

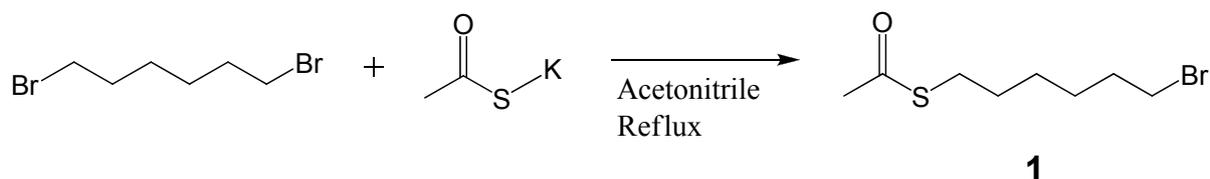
*Electronic Supplementary Information*

**Molten Matrix Sputtering Synthesis of Water-soluble Luminescent Au  
Nanoparticles with a Large Stokes Shift**

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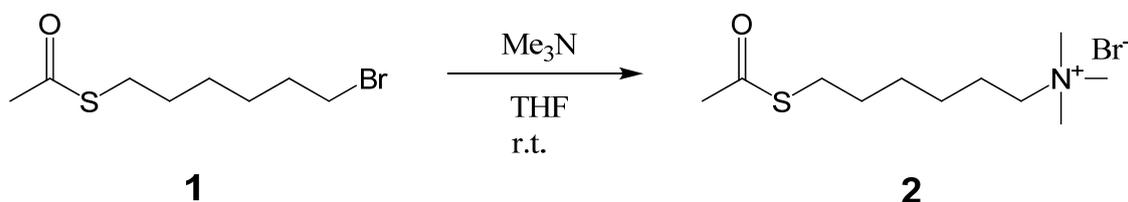
## Synthesis of 6-MTAB<sup>[1]</sup>

**1**



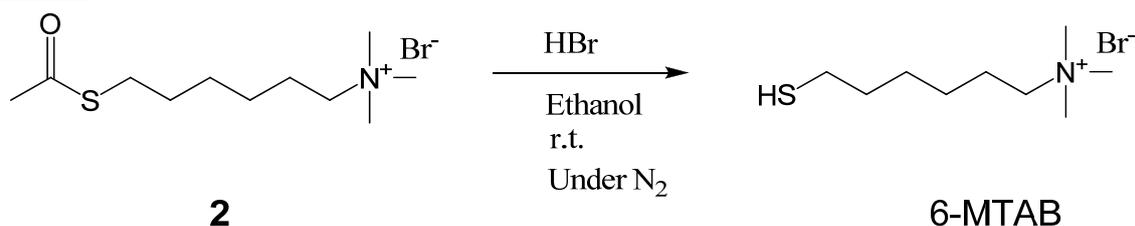
To an acetonitrile solution (150 mL) of 1,6-dibromohexane (60.0 g, 0.25 mol) and potassium thioacetate (5.7 g, 0.050 mol) were added and refluxed for 12 h. The solution was filtered at RT. and acetonitrile was removed under a reduced pressure. The obtained yellow oil was purified by silica gel column chromatography (eluent: C<sub>6</sub>H<sub>12</sub>/CHCl<sub>3</sub>), **1** was obtained in 60% yield.

**2**



A solution of **1** (3.0 g, 0.013 mol) and trimethylamine (7.7g, 0.13 mol) in dry THF (100 mL) was stirred in a sealed flask for 6 days. The colorless precipitate was filtered, washed with dry THF and dried under a reduced pressure. **2** was obtained in 84% yield.

## 6-MTAB



A solution of **2** (1.5 g, 5.03 mol) in 47% hydrobromic acid (17.2 g) and ethanol (30.3 g) was stirred for 2 days under argon. The solvent was removed under a reduced pressure. The resultant yellow oil was added in methanol and diethyl ether, the precipitate was obtained by reprecipitation. The precipitate was filtered, and the reprecipitation was carried out in a same solution for several times. The product was dried under reduced pressure, 6-MTAB was obtained in 49% yield. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 1.46 (m, 4H; CH<sub>2</sub>), 1.64 (m, 2H; CH<sub>2</sub>CH<sub>2</sub>S), 1.79 (m, 2H; CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>), 2.52 (t, 2H; CH<sub>2</sub>S), 3.14 (s, 9H; (CH<sub>3</sub>)<sub>3</sub>N<sup>+</sup>), 3.36 (t, 2H; CH<sub>2</sub>N<sup>+</sup>). Anal. Calcd for C<sub>9</sub>H<sub>22</sub>BrNS: C, 42.18; H, 8.65; N, 5.47. Found: C, 42.05; H, 8.83; N, 5.40. IR (KBr): 2925 cm<sup>-1</sup> (C-H); 2856 cm<sup>-1</sup> (C-H); 2424 cm<sup>-1</sup> (S-H).

## Reference

- [1] S. Onoue, Ph.D. Dissertation, Kyushu University, Fukuoka, JPN, 2001.

## MMS synthesis of AuNPs

In a sputter coater, 0.15 g of molten 6-MTAB by heating at 110 °C for 3 min in a glass vessel with an inner diameter of 20 mm was set, and Au sputter deposition was performed with a current of 40 mA under an air pressure of 15 Pa. The Au target was located at a distance of 23 mm from the surface of 6-MTAB. After sputtering deposition for 2 min, 6-MTAB was reheated at 110 °C for 3 min to keep it molten. Sputtering deposition was then repeated under the same conditions. By repeating this procedure several times, AuNPs were prepared with the sputtering time of 5–20 min. The obtained samples were dispersed into water (3 mL).

## The measurements of the amounts of Au

The concentration of AuNPs was obtained by inductively-coupled plasma atomic emission spectroscopy (ICP–AES) (ICPS-7500, Shimadzu, Japan), and the amount of the sputtering Au in 6-MTAB was estimated. In order to check the accuracy of the ICP–AES data, we also sputtered Au as AuNPs formation onto a glass substrate in the same sputtering condition, and measured the amount of Au by precision balance.

## Transmission Electron Microscopy

TEM images were obtained with a H-9500 (HITACHI, Japan) operation at 300 kV. Samples for TEM were made as follows. Ultra centrifugation of AuNPs was carried out with a CS150GX (HITACHI Koki, Japan) at 140,000 rpm for 2 h, and the supernatant was removed in order to eliminate the free 6-MTAB molecules. A few aliquots of the obtained AuNPs dispersion were dropped onto carbon coated copper grid. Then the grid was dried under vacuum oven overnight.

## UV/Vis absorption spectra measurements

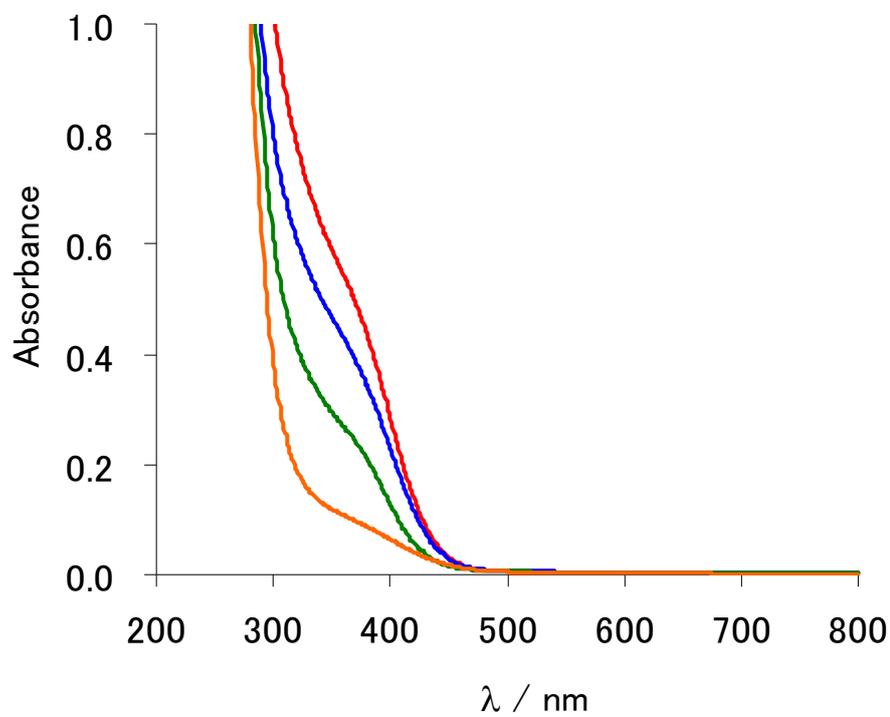
UV/Vis absorption spectra of AuNPs with various sputtering times were recorded with a spectrophotometer (V-630, JASCO, Japan) in the range of 250–800 nm. The UV/Vis samples of AuNPs were diluted with water by ten times.

## Photoluminescence (PL) and PL excitation (PLE) spectra measurements

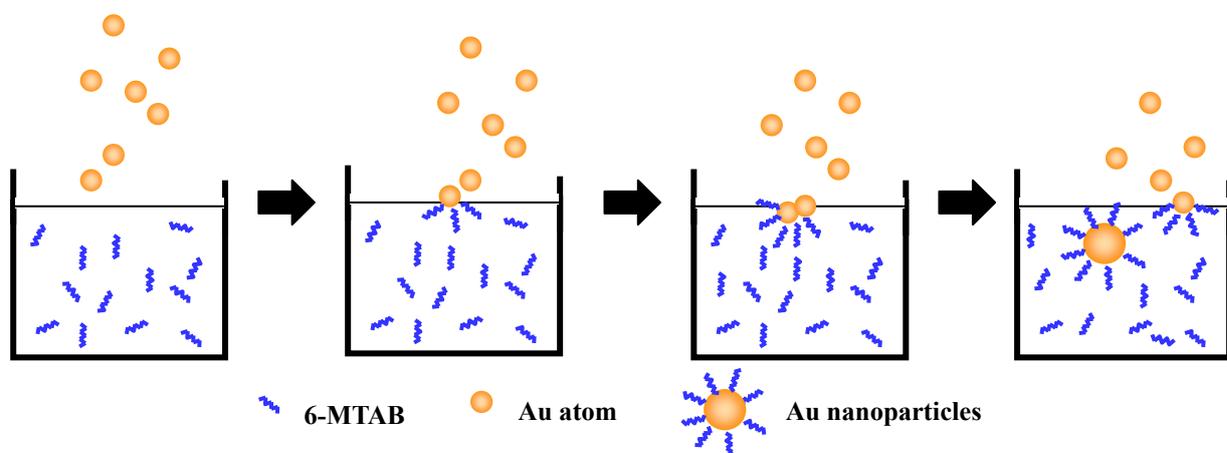
PL spectra of AuNPs (< 50 μM) were recorded with a FP-6600 spectrofluorometer (JASCO, Japan). The excitation and emission wavelengths of PL were firstly obtained using three dimensional PL spectra, and next, PLE spectra were measured at these wavelengths of PL peaks. In order to obtain PL spectra in the range of 500–1000 nm with the excitation wavelength in the range of 250–500 nm, we have used a long path filter (cut-off wavelength of 500 nm).

### **Quantum yield measurements**

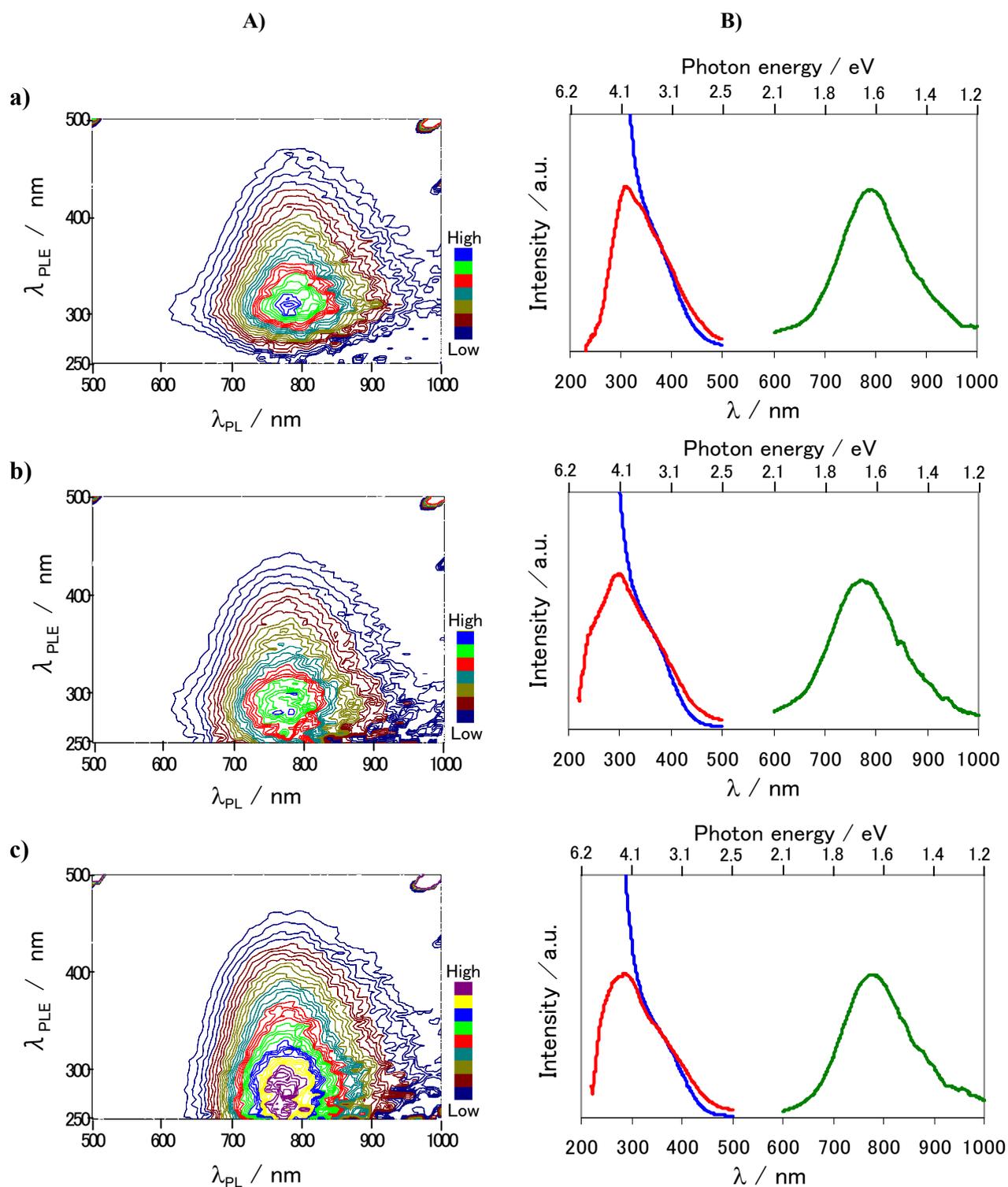
The absolute quantum yields of AuNPs were determined by a C9920-02G (Hamamatsu, Japan).



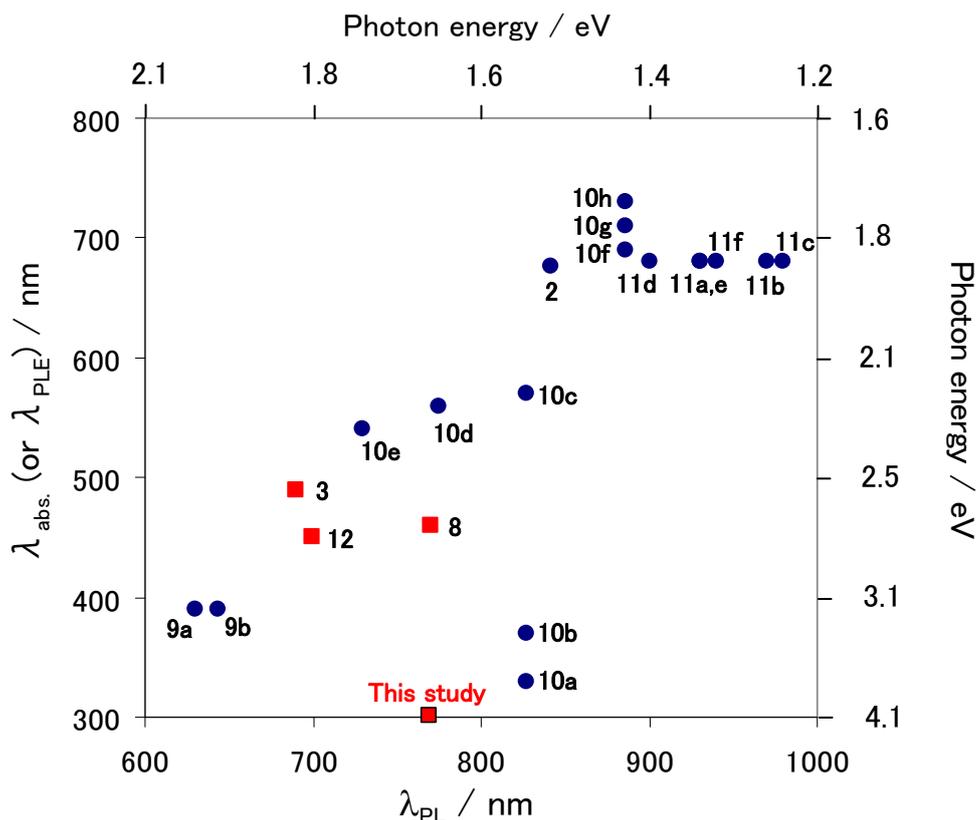
**Fig. S1** UV/Vis absorption spectra of AuNPs produced with sputtering times of 5 min (green), 10 min (orange), 15 min (blue), and 20 min (red), respectively.



**Fig. S2** Schematic illustration of formation mechanism of AuNPs.



**Fig. S3** A) Three dimensional PL spectra of AuNPs produced with various sputtering times. B) Optical absorption (blue), PL (green), and PLE (red) spectra of AuNPs produced with various sputtering times. Sputtering time (min),  $\lambda_{PL}^{\max}$  (nm),  $\lambda_{PLE}^{\max}$  (nm), quantum yield, and Stokes shift (eV): sample a), (5, 785, 310, 0.011, 2.4); sample b), (10, 772, 297, 0.012, 2.6); sample c), (15, 778, 289, 0.009, 2.7); respectively.



References	NP size (nm)	Stokes shift (eV)	Quantum yield	Protencing agents
This study (sputtering time of 20 min)	1.3	2.5	$1 \times 10^{-2}$	6-MTAB
10	a (Au <sub>10</sub> , Au <sub>11</sub> , Au <sub>12</sub> )	2.3	$1 \times 10^{-4}$	Glutathione (GSH)
	b 0.9 (Au <sub>15</sub> )	1.9	$2 \times 10^{-4}$	
	c 0.9 (Au <sub>18</sub> )	0.7	$4 \times 10^{-3}$	
	d 0.9 (Au <sub>22</sub> (SG) <sub>16</sub> )	0.6	$4 \times 10^{-3}$	
	e 0.9 (Au <sub>22</sub> (SG) <sub>17</sub> )	0.6	$2 \times 10^{-3}$	
	f 0.9 (Au <sub>29</sub> )	0.4	$3 \times 10^{-3}$	
	g 1.0 (Au <sub>33</sub> , Au <sub>35</sub> )	0.4	$2 \times 10^{-3}$	
	h 1.1 (Au <sub>38</sub> , Au <sub>39</sub> )	0.3	$2 \times 10^{-3}$	
9	a 0.8 (Au <sub>12</sub> )	1.2	$1 \times 10^{-6}$	meso-2,3-dimercaptosuccinic acid (DMSA)
	b 0.8	1.3	$3 \times 10^{-5}$	DMSA-tetraoctylammonium
8	1.8	1.1	$3 \times 10^{-3}$	Tiopronin
12	1.1	1.0	$3 \times 10^{-2}$	pentaerythritol tetrakis(3-mercaptopropionate)-terminated polymethacrylic acid
11	3	1.6	$1.8 \times 10^{-2}$	dihydrolipoic acid
	a 1.1 (Au <sub>38</sub> )	0.5	-	4-nitrothiophenol
	b 1.1 (Au <sub>38</sub> )	0.5		p-toluenethiol
	c 1.1 (Au <sub>38</sub> )	0.5		4-methoxybenzenethiol
	d 1.1 (Au <sub>38</sub> )	0.4		3-mercaptopropionic acid
	e 1.1 (Au <sub>38</sub> )	0.5		hexanethiol
f 1.1 (Au <sub>38</sub> )	0.5	phenylethylenethiol		
2	0.8	0.3	$3 \times 10^{-7}$	dodecanethiol

**Fig. S4** Summary of PL properties of various AuNPs. The reference numbers in the figure and table are correlated with that of the main manuscript. The Stokes shift was determined from either (energy of  $\lambda_{\text{abs.}}^{\text{max}}$  (eV)) – (energy of  $\lambda_{\text{PL}}^{\text{max}}$  (eV)) (blue dot references) or (energy of  $\lambda_{\text{PLE}}^{\text{max}}$  (eV)) – (energy of  $\lambda_{\text{PL}}^{\text{max}}$  (eV)) (red dot references).