

Supporting Information

Photoluminescent gold nanodots: role of the accessing ligands

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Experimental

Chemicals. Tetrakis(hydroxymethyl)phosphonium chloride (THPC), 11-mercaptoundecanoic acid (11-MUA), (11-mercaptoundecyl)trimethylammonium bromide (11-MUNT), α -lipoic acid (LA), 6-mercaptohexanoic acid (6-MHA), hexadecyltrimethylammonium bromide (CTAB), DL-dithiothreitol (DTT), and all the metal salts used in this study were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Sodium tetraborate and hydrogen tetrachloroaurate (III) trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) were obtained from Acros (Geel, Belgium). Ammonium hydroxide and boric acid obtained from J. T. Baker (Phillipsburg, NJ, USA) were used to prepare the ammonia-boric acid buffer (50 mM, pH 9.0). Sodium phosphate buffer solution (100 mM, pH 5.0) was prepared from H_3PO_4 (100 mM) and Na_3PO_4 (100 mM) solutions. The ultrapure water used in all the experiments was from a Milli-Q (18.2 M Ω cm; Millipore, Billerica, MA) system.

Synthesis and Characteristics of Gold Nanoparticles. Gold nanoparticles (Au NPs) were synthesized by THPC-mediated reduction of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$.^[1] A THPC solution prepared by mixing 80% THPC solution (12 μL) with 1 M aqueous NaOH (0.5 mL) was added to water (46.0 mL). The mixture was stirred for 5 min and then 1 wt% $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (1.5 mL) was rapidly added to it. After 10 s of stirring, the solution changed color to brown, indicating the formation of THPC–Au NPs. The solution was stirred for another 15 min and then stored at 4 °C in the dark until required for use. The average size of the Au NPs, determined using a transmission electron microscope (Tecnai 20 G2 S-Twin TEM, Philips/FEI, Hillsboro, Oregon, USA), was 2.9 ± 0.5 nm (from 100 counts). The particle concentration of the Au NP solution was determined to be 0.95 μM .^[2]

Synthesis of Photoluminescent 11-MUA–Au NDs in the Presence of Salt. DI water (0.1 mL), ammonia-boric acid buffer (50 mM, pH 9.2, 0.2 mL), 11-MUA (100 mM, 0.1 mL), metal salts (NaCl, KCl, MgCl_2 , or CaCl_2 , 0–2.5 M, 0.1 mL), and the as-prepared Au NPs (0.5 mL) were added sequentially to a 1.7 mL microcentrifuge tube. The mixtures were then left to react in the dark at room temperature and their

absorption and photoluminescence (PL) spectra were recorded at regular intervals for 100 h.

Synthesis of 11-MUA/11-MUNT–Au NDs, 11-MUA/LA–Au NDs, 11-MUA–Au NDs, MUNT–Au NDs, and LA–Au NDs. First, we prepared the alkanethiol solutions (0.1 mL) with [11-MUA]/[11-MUNT] and [11-MUA]/[LA] concentration ratios of 19, 9, 3, and 1 at a constant total alkanethiol concentration (100 mM). Solutions containing one of 11-MUA, 11-MUT, or LA were prepared for controls. They were then separately added to 1.7 mL microcentrifuge tubes containing DI water (0.3 mL), trisodium tetraborate (50 mM, pH 9.2, 0.1 mL), and the as-prepared Au NPs (0.5 mL) to prepare various Au NDs including 11-MUA/11-MUNT–Au NDs, 11-MUA/LA–Au NDs, 11-MUA–Au NDs, MUNT–Au NDs, and LA–Au NDs. The mixtures were then left to react for 100 h. The absorption and PL spectra of the as-prepared Au NDs were observed at regular intervals of 4 h in the dark at room temperature.

Characterization of Au NDs. The PL spectra of the as-prepared Au ND solutions were recorded using a spectrofluorometer (Varian, Walnut Creek, CA, USA) with an excitation wavelength of 375 nm. The absorption spectra of the as-prepared Au ND solutions were measured using a double beam UV-Vis spectrophotometer (Cintra 10e; GBC, Victoria, Australia). Diluted solutions of Au NDs were placed in a 1 cm quartz cuvette before absorption and PL measurements for the determination of their quantum yield (QY) values. The QY values were determined by comparison with that of quinine (QY = 53% in 0.1 M H₂SO₄). The zeta potential (ζ) values of the photoluminescent Au NDs in various solutions were assessed using a Zetasizer (Nano ZS, Malvern Instruments, Worcestershire, UK). For TEM measurements using a Tecnai 20 G2 S-Twin transmission electron microscope operating at 200 kV, each of the purified Au NDs (50 nM, 50 μ L) was deposited onto a TEM grid with a thin layer of carbon. X-ray photoelectron spectroscopy (XPS) was performed using an ES-CALAB 250 spectrometer (VG Scientific, East Grinstead, UK) with Al K α X-ray radiation as the X-ray source for excitation. Binding energies were corrected using the C 1s peak at 284.6 eV as a standard. The samples for XPS measurements

were prepared by depositing drops of the Au ND solution (10 μM , 100 μL) onto Si substrates in which the solvents evaporated at ambient temperature and pressure. The PL lifetimes of the Au NDs were recorded using a photo-counting PicoHarp 300 system (PicoPicoQuant, Berlin, Germany) and a diode laser emitting at 375 nm (FluoTime 300) as the light source.

Before conducting matrix-assisted laser desorption/ionization-mass spectrometry analyses, the as-prepared Au ND solutions (0.5 mL) were centrifuged at 18000 g for 30 min. After removal of the supernatant solution, the precipitate was resuspended in water. Mass spectrometry (MS) experiments were performed in the reflectron negative- and positive-ion modes for analysis of 11-MUA–Au NDs and 11-MUA/11-MUNT–Au NDs, respectively, using an AutoflexIII LDI time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Bremen, Germany). The samples were irradiated using pulsed laser irradiation (355-nm Nd:YAG, 100 Hz; pulse width: 6 ns). A total of 1000 pulsed laser shots at a laser density of $6.37 \times 10^4 \text{ W cm}^{-2}$ were applied to five random positions on the LDI target. The electrospray ionization (ESI) samples were prepared by collecting the RS–Au⁺ complexes from 11-MUA–Au NDs and 11-MUA_{9,0}/LA_{1,0}–Au ND solutions after using centrifugal filtration (12000 g) for 40 min through a filter with a cutoff of 10 kDa. To determine the molar ratio of alkanethiol ligands (11-MUA/11-MUNT and 11-MUA/LA) on Au NDs, NaCN (1.0 mM) was used for the dissolution of Au NDs to liberate the thiolate ligands. The dissolute solutions were further treated with DTT (100 mM) to avoid the formation of disulfide bonds (RSSR) of alkanethiol ligands. For the determination of 11-MUNT in the positive mode of ESI-MS, CTAB (m/z 248.33) was used as internal standard; while in the native mode, 6-MHA (m/z 147.05) was used as internal standard. A Bruker Q-ToF system, hybrid quadrupole-TOF mass spectrometer operating in the positive or native mode (sample injection rate 180 $\mu\text{L min}^{-1}$; capillary voltage 4.5 kV; nebulizer 0.4 bar; dry gas 4.0 L min^{-1} at 160 $^\circ\text{C}$; and m/z 100–1000) was used for ESI-MS.

References

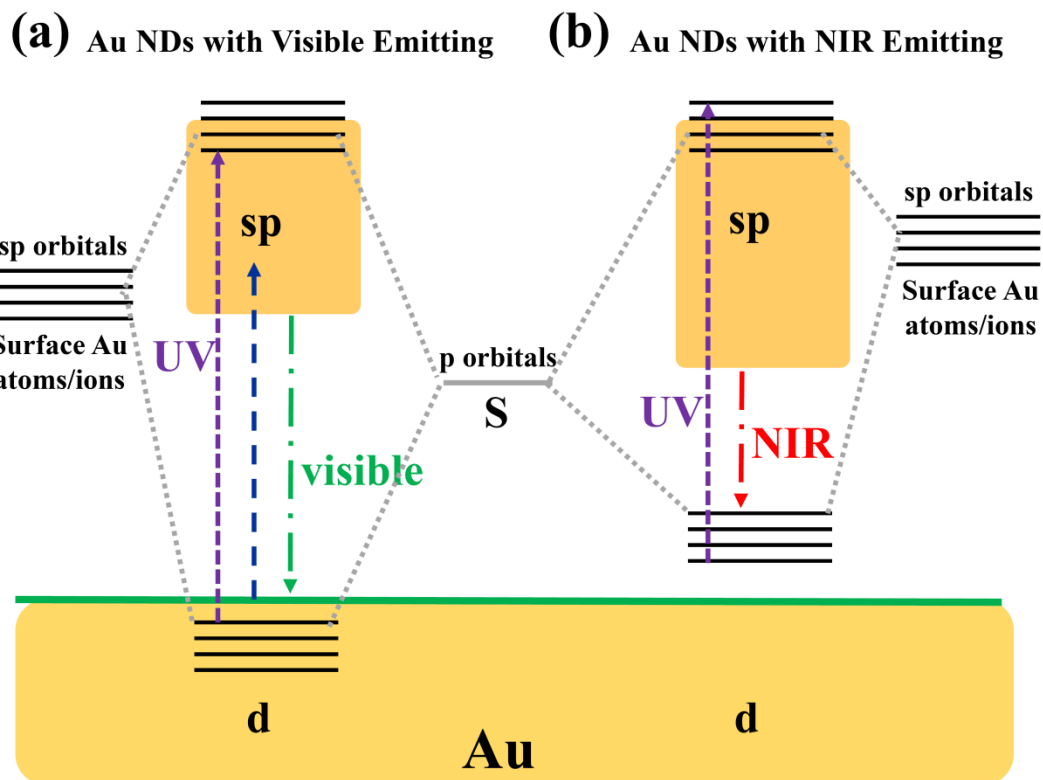
1. D. G. Duff, A. Baiker and P. P. Edwards, *Langmuir* 1993, **9**, 2301.

2. C.-C. Huang, Z. Yang, K.-H. Lee and H.-T. Chang, *Angew. Chem. Int. Ed.*, 2007, **46**, 6824.

Table S1. Optical properties of as-prepared Au NDs.

	λ_{max}^{abs} (nm) ^a	λ_{max}^{ex} (nm) ^b	λ_{max}^{em} (nm) ^c	QY (%)	absorption coefficient (ϵ , M ⁻¹ cm ⁻¹) ^d	lifetime (τ_1/τ_2 , ns)
11-MUA–Au NDs (w/o salt) ^e	N/A ^f	378	545	2.5	0.7×10^6 ^g	1.7 (89.6%)/52.4 (10.4%)
11-MUA–Au NDs (100 mM NaCl) ^h	375	378	550	11.7	1.8×10^6	9.6 (60.0%)/84.8 (40.0%)
11-MUA–Au NDs ⁱ	375	375	530	4.6	3.0×10^6	9.3 (66.2%)/74.8 (33.8%)
11-MUA _{9.0} /11-MUNT _{1.0} –Au NDs ⁱ	380	380	530	7.8	2.6×10^6	4.9 (71.8%)/59.6 (28.2%)
11-MUA _{9.5} /LA _{0.5} –Au NDs ⁱ	385	382	518	15.6	2.7×10^6	6.6 (55.3%)/108.8 (44.7%)

^aAbsorption-band maxima at wavelength. ^bExcitation-band maxima at wavelength. ^cEmission-band maxima at wavelength. ^dAbsorption coefficient at the wavelength of the absorption-band maxima. ^e, ^hAu NDs prepared in 10 mM ammonia-boric acid solution (pH 9.0) in the absence^e and presence^h of 100 mM NaCl. ^fNot available. ^gAbsorption coefficient at the wavelength at 378 nm. ⁱAu NDs prepared in 5 mM sodium tetraborate solution (pH 9.2) in the presence of alkanethiols.



Scheme S1. Schematic representation of the proposed energy level of photoluminescent (a) 11-MUA–Au NDs and (b) 11-MUNT–Au NDs. The thiolated ligands form hybrid electronic states with surface gold atoms and ions. The absorption and emission wavelengths of Au NDs were significantly affected by the ligand (S)-to-metal (Au) charge transfer and valence states of surface Au atoms.

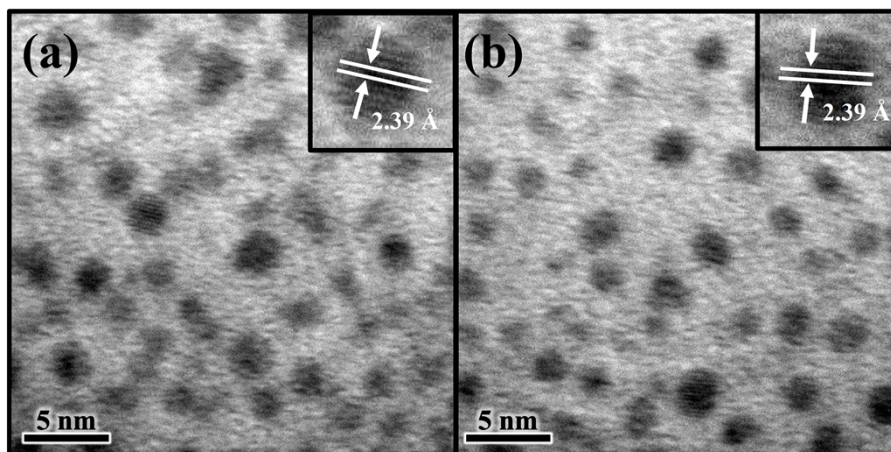


Figure S1. TEM images of 11-MUA–Au NDs obtained from the reaction of THPC–Au NPs (3 nm) with 11-MUA (10 mM) in 10 mM ammonia-boric acid solution (pH 9.0) (a) with and (b) without containing 100 mM NaCl at ambient temperature for 48 h. Insets: HRTEM images. The particle sizes of 11-MUA–Au NDs prepared in the (a) absence and (b) presence of 100 mM NaCl (calculated from 100 counts for each) were 2.2 ± 0.6 and 2.1 ± 0.5 nm, respectively. Other conditions were the same as those described in Fig. 1.

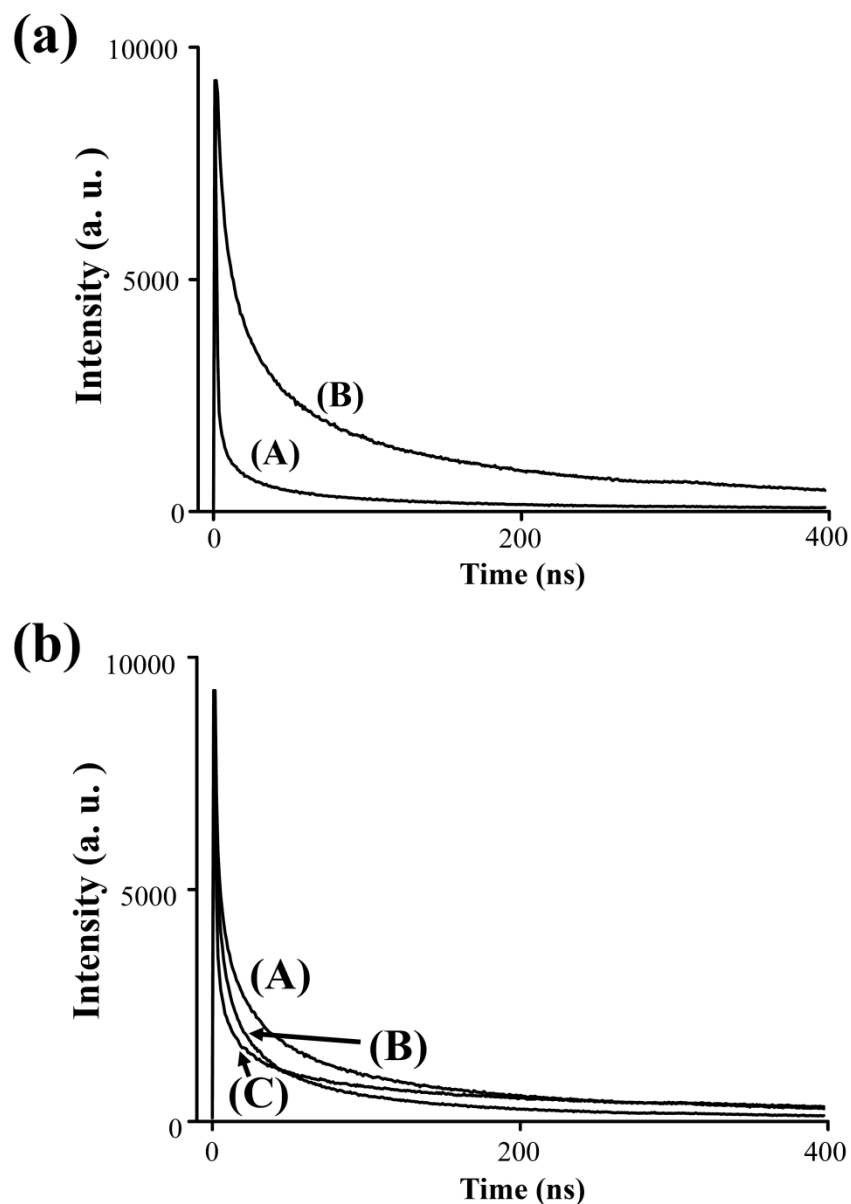


Figure S2. Photoluminescence lifetime, after excitation at 375 nm, of (a) the 11-MUA–Au NDs prepared from the THPC–Au NPs and 11-MUA in the (A) absence and (B) presence of NaCl (100 mM); (b) the as-prepared (A) 11-MUA–Au NDs, (B) 11-MUA_{9.0}/11-MUNT_{1.0}–Au NDs, and (C) 11-MUA_{9.0}/LA_{1.0}–Au NDs. The photoluminescence decay was fitted to a biexponential decay. Other conditions were the same as those described in Fig. 1b, 3b, and 5b.

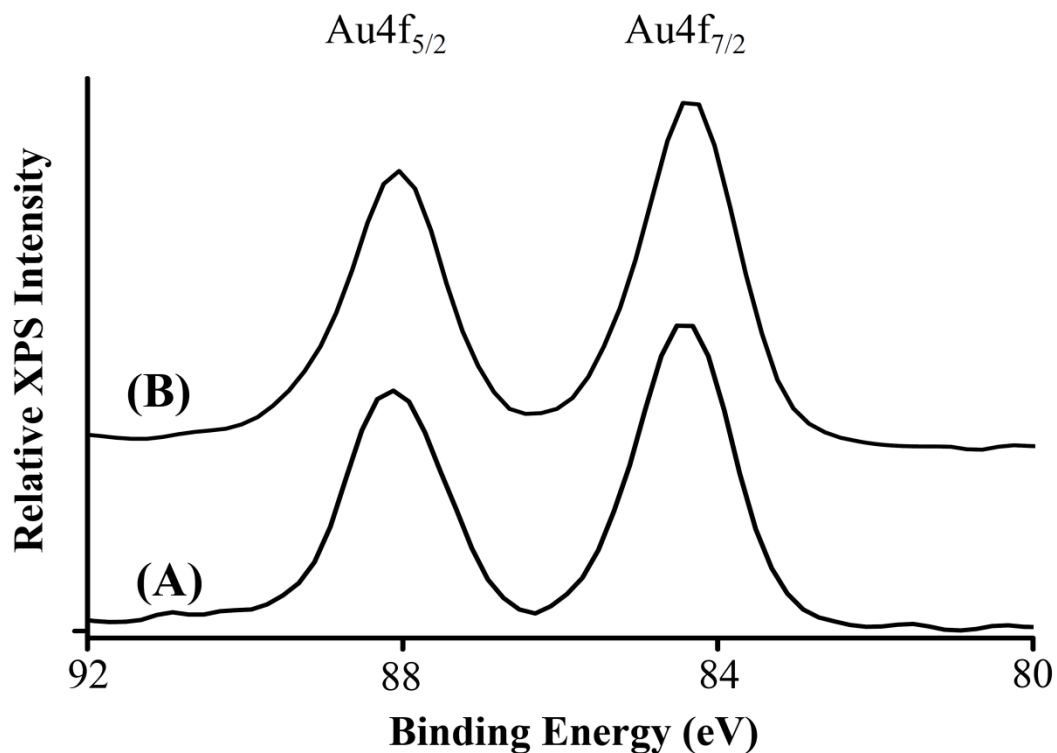


Figure S3. Au(4f) X-ray photoelectron spectroscopy (XPS) spectra of 11-MUA–Au NDs obtained from the reaction of THPC–Au NPs (3 nm) with 11-MUA (10 mM) in 10 mM ammonia-boric acid solution (pH 9.0) (A) with and (B) without containing 100 mM NaCl at ambient temperature for 48 h. Other conditions were the same as those described in Fig. 1.

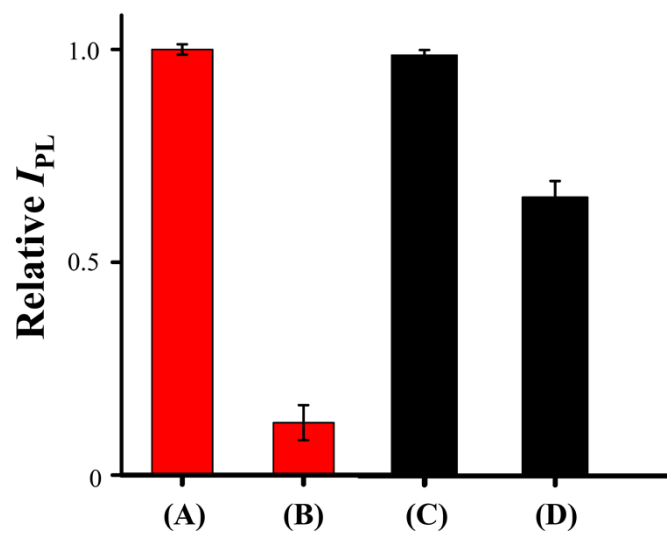


Figure S4. Relative photoluminescence intensity at 550 nm of 11-MUA–Au NDs synthesized in the (A, B) absence and (C, D) presence of NaCl (100 mM) after treating with (A, C) 0 and (B, D) 10 mM NaBH₄ in 5 mM phosphate buffer (pH 5.0) for 2 h. Error bars represent standard deviations from three repeated experiments. Other conditions were the same as those described in Fig. 1b.

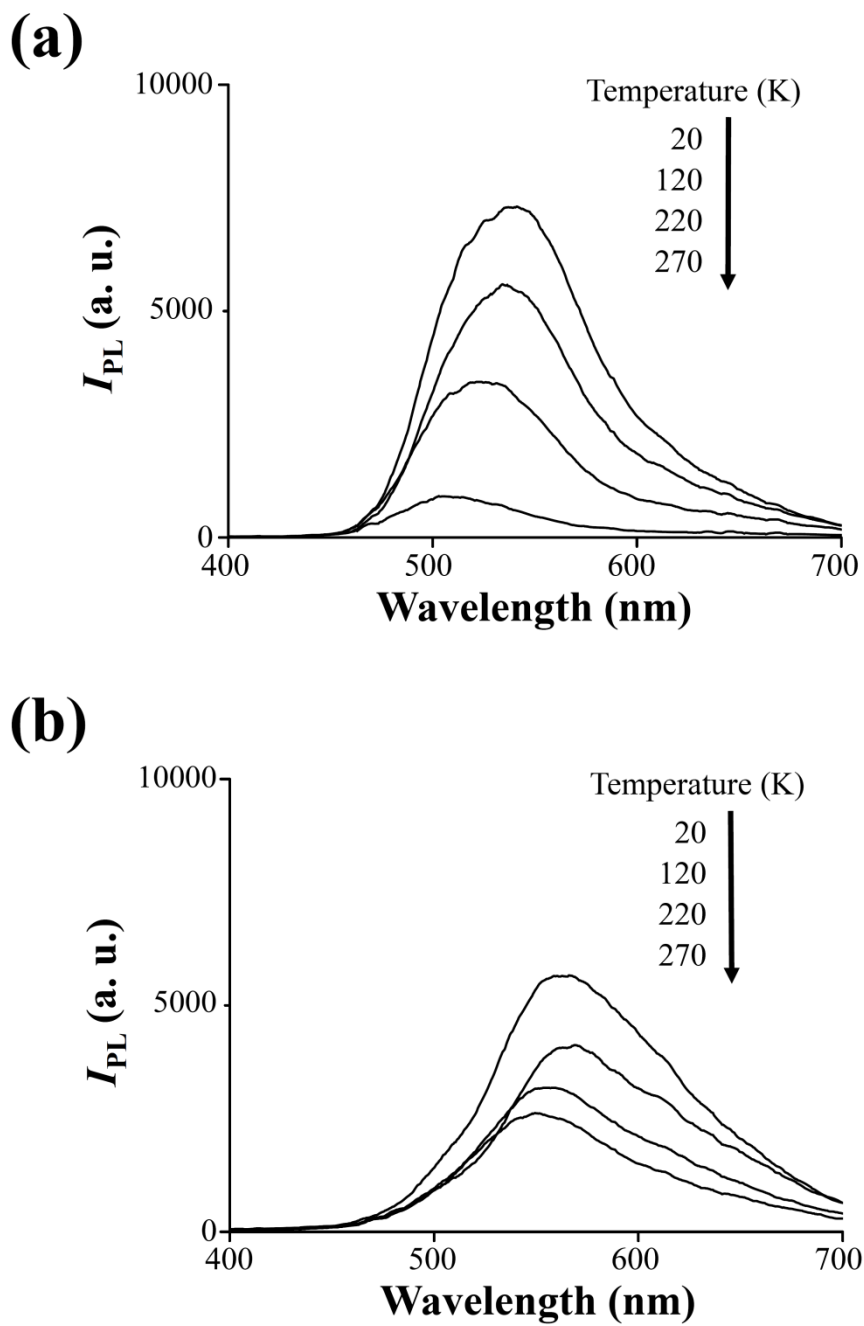


Figure S5. Temperature-dependent (20–270 K) emission spectra of 11-MUA–Au NDs prepared in the (a) absence and (b) presence of 100 mM NaCl. Other conditions were the same as those described in Fig. 1b.

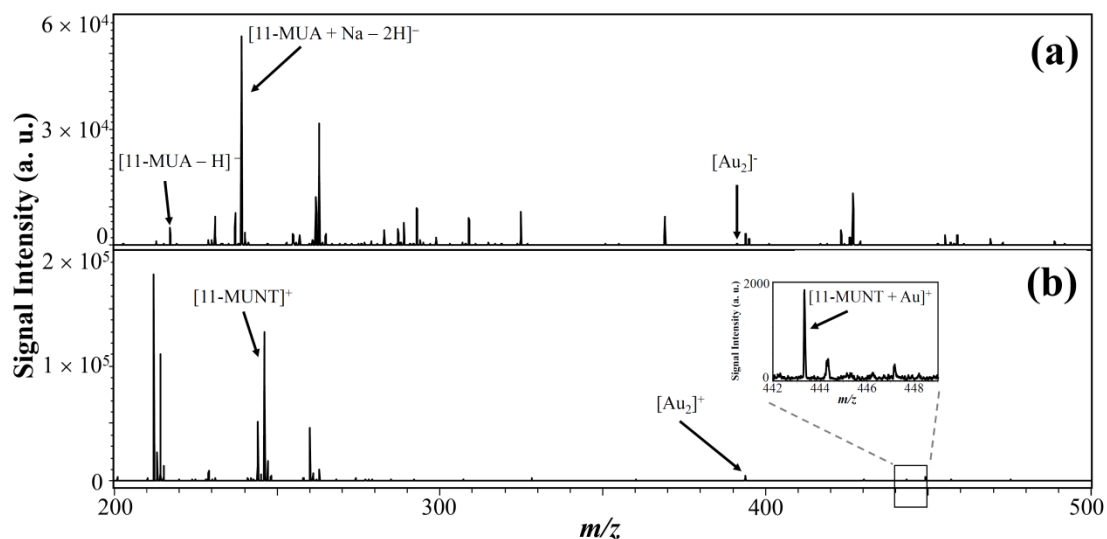


Figure S6. Mass spectra of the purified 11-MUA_{9.0}/11-MUNT_{1.0}-Au NDs through laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS) operated in the (a) negative and (b) positive modes. Signals at m/z 217.18, 239.16, and 393.88 in (a) are assigned to $[11\text{-MUA} - \text{H}]^-$, $[11\text{-MUA} + \text{Na} - 2\text{H}]^-$, and $[\text{Au}_2]^-$ ions, respectively. Signals at m/z 246.73, 393.83, and 443.19 in (b) are assigned to $[11\text{-MUNT}]^+$, $[\text{Au}_2]^+$, and $[11\text{-MUNT} + \text{Au}]^+$, respectively. A total of 1000 pulsed laser shots were applied to accumulate the signals from five LDI target positions under a laser power density of $6.37 \times 10^4 \text{ W cm}^{-2}$. MS signal intensities are plotted in arbitrary units (a. u.).

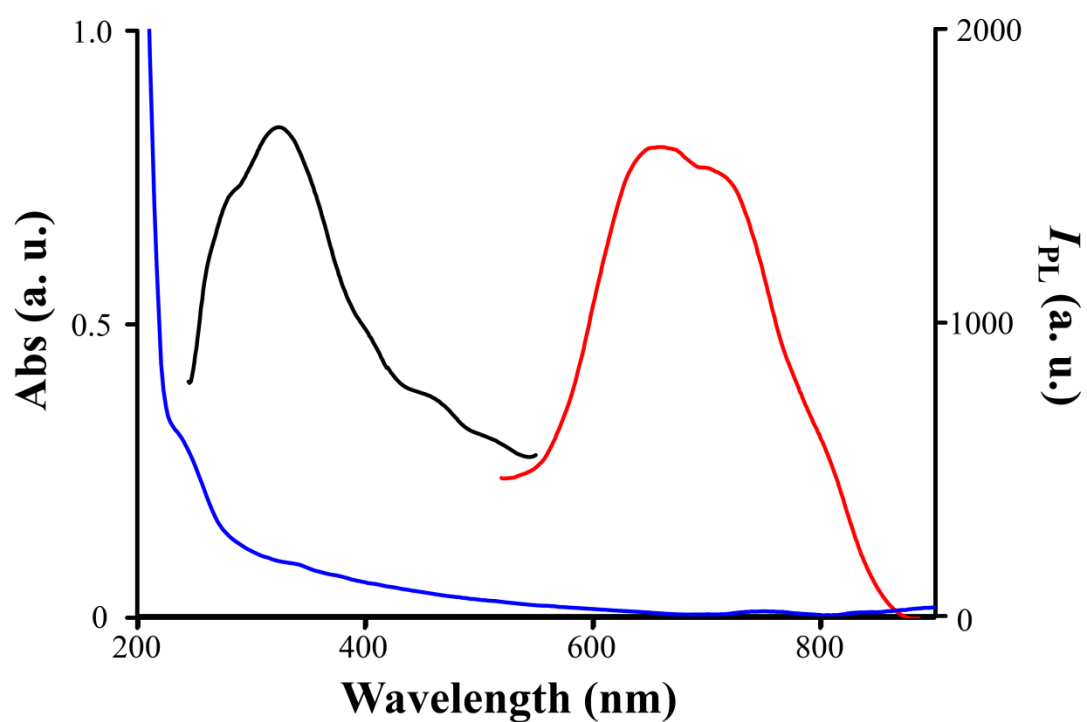


Figure S7. UV-Vis absorption (blue), excitation (black), and photoluminescence (red) spectra of the as-prepared 11-MUNT–Au NDs. The concentration of Au ND particles was 100 nM. The absorbance (Abs) and photoluminescence intensity (I_{PL}) are plotted in arbitrary units (a. u.). Other conditions were the same as those described in Fig. 3b.

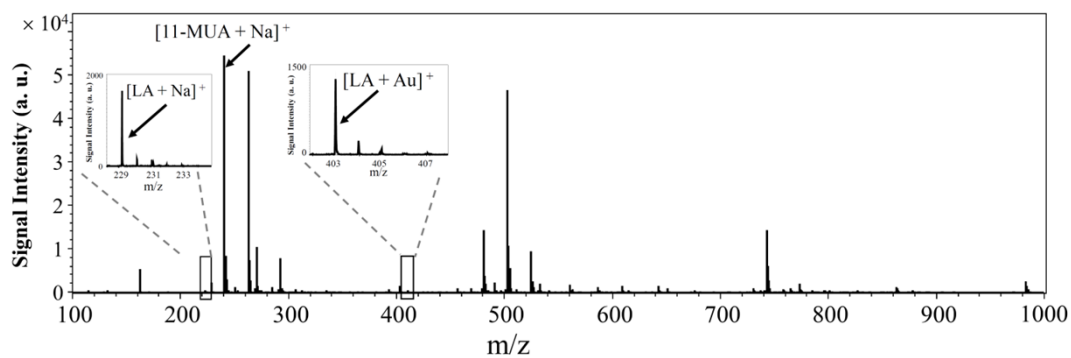


Figure S8. Characterization of RS–Au⁺ species using ESI-MS from the leaching solution of 11-MUA_{9,0}/LA_{1,0}–Au NDs in the positive mode. Signals at m/z 229.04, 241.13, and 403.04 are assigned to [LA + Na]⁺, [11-MUA + Na]⁺, and [LA + Au]⁺ ions, respectively. MS signal intensities are plotted in arbitrary units (a. u.). Other conditions were as described in Fig. 4.