in deaerated THF (pumped at 640 nm).

number when the charge number ( $z$ ) was  $+2$  ( $m/z$  4151.6). The result confirms that the  $\text{Au}_{25}$ -rods were the dominantly formed product. The absorption and PL spectra of this sample are shown in Fig. 1b. The absorption spectrum with a weak absorption tail from 730 to 900 nm excellently agrees with the literature.<sup>12,22</sup> However, the peak around 900 nm in the PL spectrum is an artefact caused by a sharp drop in the sensitivity of the detector in this wavelength range (Fig. S1†), and the PL actually peaks at  $\sim 990$  nm.<sup>22</sup> This NIR PL is observed in the wavelength region much longer than the lowest absorption band around 670 nm and is moderately weakened under aerated conditions, regardless of the excitation wavelength (Fig. 1b and Fig. S2†). The PL decay curve (depicted in Fig. 1c) was fitted to single and double exponential functions. The double exponential fit better reproduced the observed profile than the single exponential fit (see the residuals and  $\chi^2$  values in the lower part of Fig. 1c). Two lifetime components were identified,  $\tau_1 = 0.80 \mu\text{s}$  (3%) and  $\tau_{\text{II}} = 3.36 \mu\text{s}$  (97%), with the average lifetime of  $3.29 \mu\text{s}$ . Under aerated conditions, the PL lifetime and PL intensity were reduced by 10–20% compared to those under deaerated conditions (Fig. 1b, Fig. S2 and Table S1†), suggesting the involvement of oxygen in the PL quenching and the observed PL is assumed to stem from phosphorescence. The trace component ( $\tau_1$ ) was observed in the same wavelength range as the major component, and the PL lifetime was shortened and the fractional population slightly increased by the addition of a large excess of  $\text{SbF}_6^-$  (Table S2†), suggesting that the ion pairs of the  $\text{Au}_{25}$ -rod and  $\text{SbF}_6^-$  might be formed at a very low ratio by association–dis-

sociation equilibrium in solution.<sup>24,25</sup> The lifetime of the dominant component excellently agrees with the reported average lifetime of the  $\text{Au}_{25}$ -rod ( $\sim 3.2 \mu\text{s}$ ).<sup>22</sup> Therefore, only the main component ( $\tau_{\text{II}}$ ) will be discussed below. Fig. 1d shows the sub-nanosecond transient absorption (TA) spectra of the  $\text{Au}_{25}$ -rod in deaerated THF. As reported in the literature, the overall feature of the TA spectrum (*i.e.*, excited-state absorption bands at around 480, 610, and  $>700$  nm and ground-state bleaching at 650–700 nm) was unchanged at all time delays.<sup>16</sup> These excited-state absorption bands are attributed to the T-T absorption of the  $\text{Au}_{25}$ -rod, as described later.

To experimentally confirm that the PL of the  $\text{Au}_{25}$ -rod is phosphorescence, PL quenching experiments were implemented on the  $\text{Au}_{25}$ -rod exposed to two highly fluorescent organic molecules, 9,10-bis(phenylethynyl)anthracene (BPEA) and rubrene, as the quenchers. When the  $\text{Au}_{25}$ -rod is combined with the BPEA or rubrene quencher, the expected main quenching pathway is triplet energy transfer (TET) (Fig. 2a and S3†). Indeed, both quenchers decreased the PL intensity and lifetime (Fig. 2b and c), but did not change the spectral shape of the  $\text{Au}_{25}$ -rod PL. Furthermore, there was no change in the absorption spectrum of the  $\text{Au}_{25}$ -rod up to the quencher concentration of 10 mM and no isosbestic point (Fig. S4†), thus ruling out the formation of association complexes between the  $\text{Au}_{25}$ -rod and BPEA (or rubrene). In the BPEA case, the Stern–Volmer plot of  $\tau_{\text{II}}$  was a linear function of BPEA concentration up to 5 mM, but somewhat saturated at higher BPEA concentrations (Fig. 2d). As can be seen from the absorption spectrum in Fig. S4a,† BPEA aggregates begin to form when the BPEA concentration exceeds  $\sim 5$  mM. Thus, the decrease in the effective quencher concentration due to the aggregation is considered to be the main cause of the downward deviation in Fig. 2d. In the presence of rubrene, the quenching effect was much more pronounced (Fig. 2c) and the linearity of the plot was maintained up to 10 mM (Fig. 2e). This result can be explained by the increased TET driving force due to the approximately 0.4 eV lower  $T_1$  energy of rubrene [ $E_T = 1.14$  eV] than that of BPEA [ $E_T = 1.53$  eV] (Fig. 2a)<sup>26</sup> and the lack of rubrene aggregation in THF (Fig. S4b†). The linear dependence in the Stern–Volmer plot is a typical signature of dynamic quenching,<sup>27</sup> indicating that this quenching is solely based on collisions *via* diffusion. The Stern–Volmer constants ( $K_{\text{sv}}$ ) obtained from the linear fits were  $15.5 \text{ M}^{-1}$  for BPEA and  $320.1 \text{ M}^{-1}$  for rubrene. From the relation  $K_{\text{sv}} = k_{\text{TET}} \cdot \tau_{\text{II}}$ , the TET rate constants ( $k_{\text{TET}}$ ) in the presence of BPEA and rubrene were calculated as  $4.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $9.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. When anthracene [ $E_T = 1.84$  eV]<sup>28</sup> was used as the quencher, no quenching was observed at an anthracene concentration of 10 mM (Fig. S5 and Table S3†). Thus, we inferred that the  $T_1$  state of the  $\text{Au}_{25}$ -rod is located around 1.6–1.7 eV. The magnitude of  $k_{\text{TET}}$  is obviously correlated with the energy gap between the  $T_1$  states of the  $\text{Au}_{25}$ -rod and the quenchers (roughly +0.5 eV for rubrene, +0.1 eV for BPEA, and  $-0.2$  eV for anthracene), indicating that the observed quenching is indeed caused by the TET process. Interestingly, even though the  $\text{Au}_{25}$  biicosahedral core is almost completely shielded by phosphine



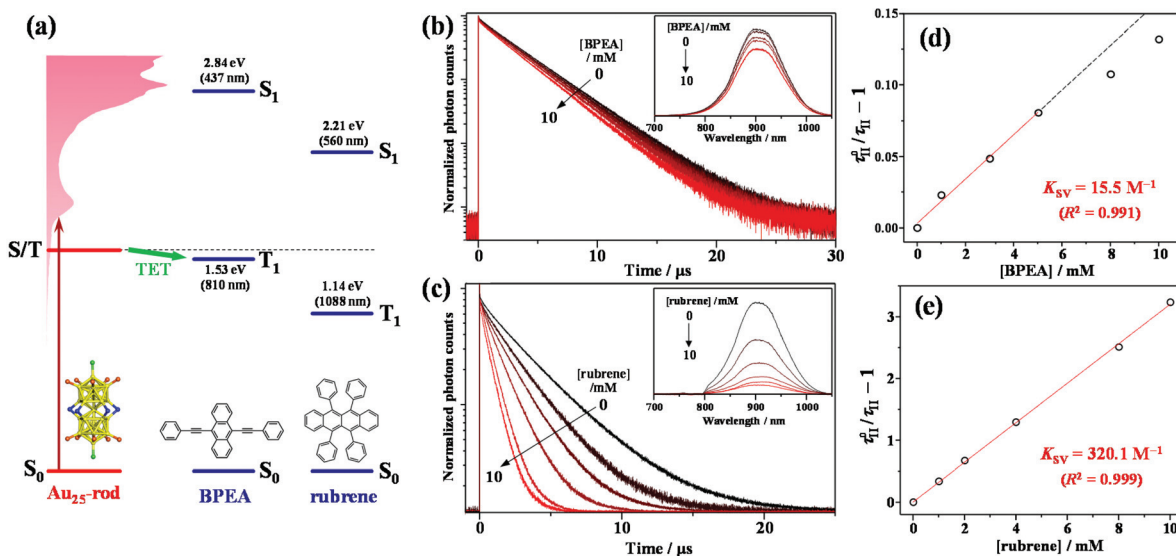


Fig. 2 (a) Energy-level diagram of the Au<sub>25</sub>-rod sensitizer combined with a BPEA or rubrene emitter. (b and c) Emitter-concentration-dependent PL decay curves of the Au<sub>25</sub>-rod (7 μm) in deaerated THF solution (excitation wavelength λ<sub>ex</sub> = 634 nm). Insets in panels (b) and (c) show the corresponding PL spectra obtained under excitation with 640 and 785 nm CW lasers, respectively. (d and e) Stern-Volmer plots of the main component lifetime (τ<sub>1</sub>). K<sub>SV</sub> and R<sup>2</sup> represent the Stern-Volmer constant and coefficient of determination, respectively.

and thiolate ligands in the Au<sub>25</sub>-rod (Fig. S6<sup>†</sup>),  $k_{\text{TET}}$  of the Au<sub>25</sub>-rod for the rubrene acceptor is comparable to that of the PtAg<sub>24</sub> clusters ( $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ), where the triplet excitation energy is transferred to the surface staple.<sup>29</sup> Notably, the Cl atoms bound to both ends of the long axis of the biicosahedral core are not completely shielded by the PPh<sub>3</sub> ligands. Moreover, in both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), the p orbital of the Cl atom extends outward along the long axis direction of the Au<sub>25</sub> core.<sup>30</sup> Therefore, these are presumed to be the effective sites for short-range Dexter-type TET to occur.

We attempted to measure the triplet-triplet (T-T) absorption of <sup>3</sup>BPEA\* and <sup>3</sup>rubrene\* sensitized by the TET from the Au<sub>25</sub>-rod. However, the T-T absorption band overlapped with its own extremely strong S<sub>0</sub>-S<sub>1</sub> absorption and could not be observed. If triplet sensitization is indeed caused by the Au<sub>25</sub>-rod, we should observe upconverted fluorescence *via* triplet-triplet annihilation (TTA) between the <sup>3</sup>BPEA\* (or <sup>3</sup>rubrene\*) molecules (*i.e.*, delayed fluorescence). As shown in Fig. 3, when a deaerated mixture of the Au<sub>25</sub>-rod and BPEA or rubrene was excited at 640 or 785 nm, respectively, upconverted fluorescence was clearly observed at wavelengths shorter than the excitation wavelength. Both fluorescences exhibited very long decays (in the order of 100 μs; see Fig. 3, insets). The time evolution of the UC intensity  $I_{\text{UC}}(t)$ , derived from the rate equation of the time dependence of the concentration of triplet emitter (<sup>3</sup>E\*) molecules considering the TTA process between <sup>3</sup>E\*, is given by

$$I(t) = I(0) \left( \frac{1 - \beta}{\exp(t/\tau_T) - \beta} \right)^2, \quad (1)$$

where τ<sub>T</sub> is the lifetime of the <sup>3</sup>E\* molecules and β is a dimensionless parameter between 0 and 1.<sup>31</sup> Eqn (1) accurately repro-

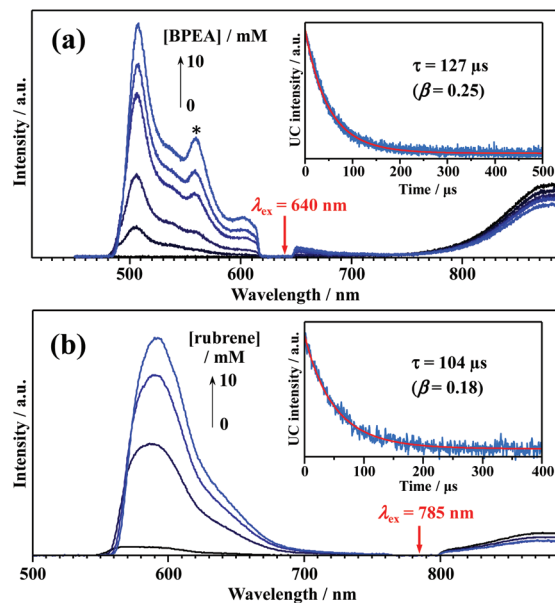


Fig. 3 PL emission spectra of (a) Au<sub>25</sub>-rod (13 μm)/BPEA (0–10 mM) excited at 640 nm (10 W cm<sup>-2</sup>) and (b) Au<sub>25</sub>-rod (40 μm)/rubrene (0–10 mM) excited at 785 nm (5.5 W cm<sup>-2</sup>) in deaerated THF. The asterisked peak in panel (a) begins to appear when the BPEA concentration exceeds ~5 mM and is assigned to the emission from BPEA aggregates (Fig. S4a<sup>†</sup>). Insets in panels (a) and (b) show the decay curves obtained by monitoring only the upconverted emission from BPEA and rubrene, respectively.

duces the observed decay profiles with τ<sub>T</sub> = 127 μs and β = 0.25 for BPEA and τ<sub>T</sub> = 104 μs and β = 0.18 for rubrene. These values are approximately four orders of magnitude longer than the fluorescence lifetimes of BPEA (3.3 ns in THF) and rubrene

(10.8 ns in THF) shown in Fig. S7.† These facts confirm that the observed upconverted fluorescence is delayed fluorescence *via* the TTA between the BPEA (or rubrene) triplets sensitized by the Au<sub>25</sub>-rod.

Recently, we proposed a relative method that estimates the  $\Phi_{\text{ISC}}$  value of sensitizers by a TF-UC analysis.<sup>29,32</sup> The formation yield of the UC state ( $\Phi_{\text{UCs}}$ ), *i.e.*, the number of excited singlet states of the emitter ( $^1\text{E}^*$ ) generated per number of photons absorbed by the sensitizer, can be experimentally evaluated as (see also Fig. S8†):<sup>33</sup>

$$\Phi_{\text{UCs}} = \frac{\Phi_{\text{UC}}}{\Phi_{\text{out}}(1 - \Phi_{\text{q}})\Phi_{\text{f}}}, \quad (2)$$

where  $\Phi_{\text{UC}}$  is the uncorrected UC yield determined by the common relative method using an organic dye with a known fluorescence quantum yield (eqn (S1)).  $\Phi_{\text{out}}$  represents the output coupling yield and corresponds to the correction for the loss of upconverted photons due to reabsorption by the sensitizer and emitter molecules.  $\Phi_{\text{q}}$  is the quenching yield of  $^3\text{E}^*$  by the sensitizer, and  $\Phi_{\text{f}}$  is the fluorescence quantum yield of the emitter under UC measurement conditions (*i.e.*, at a very high emitter concentration). The  $\Phi_{\text{UCs}}$  value is unique to the system and is determined by<sup>33</sup>

$$\Phi_{\text{UCs}} = \Phi_{\text{ISC}}\Phi_{\text{TET}}\Phi_{\text{TTA}}, \quad (3)$$

where  $\Phi_{\text{TET}}$  and  $\Phi_{\text{TTA}}$  represent the TET and TTA quantum yields, respectively. By definition,  $\Phi_{\text{TTA}}$  is the product of the spin statistic factor  $\eta_{\text{c}}$  and the fraction of  $^3\text{E}^*$  undergoing second-order decay  $f_2$ : explicitly,  $\Phi_{\text{TTA}} = f_2\eta_{\text{c}}/2$  (maximum value 0.5) where  $f_2$  is given by<sup>34</sup>

$$f_2 = 1 - \frac{\beta - 1}{\beta} \ln(1 - \beta). \quad (4)$$

The value of  $f_2$  can be calculated from the  $\beta$  value of the UC decay fit using eqn (1). Finally, eqn (3) can be rewritten as

$$\Phi_{\text{UCs}} = \Phi_{\text{ISC}}\Phi_{\text{TET}}f_2\eta_{\text{c}}/2. \quad (5)$$

If the  $\Phi_{\text{UCs}}$  value of the Au<sub>25</sub>-rod/BPEA system is evaluated under the same experimental conditions (the same emitter concentration, solvent, and excitation source) as when evaluating  $\Phi_{\text{UCs}}^{\text{r}}$  of the PdTPBP ( $\Phi_{\text{ISC}} = 0.97$ )<sup>35</sup>/BPEA reference system, the ratio  $\Phi_{\text{UCs}}/\Phi_{\text{UCs}}^{\text{r}}$  based on eqn (2) can be combined with eqn (5) to give the  $\Phi_{\text{ISC}}$  value of the Au<sub>25</sub>-rod. The formulation is as follows:

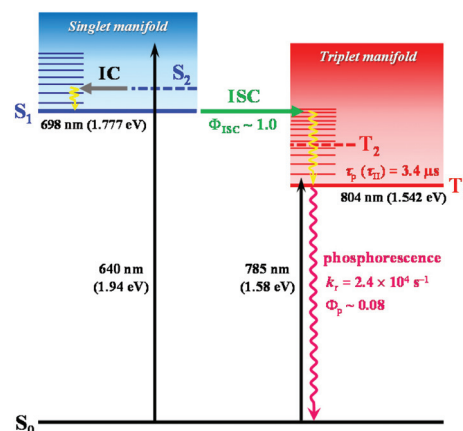
$$\Phi_{\text{ISC}} = \Phi_{\text{ISC}}^{\text{r}} \cdot \frac{\Phi_{\text{TET}}^{\text{r}}f_2^{\text{r}}}{\Phi_{\text{TET}}f_2} \cdot \frac{\Phi_{\text{UC}}/\Phi_{\text{out}}(1 - \Phi_{\text{q}})}{\Phi_{\text{UC}}^{\text{r}}/\Phi_{\text{out}}^{\text{r}}(1 - \Phi_{\text{q}}^{\text{r}})}. \quad (6)$$

In eqn (6), the superscript “r” refers to the reference system. Under the above-described experimental conditions,  $\eta_{\text{c}}$  can be regarded as identical in both systems and thereby cancels out. However, if the  $\beta$  values largely differ between the experimental and reference systems, the ratio  $f_2$  must be retained in eqn (6). From the data and parameters shown in Fig. S9 and S10 and Tables S4–S6,† the  $\Phi_{\text{ISC}}$  value of the Au<sub>25</sub>-rod was determined as  $0.99 \pm 0.05$ . Thus, the phosphorescence quantum yield ( $\Phi_{\text{p}}$ )

was calculated as  $\sim 0.08$  from the relation  $\Phi_{\text{PL}} = \Phi_{\text{ISC}}\Phi_{\text{p}}$  ( $\sim 0.08$ )<sup>22</sup> and the radiative rate constant ( $k_{\text{r}}$ ) was calculated as  $2.4 \times 10^4 \text{ s}^{-1}$  from the relation  $\Phi_{\text{p}}\tau_{\text{p}}^{-1} = (\Phi_{\text{p}}\tau_{\text{p}})^{-1}$ , where  $\tau_{\text{p}}$  represents the phosphorescence lifetime).

In a previous femtosecond TA spectroscopy study of the Au<sub>25</sub>-rod,<sup>16</sup> excitation at 415 nm elicited sub-picosecond internal conversion ( $\sim 0.8$  ps) early time dynamics, but excitation at 775 nm yielded a constant feature of the TA spectra over a wide range of timescales (sub-ps to  $\mu\text{s}$ ). In the present study, we showed that under excitation at 785 nm, the observed PL emission from the Au<sub>25</sub>-rod is also phosphorescence (Fig. S2†); moreover, this coexistence with rubrene can induce the TF-UC phenomenon (Fig. 3b and Table S7†). Based on these experimental facts, we attributed the unchanged excited-state absorption signal to the  $\text{T}_1$ – $\text{T}_n$  absorptions of the Au<sub>25</sub>-rod, and the weak absorption shoulder at 730–900 nm mainly to the direct spin-forbidden transitions from  $\text{S}_0$  to  $\text{T}_1$  of the Au<sub>25</sub>-rod, as shown in Fig. 4. The  $\text{T}_1$ – $\text{T}_n$  absorption has been observed within a few picoseconds,<sup>16</sup> suggesting the occurrence of ultrafast ISC ( $\sim 10^{12} \text{ s}^{-1}$ ). This inference is consistent with the almost 100% ISC efficiency and absence of fluorescence at room temperature. In time-dependent density functional theory calculations, the transitions between  $\text{S}_0$  and  $\text{S}_1$  were suggested to be symmetrically forbidden and their oscillator strength was zero (Fig. S11†).<sup>22</sup> In other words, the Au<sub>25</sub>-rod cluster has the “dark”  $\text{S}_1$  and “bright”  $\text{T}_1$  states at room temperature.

In the biicosahedral Au<sub>25</sub> core, the significant spin–orbit coupling effect provided by 25 Au atoms and the small S–T energy gap ( $< 0.2$  eV) is presumed to inevitably result in strong S–T mixing. Therefore, it may be more appropriate to view the excited states of such gold clusters as coherent superpositions of singlet and triplet states,<sup>36</sup> as in semiconductor nanocrystals with ill-defined spin quantum numbers.<sup>37</sup> If this is true, a clear distinction between fluorescence and phosphorescence



**Fig. 4** Excited state deactivation pathway and related photophysical parameters for the Au<sub>25</sub>-rod in deaerated THF. The vertical transition energy from  $\text{S}_0$  to  $\text{S}_1$  or  $\text{T}_1$  obtained from theoretical calculations is also shown. The  $\text{S}_2$  and  $\text{T}_2$  states theoretically predicted to exist in the energetic vicinity of the  $\text{S}_1$  and  $\text{T}_1$  states (Fig. S11†) are shown as dashed lines.

would no longer be possible. Therefore, theoretical considerations based on total angular momenta (*i.e.*, the sum of orbital and spin angular momenta) may be necessary to better understand the electronic excited states and PL properties of noble metal clusters.

In conclusion, the observations and analysis of PL quenching and TF-UC of the biicosahedral Au<sub>25</sub>-rod clusters confirmed that the PL from the Au<sub>25</sub>-rod is phosphorescence from the excited triplet state formed with almost 100% ISC quantum yield. Moreover, this cluster behaves as a triplet sensitizer undergoing direct S–T transitions in the NIR region, which can induce NIR-to-visible photon upconversion. This gold superatomic molecule is capable of modifying its electronic states, photophysical properties, and hydrophobicity/hydrophilicity by altering thiolate ligands<sup>15,23</sup> or replacing the terminal Cl atoms with alkynyl ligands.<sup>38</sup> Hence, it is expected to be a nanomaterial with potential use as a triplet sensitizer in TF-UC applications.

## Author contributions

MM conceptualized and designed the study, performed the computational work and wrote the manuscript. YW, RK, DA and YN performed experimental work and data analyses. All the authors discussed the results and contributed to the writing of the manuscript.

## Conflicts of interest

There are no conflicts to declare.

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