

(Supporting Information)

## Bright Near-Infrared Emission from the Au<sub>39</sub>(SR)<sub>29</sub> Nanocluster

Zhongyu Liu,<sup>†a</sup> Lianshun Luo,<sup>†a</sup> Jie Kong,<sup>b</sup> Ellen Kahng,<sup>a</sup> Meng Zhou<sup>b</sup> and Rongchao Jin<sup>a\*</sup>

<sup>a</sup> Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213, USA

<sup>b</sup> Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

[†] These authors contributed equally to this work.

\* To whom correspondence should be addressed, email: rongchao@andrew.cmu.edu

### Chemicals

Tetrachloroauric(III) acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O, >99.99% metal basis, Aldrich), tetraoctylammonium bromide (TOAB, ≥98%, Aldrich), 2-phenylethanethiol (PET, 98%, Aldrich), borane-tert-butylamine complex ((CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>·BH<sub>3</sub>, 97.0%, Aldrich), benzimidazole (98%, Aldrich), 2-bromopropane (99%, Aldrich), dimethyl sulfide (>99%, Aldrich), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>, 99%, Aldrich), polystyrene (PS, Aldrich). Solvents: 2-methyltetrahydrofuran, deuterated chloroform, methanol, ethanol, ethyl ether, ethyl acetate, pentane, dichloromethane (DCM), chloroform, acetone, hexane, and acetonitrile (HPLC grade for all solvents). All chemicals were used without further purification. Deionized water was prepared with Barnstead NANOpure Diamond (18.2 MΩ·cm). Thin-layer chromatography (TLC) plates (iChromatography, silica gel, 250 μm).

### Synthesis of chloro(dimethylsulfide)gold(I) (AuCl(SMe<sub>2</sub>))

500 mg HAuCl<sub>4</sub>·3H<sub>2</sub>O (1.27 mmol) was dissolved in 20 mL ethanol, followed by the addition of 280 μL dimethyl sulfide (3.81 mmol). The reaction was allowed to continue for 2 hours. Following that, the white precipitate was collected by centrifugation and ethyl ether was used to wash the crude products for 5 times. The as-obtained product was finally dried to yield a white powder.

### Synthesis of 1,3-diisopropylbenzimidazolium bromide (<sup>i</sup>Pr<sub>2</sub>-bimy·HBr)

1.18 g benzimidazole (10 mmol) and 760 mg K<sub>2</sub>CO<sub>3</sub> (5.5 mmol) were mixed in acetonitrile (8 mL) and vigorously stirred for 1 hour. Then, 5.4 mL 2-bromopropane (7.5 mmol) was added to the suspension, and the reaction mixture was stirred under reflux conditions for 24 hours, followed by the addition of the second portion of 2-bromopropane (5.4 mL, 57.5 mmol). The reaction mixture was vigorously stirred under reflux for additional 48 hours. After removing the solvent under reduced pressure, DCM was added to the residue, and the upper supernatant after centrifugation was collected. The solvent of the supernatant was removed under reduced pressure to produce a spongy solid, which was washed by ethyl acetate to afford the desired product as a white powder.

### Synthesis of NHC-Au-Br complex (<sup>i</sup>Pr<sub>2</sub>-bimy·AuBr)

<sup>i</sup>Pr<sub>2</sub>-bimy·HBr (1337.4 mg, 4.725 mmol), AuCl(SMe<sub>2</sub>) (1393.4 mg, 4.725 mmol), and K<sub>2</sub>CO<sub>3</sub> (653.5 mg, 4.725 mmol) were added into acetone (20 mL) and vigorously stirred under reflux conditions for 2 hours. After that, the solvent in the suspension was removed under reduced pressure. DCM was added to the residue, and the upper supernatant after centrifugation was collected. The solvent of the supernatant was removed under reduced pressure to give the solid product, which was washed with pentane and finally dried to afford the desired product as a gray powder.

## **Synthesis of Au<sub>39</sub>(PET)<sub>29</sub>**

<sup>1</sup>Pr<sub>2</sub>-bimy·AuBr (120 mg, 0.25 mmol) and PET (67 μL, 0.5 mmol) were dissolved in a mixture of chloroform (15 mL) and ethanol (5 mL), and the mixture gradually turned cloudy white within 10 minutes under stirring due to the formation of Au<sup>I</sup>-PET. Following that, the suspension was reduced to NCs by the addition of (CH<sub>3</sub>)<sub>3</sub>CNH<sub>2</sub>·BH<sub>3</sub> (434 mg, 5 mmol), indicated by the formation of a brown solution. The reaction was continued for 6 hours, and then the solvent was removed under reduced pressure. The mixture of Au NCs was thoroughly washed with methanol, extracted with DCM, and concentrated for TLC separation. The mixture of Au NCs was pipetted onto the TLC plate, and the separation was conducted in a developing tank (developing solvent 1:1 (v/v) DCM:*n*-hexane) (**Figure S1**). The reddish-brown band corresponding to Au<sub>39</sub>(PET)<sub>29</sub> was cut off and dissolved in DCM. The TLC separation is repeated until no other band can be observed on the TLC plate.

## **Preparation of Au NCs/polystyrene composite thin film.**

A drop-cast method was used to prepare the solid thin film. First, a stock solution of Au<sub>39</sub>(PET)<sub>29</sub> was prepared by dissolving Au<sub>39</sub>(PET)<sub>29</sub> (1 mg) in DCM (1 mL). Meanwhile, a polystyrene stock solution was prepared by dissolving polystyrene (80 mg) in DCM (1 mL). Then, 20 μL of as-obtained Au NCs solution and 10 μL of polystyrene solution were mixed together to afford an ink-like solution. Finally, the solution was dropped onto a quartz plate, which was dried slowly at room temperature.

## **Steady-state UV-Vis-NIR measurements**

UV-Vis-NIR spectra of Au nanoclusters were collected with a UV-3600 Plus UV-VIS-NIR spectrophotometer (Shimadzu).

## **Steady-state photoluminescence and cryogenic measurements**

Steady state photoluminescence spectra were measured on a FLS-1000 spectrofluorometer (Edinburgh). Near infrared PL was measured using a wide range InGaAs detector cooled by liquid nitrogen (-80 °C). Cryogenic PL was done on a home-built low temperature system including the FLS-1000 spectrofluorometer, a vacuum pump, an Optistat CF2 cryostat (Oxford Instruments) and a temperature controller. Liquid nitrogen was used as the cryogen.

## **Time-resolved photoluminescence measurements**

Both time-correlated single-photon counting (TCSPC) and multi-channel scaling (MCS) single photon counting measurements were performed using an EPL-450 picosecond pulsed diode laser (Edinburgh Instruments). The excitation wavelength from EPL-450 centers at 450 nm with a variance smaller than 5 nm. The pulse duration is less than 100 ps. For both TCSPC and MCS measurements, the detection wavelength was set at 850 nm.

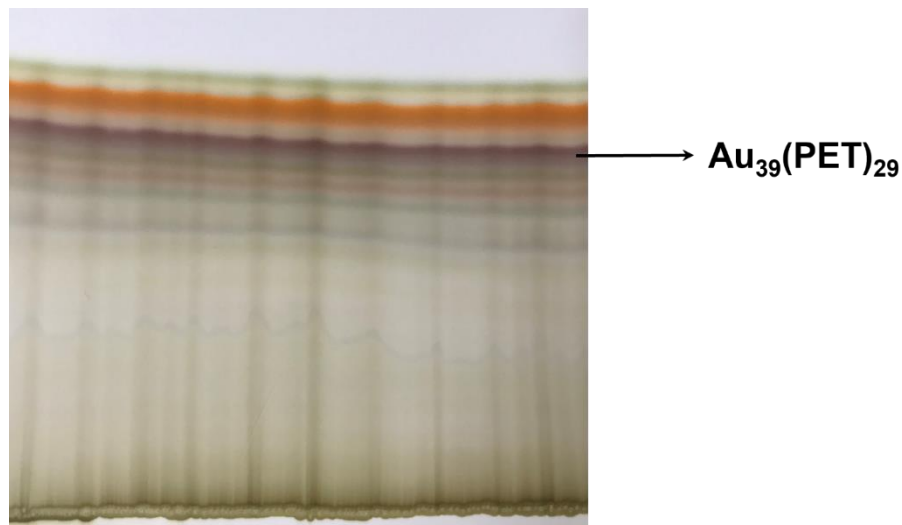
## **Quantum yield measurement by integrating sphere**

For the absolute QY measurements, the normal sample holder is removed and the integrating sphere is mounted in FLS1000. The blank spectrum (blue line in Figure S2) was obtained by putting a blank sample into the sphere and making the emission scan (repeat 5 times) from 530 nm to 1600 nm with a 550 nm excitation. The sample spectrum (yellow) was measured by replacing the blank sample with a dilute Au<sub>39</sub> solution (0.1 OD at 550 nm) and repeat the emission (repeat 5 times) scan from 530 nm to 1600 nm with a 550 nm excitation. The PLQY is calculated by eq. S1:

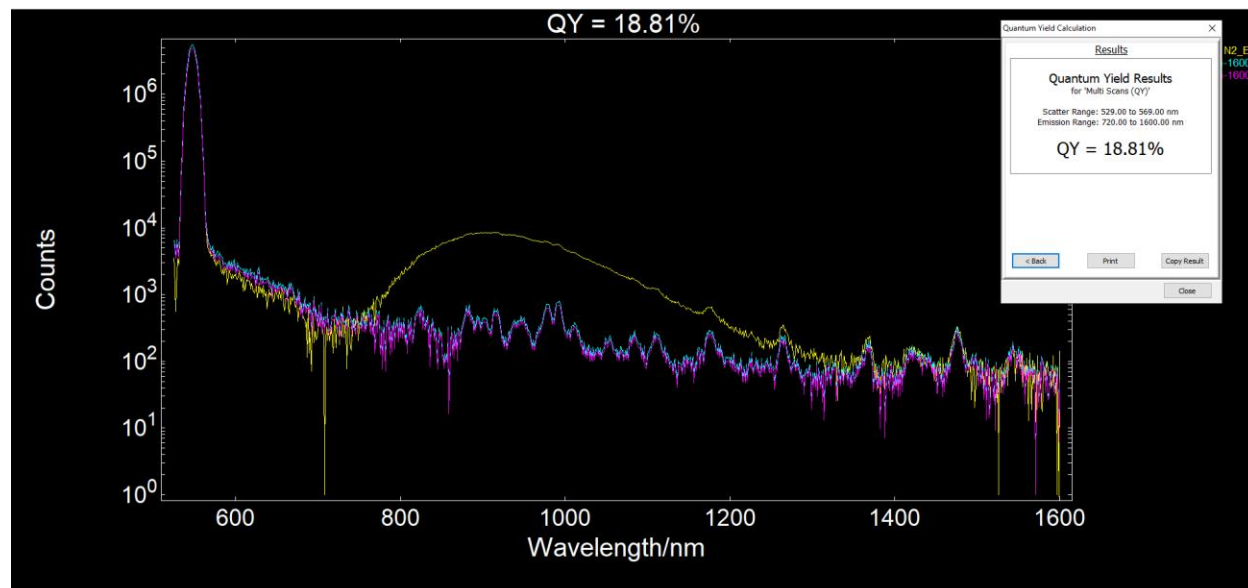
$$\eta = \frac{L_{sample}}{E_{blank} - E_{sample}}$$

Where,  $E_{blank}$  is the area under the blue line between 530 nm and 570 nm,  $E_{sample}$  is the area under the yellow line between 530 nm and 570 nm,  $L_{sample}$  is the area under the yellow line between 720 nm and 1600 nm.

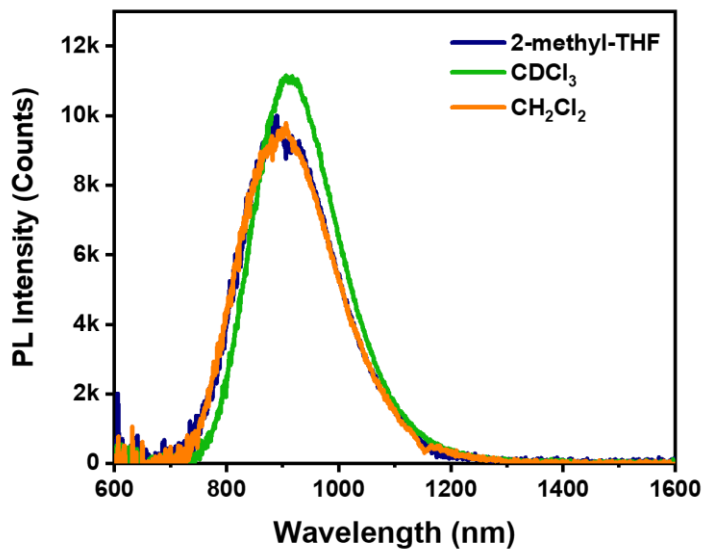
Supporting figures:



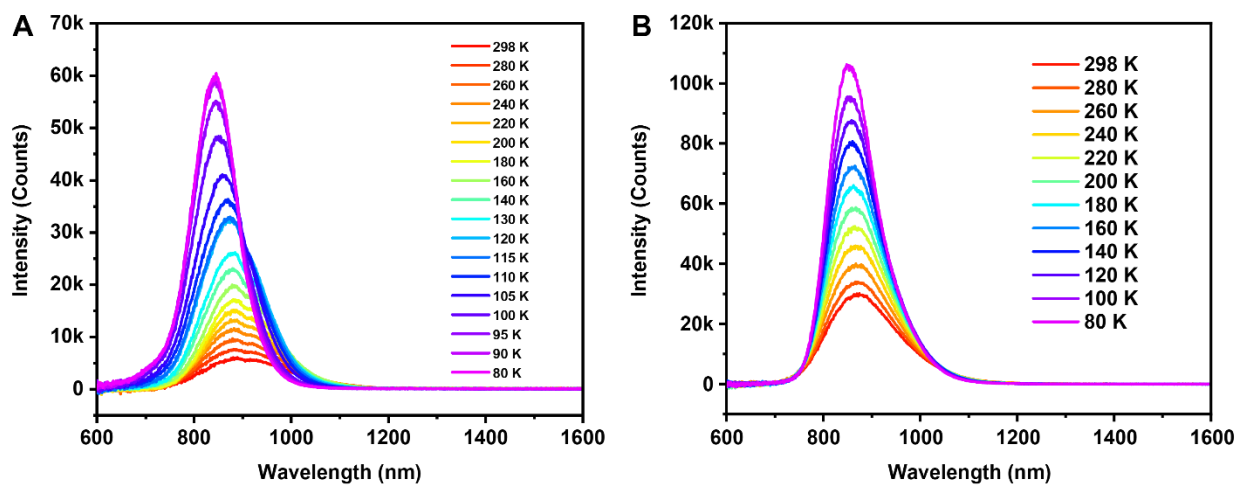
**Figure S1.** TLC separation of Au<sub>39</sub> from the product mixture. On a note, the top-most band is Au<sub>25</sub>(PET)<sub>18</sub><sup>-</sup> and the next (orange) major band is Au<sub>24</sub>(PET)<sub>20</sub>; our target is band #3 (Au<sub>39</sub>(PET)<sub>29</sub>), while other minor products are not pursued.



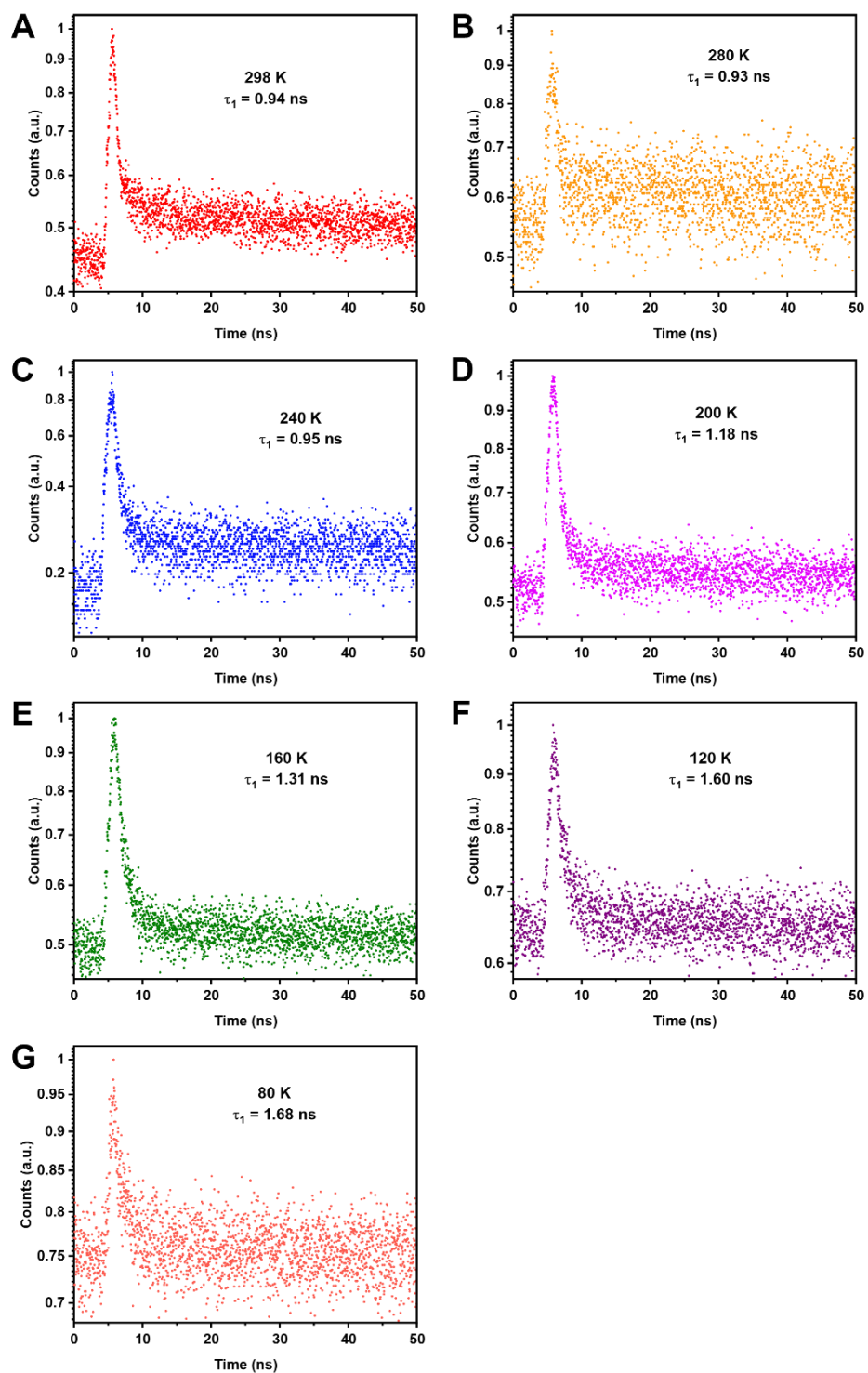
**Figure S2.** PLQY of Au<sub>39</sub> in deaerated CDCl<sub>3</sub> at room temperature measured by an integrating sphere.



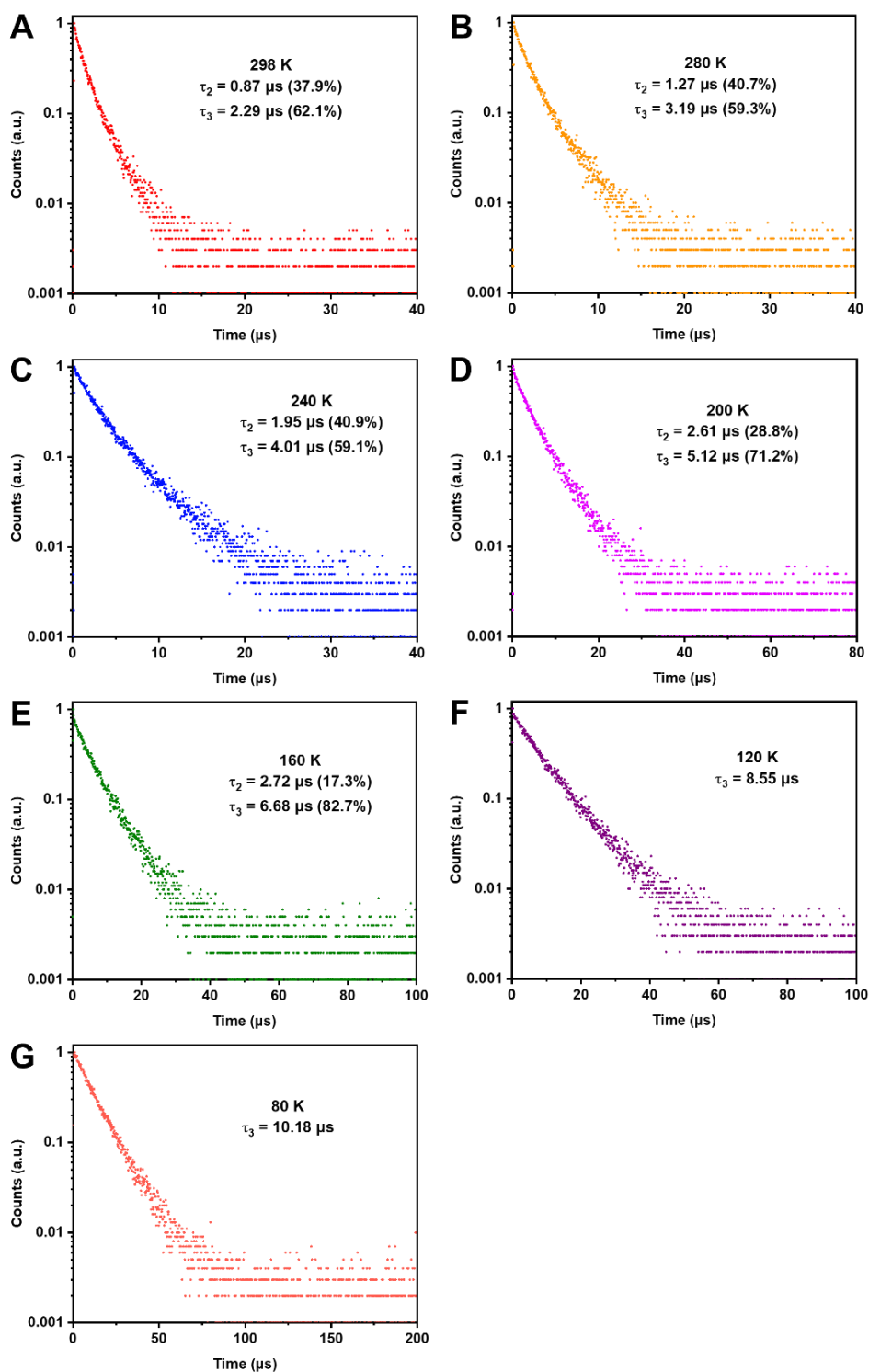
**Figure S3.** PL spectra of Au<sub>39</sub>(SR)<sub>29</sub> in different solvents. For PL measurements: excitation at 400 nm, slit width 5 nm, and emission slit 5 nm.



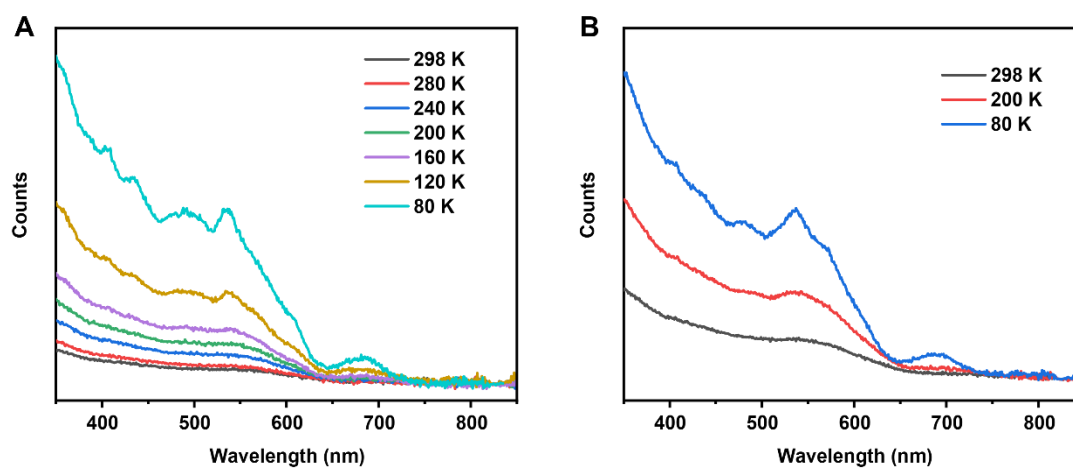
**Figure S4.** Temperature-dependent PL spectra of Au<sub>39</sub>(PET)<sub>29</sub> in (A) 2-methyl-THF and (B) PS thin film.



**Figure S5.** Nanosecond decay profile of  $\text{Au}_{39}(\text{PET})_{29}$  in 2-Me-THF at (A) 298 K, (B) 280 K, (C) 240 K, (D) 200 K, (E) 160 K, (F) 120 K, and (G) 80 K. Insets: the fitted lifetimes.

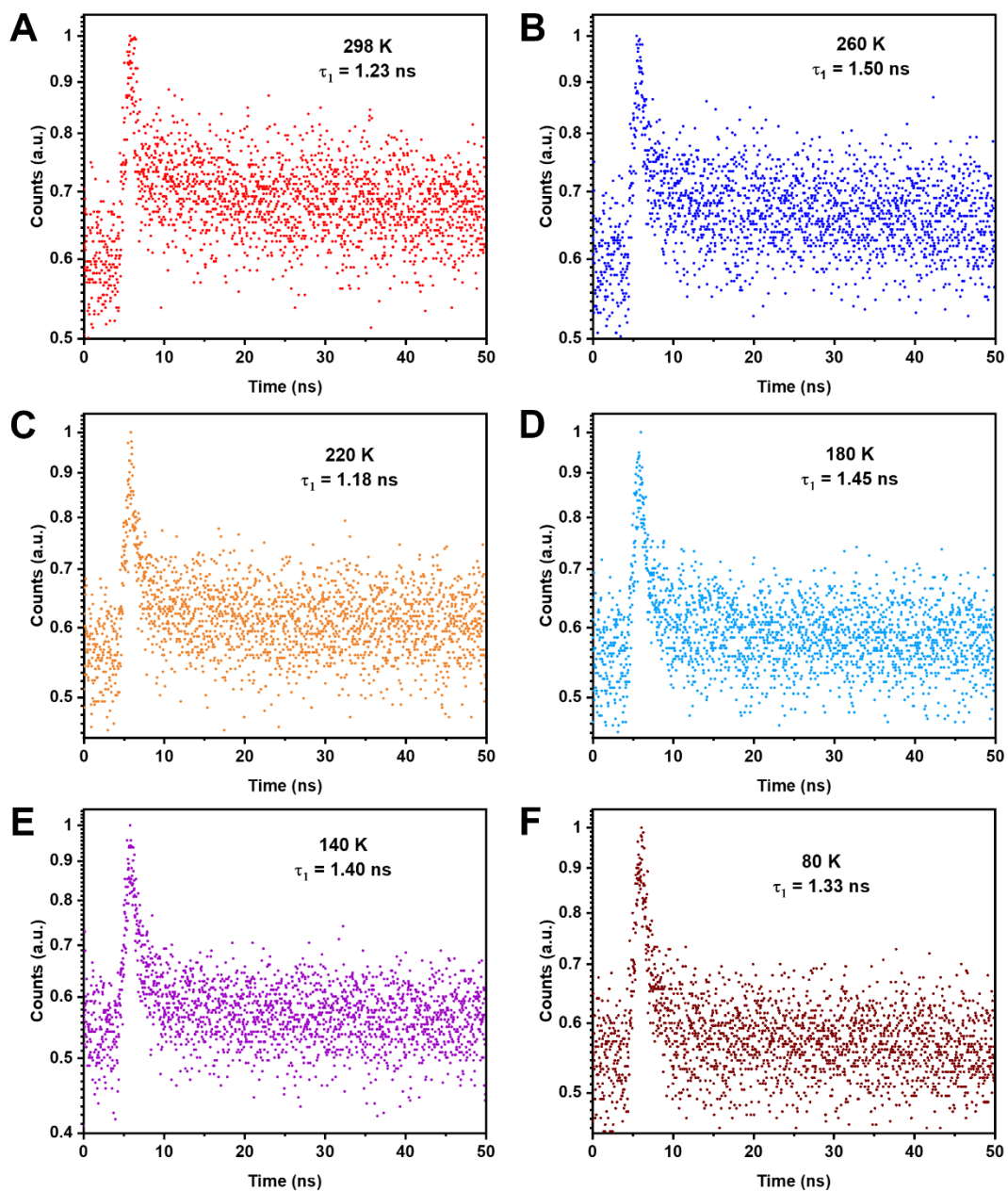


**Figure S6.** Microsecond decay profile of  $\text{Au}_{39}(\text{PET})_{29}$  in 2-Me-THF at (A) 298 K, (B) 280 K, (C) 240 K, (D) 200 K, (E) 160 K, (F) 120 K, and (G) 80 K. Insets: the fitted lifetimes and their intensity percentages (i.e., photon number ratios) in parentheses.

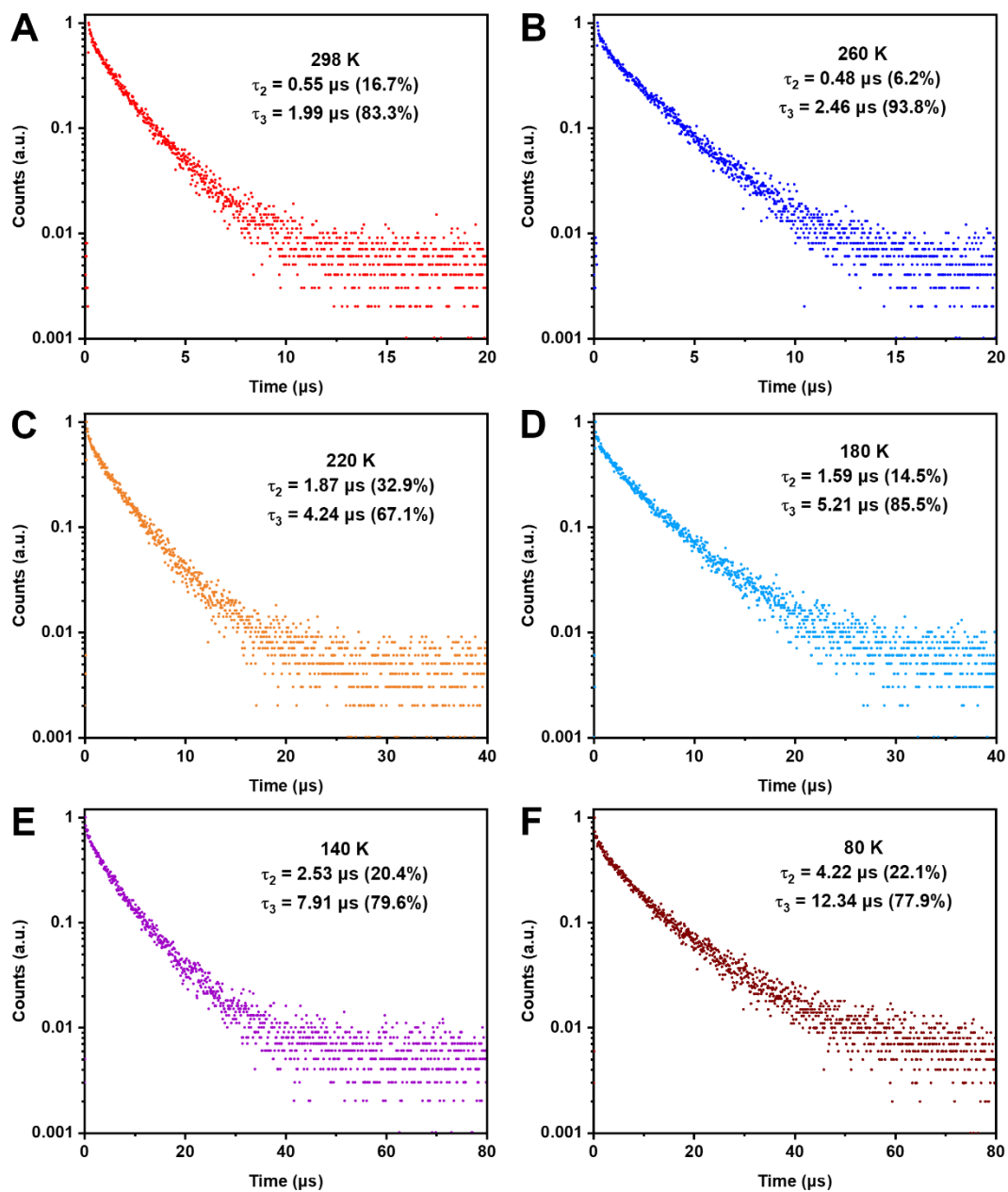


**Figure S7.** Temperature-dependent PL excitation spectra of Au<sub>39</sub>(PET)<sub>29</sub> in (A) 2-methyl-THF and (B) PS thin film.

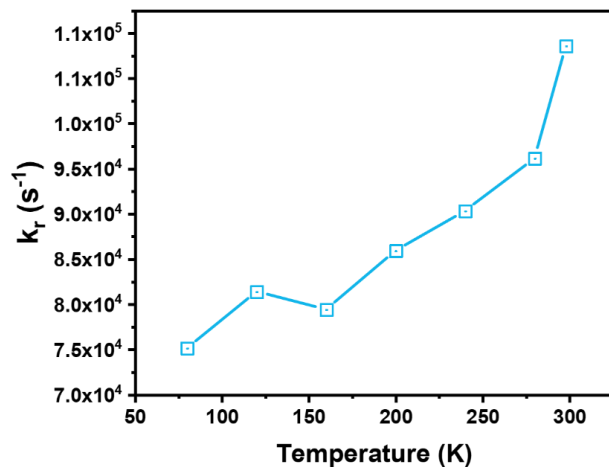




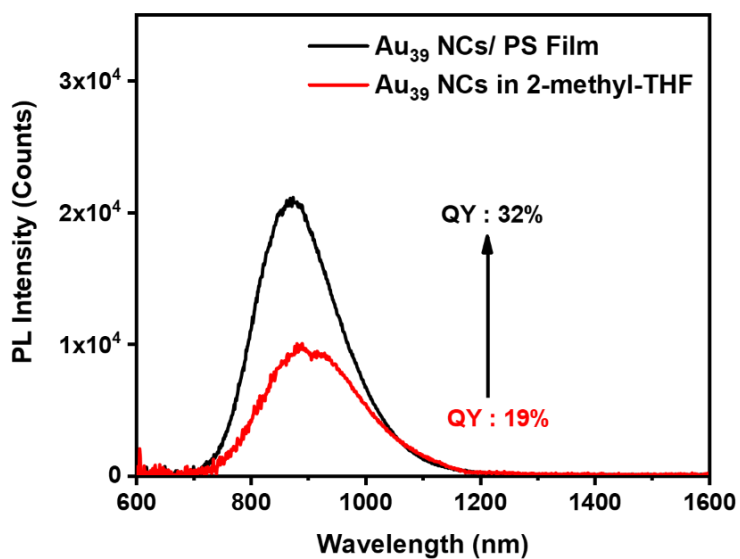
**Figure S8.** Nanosecond decay profile of  $\text{Au}_{39}(\text{PET})_{29}$  in PS thin film at (A) 298 K, (B) 260 K, (C) 220 K, (D) 180 K, (E) 140 K, and (F) 80 K. Insets: the fitted lifetimes.



**Figure S9.** Microsecond decay profile of  $\text{Au}_{39}(\text{PET})_{29}$  in PS thin film at (A) 298 K, (B) 260 K, (C) 220 K, (D) 180 K, (E) 140 K, and (F) 80 K. Insets: the fitted lifetimes and their intensity percentages.



**Figure S10.** Radiative rate of  $\text{Au}_{39}(\text{PET})_{29}$  at different temperatures. To calculate  $k_r$ , we used equations  $PLQY = \frac{k_r}{k_r + k_{nr}}$ ,  $\tau = \frac{1}{k_r + k_{nr}}$ , where  $k_{nr}$  the nonradiative rate constant and  $\tau$  is the PL lifetime.



**Figure S11.** PL spectra of  $\text{Au}_{39}(\text{PET})_{29}$  in 2-Me-THF and PS thin film. For PL measurements: excitation at 400 nm, slit width 5 nm, and emission slit 5 nm.