

Supporting Information

Self-assembly of hybridized ligands on gold nanodots: tunable photoluminescence and sensing of nitrite

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EXPERIMENTAL SECTION

Chemicals. Decanoic acid (DA), dodecanoic acid (DDA), 11-mercaptoundecanol (11-MU), tetradecanoic acid (TA), tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), and tetra(hydroxymethyl)phosphonium chloride (THPC) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Dodecyltrimethylammonium bromide (DTAB), hexadecyltrimethylammonium bromide (HTAB), and myristyltrimethylammonium bromide (MTAB) were obtained from Acros Organics (Geel, Belgium, USA). All metal salts were purchased from Sigma-Aldrich. H_3PO_4 solution (100 mM) and Na_3PO_4 solution (100 mM) were used to prepare 100 mM sodium phosphate buffer solutions (pH 3.0 and pH 7.0). Milli-Q (Millipore, Billerica, MA, USA) ultrapure water was used for all experiments.

Synthesis and Characteristics of Au NPs. 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 water (1.0 mL) was added to 10 mM aqueous NaOH (45.5 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 added rapidly. After 10 s of stirring, the solution changed color to brown, indicating formation of the 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 was determined using a transmission electron microscope (Tecnai 20 G2 S-Twin TEM, Philips/FEI, Hillsboro, Oregon, USA) to be 2.9 ± 0.5 nm. The particle concentration of the Au NP solution was determined to be $0.94 \mu\text{M}$.²

Synthesis of Photoluminescent Amphiphilic Ligand (AL)/11-MU–Au NDs. Aliquots of the as-prepared Au NPs ($0.47 \mu\text{M}$) were self-assembled with 11-MU solution, solutions of 11-MU with one of the FAs, or 11-MU with one of the QAS separately. For the preparation of 11-MU–Au NDs, as-prepared Au NPs (0.5 mL) were added to aliquots of trisodium tetraborate buffer

solution (200 mM, pH 9.2, 0.1 mL). Subsequently, a 2.5 mM 11-MU (0.4 mL) solution was added to the Au NPs solution and incubated for 48 h in the dark at ambient temperature (~25 °C). For preparation of AL/11-MU–Au NDs in a 2.0-mL vial, reagents were added in the following order: as-prepared Au NPs (0.5 mL), trisodium tetraborate (200 mM, pH 9.2, 0.1 mL), 11-MU (10 mM, 0.1 mL), appropriate concentrations (1.0–25 mM) of FAs (0.1 mL) or QASs (0.1 mL). The mixtures were then diluted to 1.0 mL with ultrapure water and left to react for 12 h in the dark at ambient temperature. Before characterization of these as-prepared Au NDs, the 11-MU–Au NDs or AL/11-MU–Au NDs were diluted with ethanol to a final concentration of 50% (v/v).

Characterization of Photoluminescent AL/11-MU–Au NDs. The PL spectra of the as-prepared AL/11-MU–Au ND solutions were recorded using a spectrofluorometer (Varian, Walnut Creek, CA, USA) with the excitation wavelength at 275 or 390 nm. The absorption spectra of the as-prepared AL/11-MU–Au ND solutions were measured using a double beam UV-vis spectrophotometer (Cintra 10e; GBC, Victoria, Australia). Diluted solutions of AL/11-MU–Au NDs (100 nM, 0.5 mL) were placed in a 1-cm quartz cuvette prior to absorption and PL measurements for determining their quantum yields (QY). The QY values were determined by comparing with that of 10^{-5} M $\text{Cs}_3[\text{Eu}(\text{dpa})_3]$ (QY = 24%, in 0.1 M Tris-HCl (pH 7.4); refractive index~1.3) or quinine (QY = 53%, in 0.1 M H_2SO_4 ; refractive index~1.3). The QYs was determined by a relative comparison method using the following equation:

$$\Phi_{unk} = \frac{A_{std}}{A_{unk}} \times \frac{F_{unk}}{F_{std}} \times \frac{n_{unk}^2}{n_{std}^2} \times \Phi_{std}$$

Φ : quantum yield; *unk*: unknown sample; *std*: standard; *n*: refractive index of solvent; *A*: absorption the selected excitation wavelength; *F*: integrated fluorescence signal in the emission region.

The absorbance values of samples kept under 0.1 at the excitation wavelength to minimize re-absorption effects. Excitation and emission slit widths were set at 5.0 nm when recording their PL spectra.

Values for the zeta potential (ζ) of the various AL/11-MU–Au NDs solutions were assessed using a Zetasizer (Nano ZS, Malvern Instruments, Worcestershire, UK). The photoluminescent TA/11-MU–Au NDs were purified through centrifugal filtration (8000 g, 20 min) using a filter having a cutoff of 10 kDa and then resuspended with 5.0 mM sodium phosphate buffer (pH 7.0). Most of the excess 11-MU and precursors and the side product(s) in the solution were removed. By comparing the absorbance of the original TA/11-MU–Au NDs solution at 390 nm to that of the resuspended solution, it was evident that approximately 95% of the TA/11-MU–Au NDs had been collected (data not shown). The PL intensity of the supernatant is negligible, revealing that the absorption and PL signal are truly from TA/11-MU–Au NDs. The as-prepared TA/11-MU–Au NDs was stable for at least 2 months when stored at 4 °C in the dark.

Before characterization of Au NDs by LDI-MS, XPS and TEM, the Au NDs were purified through centrifugal filtration (8000 g, 20 min) using a filter having a cutoff of 10 kDa and then resuspended with 5.0 mM sodium phosphate buffer (pH 7.0). For TEM measurements using a Tecnai 20 G2 S-Twin transmission electron microscope, each purified mixture 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 AL/11-MU–Au NDs onto Si substrates in which the solvents evaporated at ambient temperature and pressure. The PL lifetimes of the AL/11-MU–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.

Prior to conducting matrix-assisted laser desorption/ionization-mass spectrometry (MALDI-MS) analyses, an as-prepared Au ND solution (0.5 mL) was centrifuged at 18000 g for 30 min. After removal of the supernatant solution, the precipitate was resuspended in 0.5 mL 50% ethanol solution. After three wash-centrifuge cycles, the Au NDs samples were resuspended separately in a 50% ethanol solution (0.5 mL). MS experiments were performed in the reflectron negative-ion mode and positive mode for analysis of TA/11-MU–Au NDs and MTAB/11-MU–Au NDs, respectively, using an AutoflexIII LDI time-of-flight mass spectrometer (Bruker Daltonics, Bremen, Germany). Samples were irradiated using pulsed laser irradiation (355-nm Nd:YAG, 10 Hz; pulse width: 6 ns). A total of 200 pulsed laser shots at a laser density of $1.72 \times 10^4 \text{ W cm}^{-2}$ were applied to five random positions on the LDI target.

Detection of Nitrite Ions. Aliquots (450 μL) of 10 mM sodium phosphate (pH 3.0) containing NO_2^- ions were maintained at ambient temperature for 10 min. Solutions of 10 mM sodium phosphate (pH 3.0) containing TA/11-MU–Au NDs (50 nM, 50 μL) were added separately to each of the NO_2^- ion solutions, which were then incubated for another 5 min at ambient temperature. The final concentrations of NO_2^- ions were 0–5.0 μM . The mixtures were then transferred separately into 96-well microtiter plates, and their PL spectra were recorded using a monochromatic microplate spectrophotometer (Synergy 4, BioTek, Winooski, VT, USA) upon excitation at a wavelength of 390 nm.

Analysis of Real Samples. Tap and lake water samples were collected from the campus of the National Taiwan University; seawater samples were collected from the ocean near the National Taiwan Ocean University. The local tap water and natural water samples were filtered through

0.2 μm membranes prior to use. Aliquots of the water samples (0.50 mL) were spiked with standard solutions (100 μL) containing NO_2^- ions with the final concentration in the range of 0–5.0 μM . The mixtures were then diluted to 1.0 mL with sodium phosphate solution (pH 3.0) containing TA/11-MU–Au NDs. The final concentrations of sodium phosphate and TA/11-MU–Au NDs were 10 mM and 5.0 nM, respectively. The mixtures were equilibrated at ambient temperature for 5 min and then transferred separately into 96-well microtiter plates, and their PL spectra were recorded using a monochromatic microplate spectrophotometer upon excitation at a wavelength of 390 nm.

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1. D. G. Duff and A. Baiker, *Langmuir*, 1993, **9**, 2301–2309.
2. C.-C. Huang, Z. Yang, K.-H. Lee and H.-T. Chang, *Angew. Chem. Int. Ed.*, 2007, **46**, 6824–6828.

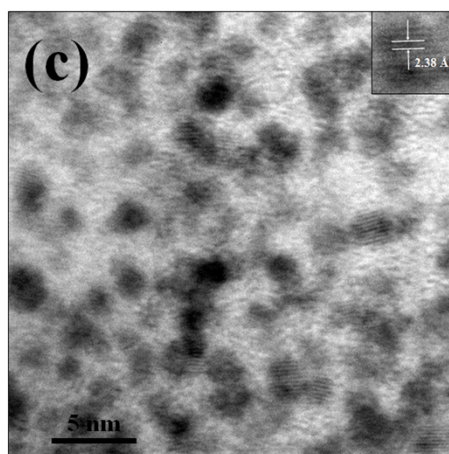
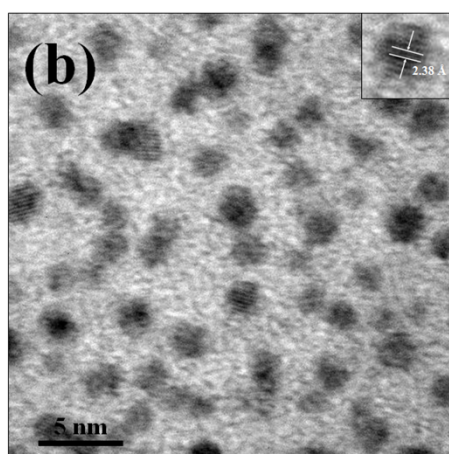
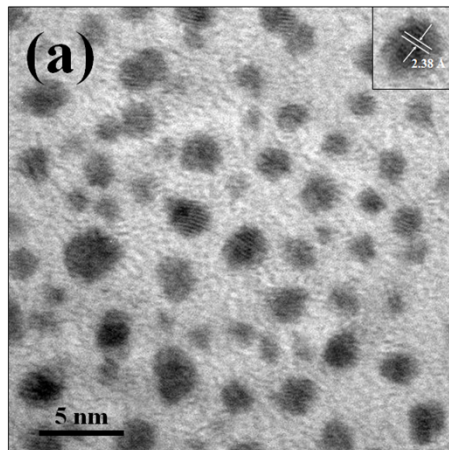


Fig. S1 TEM images of (a) 11-MU-Au NDs, (b) TA/11-MU-Au NDs, and (c) MTAB/11-MU-Au NDs. Other conditions were as described in Fig. 1.

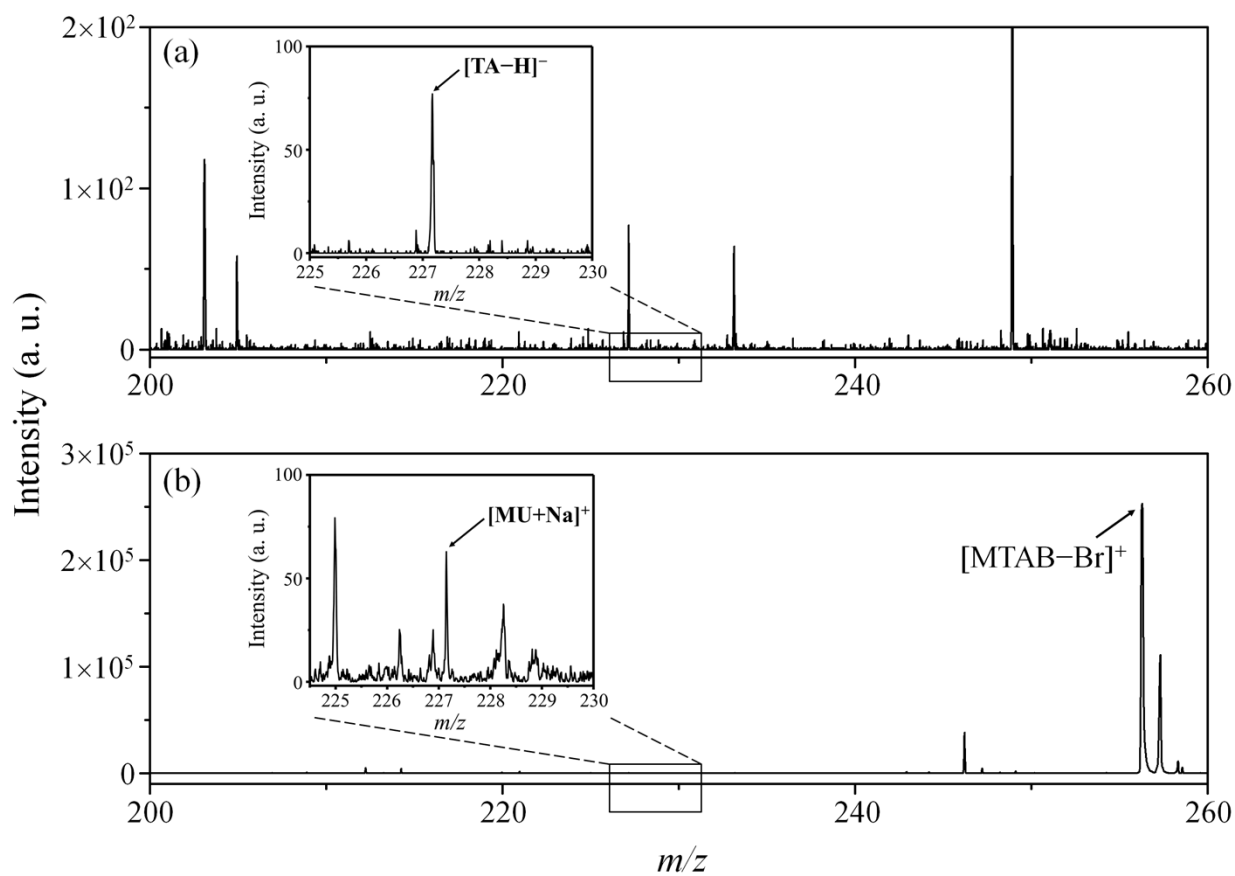


Fig. S2 LDI-MS of purified (a) TA/11-MU-Au NDs and (b) MTAB/11-MU-Au NDs in 50% ethanol solutions. Peak intensities are plotted in arbitrary units (a. u.).

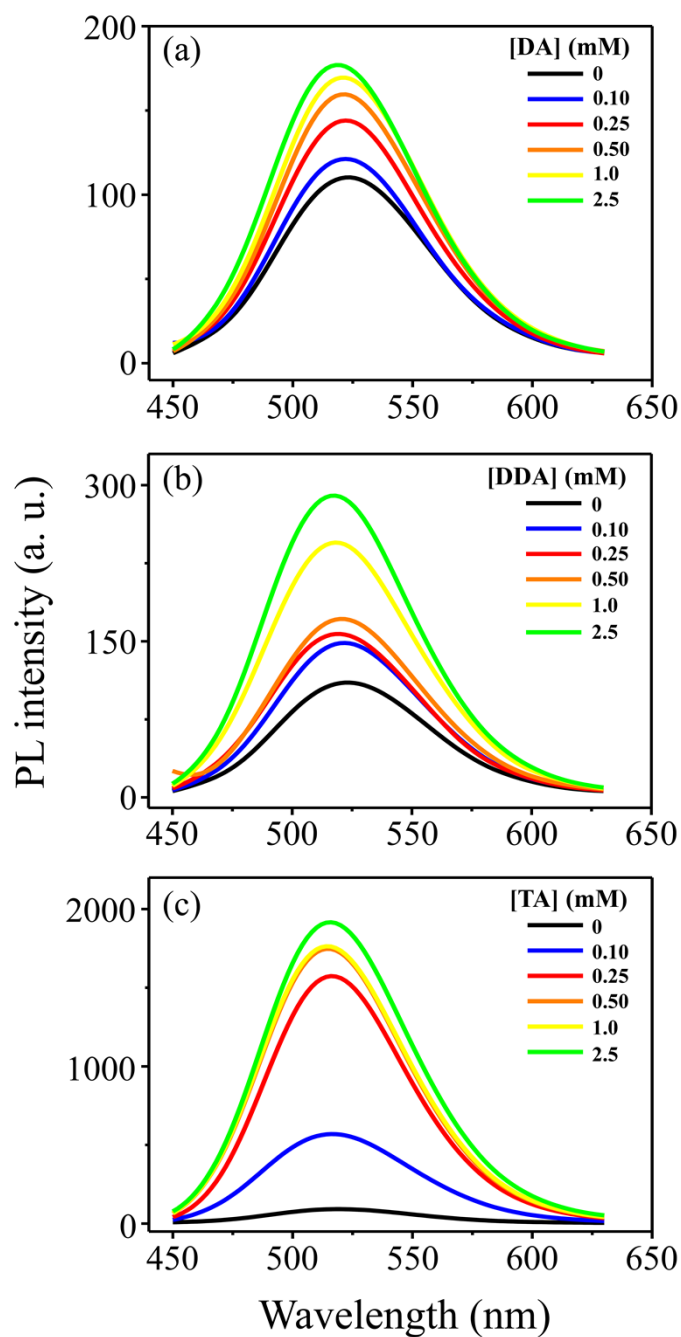


Fig. S3 PL spectra for (a) DA/11-MU-Au NPs, (b) DDA/11-MU-Au NPs, and (c) TA/11-MU-Au NPs that were prepared from the reaction of Au NP solutions with 11-MU (1.0 mM) and one of the FAs (0–2.5 mM). The excitation wavelength for FA/11-MU-Au NPs was set at 390 nm. Other conditions were as described in Fig. 1a.

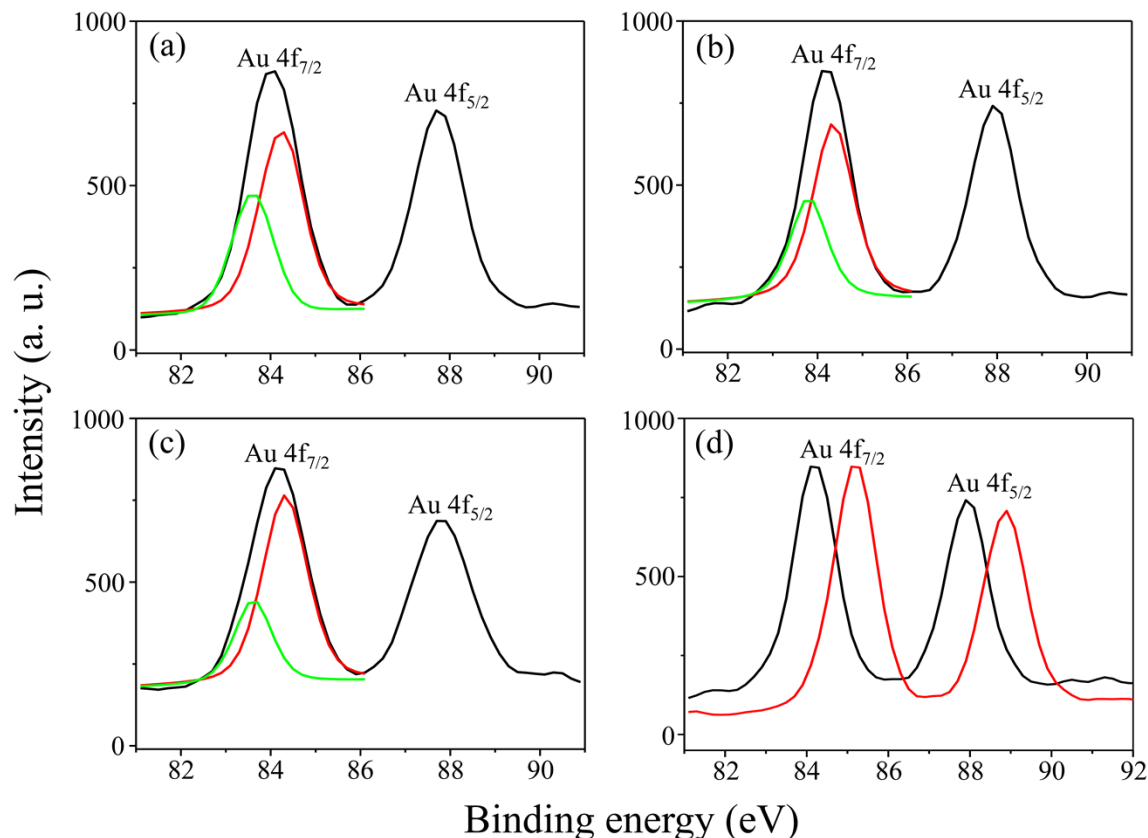


Fig. S4 XPS spectra of Au 4f core-level for solutions of (a) 11-MU–Au NDs (100 nM), (b) TA/11-MU–Au NDs (100 nM), and (c) MTAB/11-MU–Au NDs (100 nM) in 10 mM sodium phosphate (pH 7.0), and (d) TA/11-MU–Au NDs (100 nM) in the absence (black curve) and presence (red curve) of NO_2^- ions (100 μM) in 10 mM sodium phosphate (pH 3.0). The broad peak (Au 4f_{7/2}) was deconvoluted into two distinct components (green and red curves) centered at the binding energies of 83.6 and 85.0 eV, which were assigned to Au(0) and Au(I), respectively. Other conditions were as described in Fig. 1.

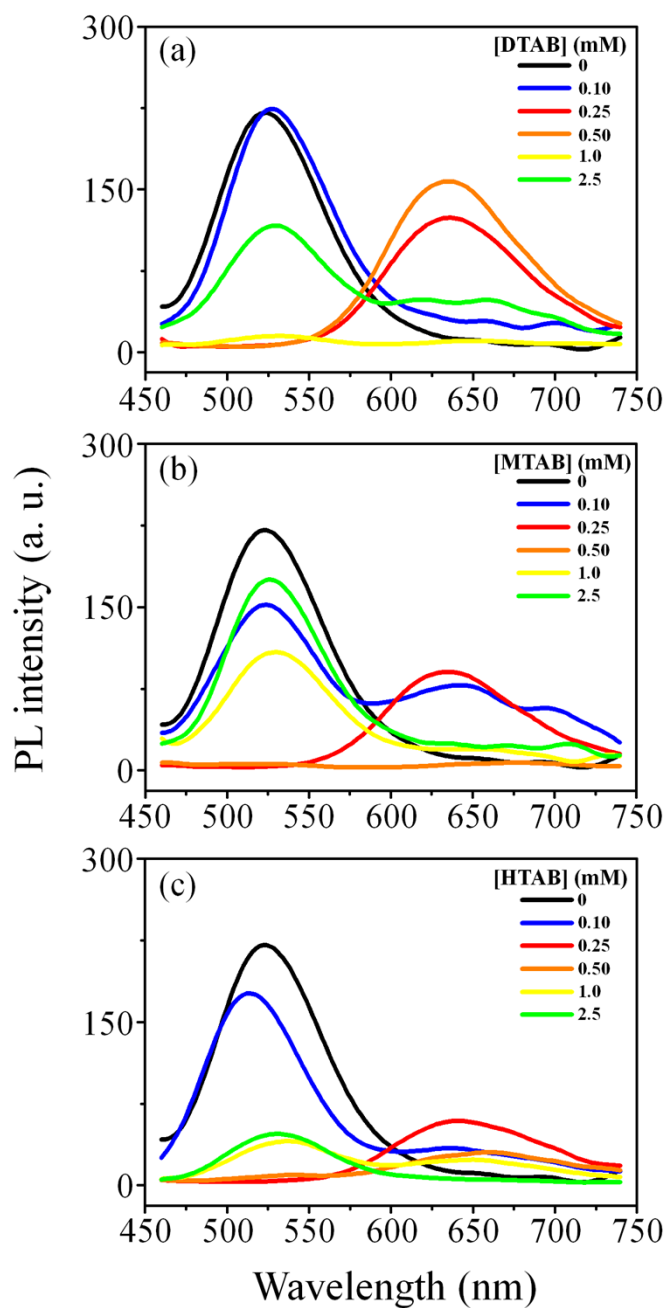


Fig. S5 PL spectra for (a) DTAB/11-MU-Au NDs, (b) MTAB/11-MU-Au NDs, and (c) HTAB/11-MU-Au NDs that were prepared from an Au NP solution in the presence of 11-MU (1.0 mM) and one of the QASs (0–2.5 mM). The excitation wavelength for the QAS/11-MU-Au ND solutions was set at 275 nm. Other conditions were as described in Fig. 1a.

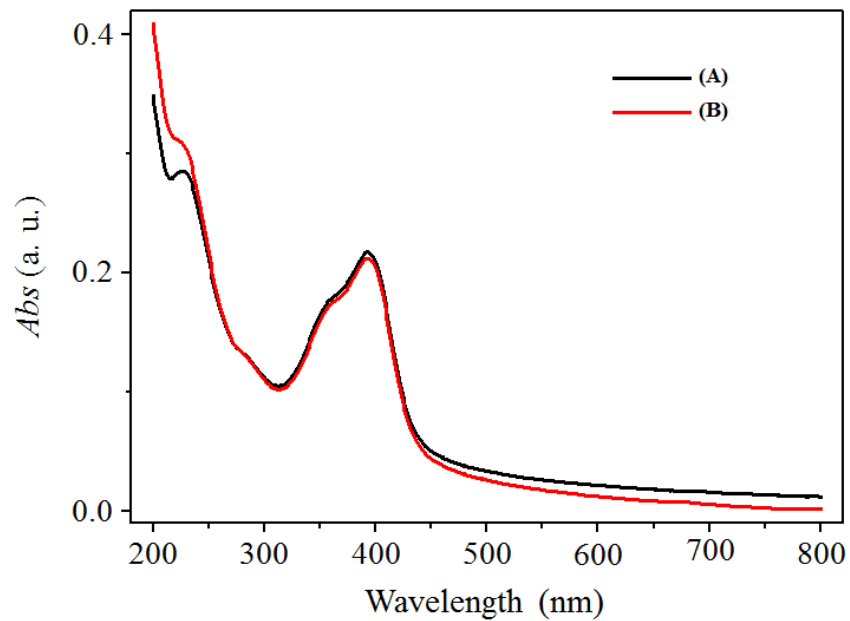


Fig. S6 UV-vis absorption spectra of TA/11-MU-Au NDs (50 nM) in sodium phosphate solution (10 mM, pH 3.0) in the (A) absence and (B) presence of NO_2^- ions (5.0 μM). Other conditions were as described in Fig. 1.

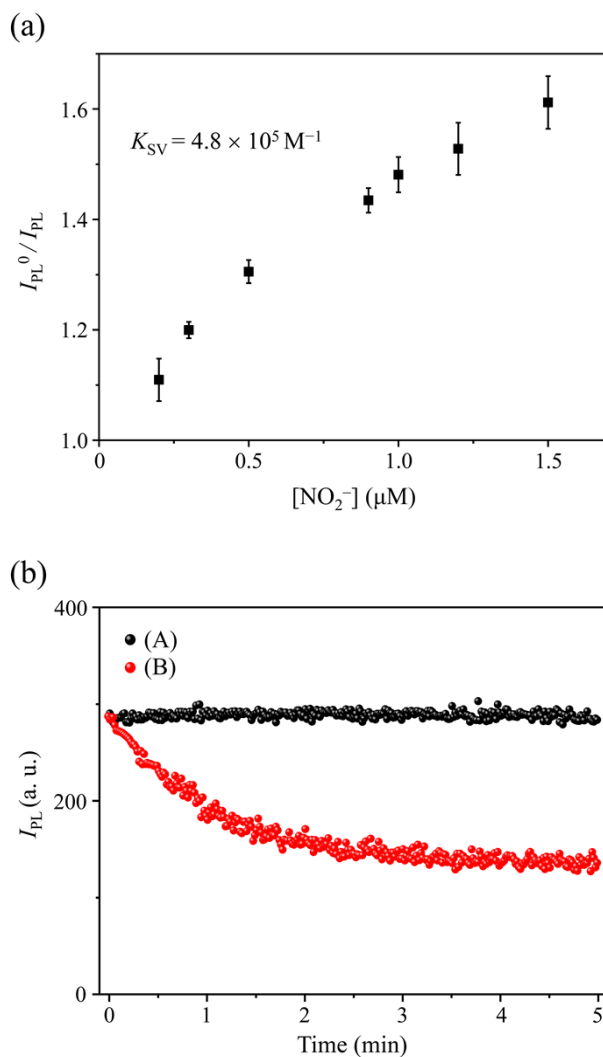


Fig. S7 (a) Stern-Volmer plot of the effect of NO_2^- ions (0–5.0 μM) on quenching efficiency of TA/11-MU–Au NDs (5.0 nM) in sodium phosphate solution (10 mM, pH 3.0). (b) Time-course measurements of PL intensity at 520 nm of sodium phosphate solution (10 mM, pH 3.0) containing (A) TA/11-MU–Au NDs (5.0 nM) and (B) TA/11-MU–Au NDs (5.0 nM) and NO_2^- ions (1.0 μM). Error bars in (a) represent standard deviations from three repeated experiments. I_{PL}^0 and I_{PL} in (a) are the PL intensities at 520 nm in the absence and presence of NO_2^- , respectively; K_{sv} is the Stern-Volmer quenching constant. Other conditions were as described in Fig. 1.

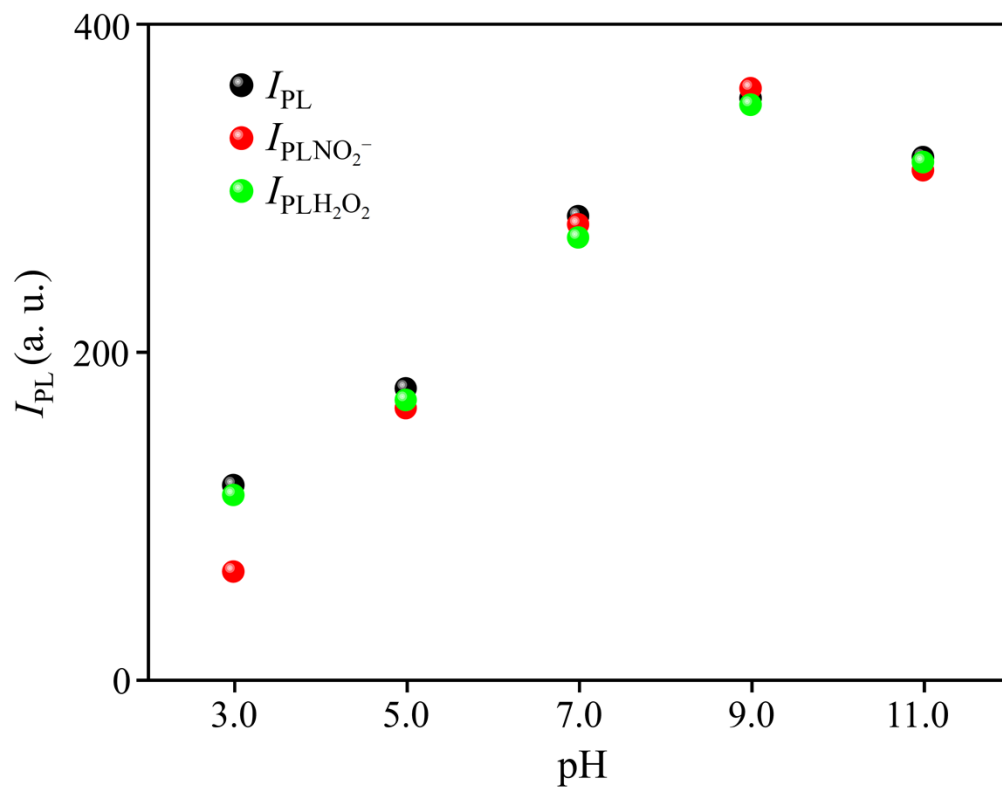


Fig. S8 Effect of pH on the PL intensity of the TA/11-MU-Au NDs (5.0 nM) at 520 nm in sodium phosphate solution (10 mM) in the absence (I_{PL}) and presence of 1.0 μM NO_2^- ions ($I_{\text{PLNO}_2^-}$) or 1.0 μM of H_2O_2 ($I_{\text{PLH}_2\text{O}_2}$). Other conditions were as described in Fig. 1.

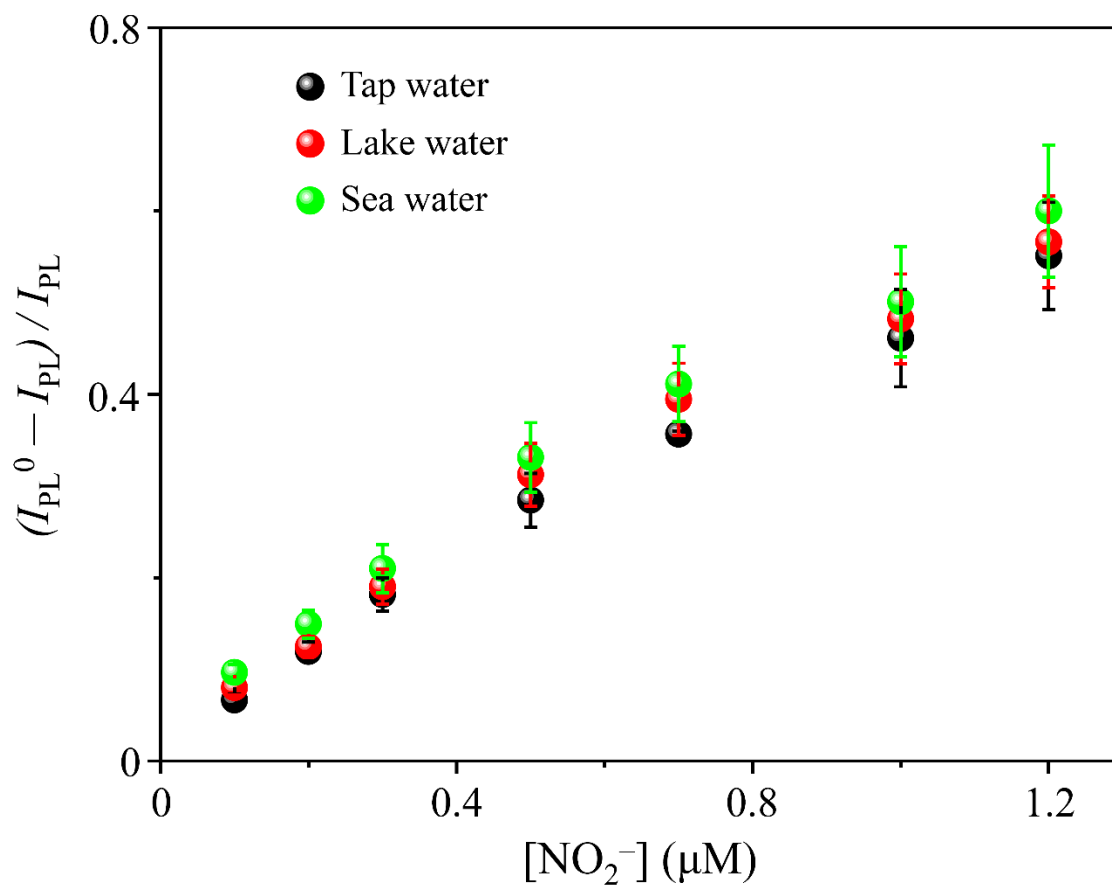


Fig. S9 Analyses of representative samples of tap water, lake water, and seawater using the TA/11-MU-Au ND probe. Diluted (two-fold) water samples were spiked with nitrite (0–1.2 μM). Error bars represent the standard deviations from three repeated experiments. Other conditions were as described in Fig. 2b.