Enhanced Quantum Yield of Dendrimer-Entrapped Gold Nanodots by a Specific Ion-Pair Association and Microwave Irradiation for Bioimaging

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Experimental Section

Preparation of All Pairs (from pair-1 to pair-4) and Synthesis of Gold Nanodots.

$HAuCl_4$ and $HAuBr_4$ (Sigma-Aldrich, 40 μL, 6 μmol, 150 mM) were added into 2 mL of deionized water containing G_4OH (Aldrich, 75.4 μL, 0.5 μmol, 10 wt % methanol solution) or G_4NH_2 (Aldrich, 87.4 μL, 0.5 μmol, 10 wt% methanol solution), respectively. The solution was incubated at 4^{o}C overnight before irradiating by microwave (CEM, Discover LabMate System, 300W/120^{o}C and 30 min). During the incubation, the color of two solutions for pair-1 and pair-3 turned brown overnight but that of the other solutions including pair-2 and pair-4 were still pale yellow. Subsequently, after microwave irradiation, the color of pair-1/pair-3 and pair-2/pair-4, respectively, became colorless and burgundy (Figure S1A). The precipitations and gold nanoparticles from all pairs after reduction were filtered through a 0.22-μm membrane filter (Millipore, PES membrane, for pair-1/pair3) and 3 KDa MWCO membrane filter (Millipore, Amico Ultra, for pair-2/pair-4). Gravimetric analysis showed that the weight percentages of precipitations and gold nanoparticles were 24.9% and 24.3%, respectively, for pair-2 and pair-3. The same analysis was applied to pair-1 and pair-4;

the percentages of precipitations and gold nanoparticles were approximately 28.6% and 31.3%, respectively. After microwave radiation, the optical absorbance properties were measured and their trends were matched to photographs (shown in Figure S1A). Finally, the photoluminescent properties of all pairs were measured after removal of the precipitations of gold nanoparticles.

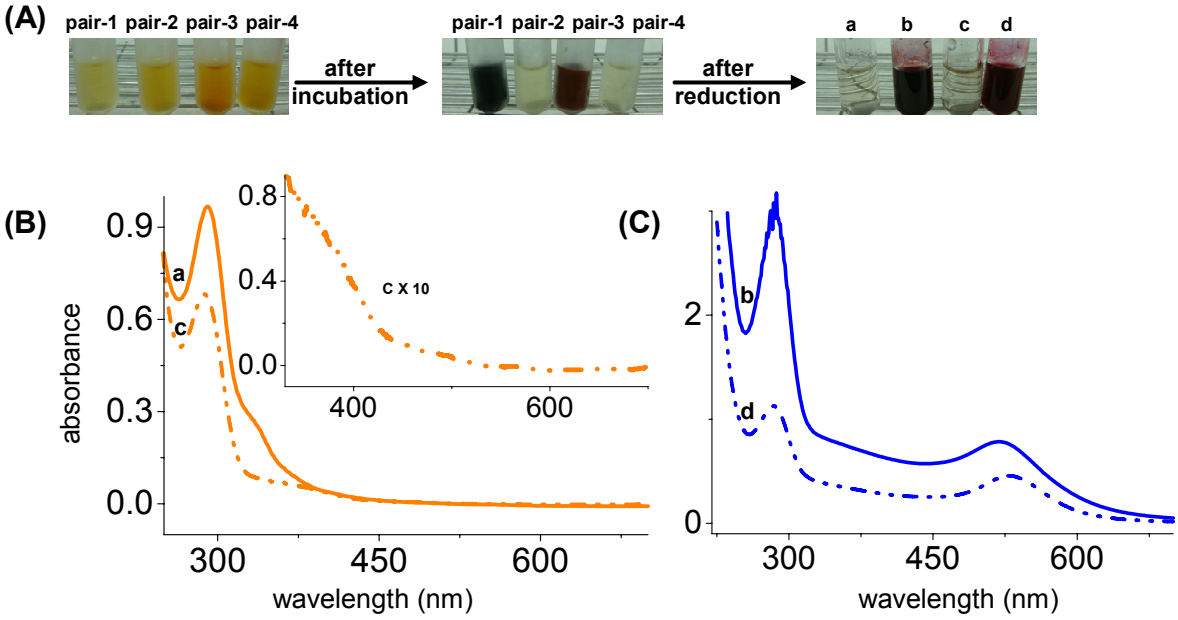

Figure S1. (A) Photographs of all pairs from incubation to reduction. (B) and (C) UV/Vis spectra from AuND-(a) to AuND-(d) after microwave irradiation.

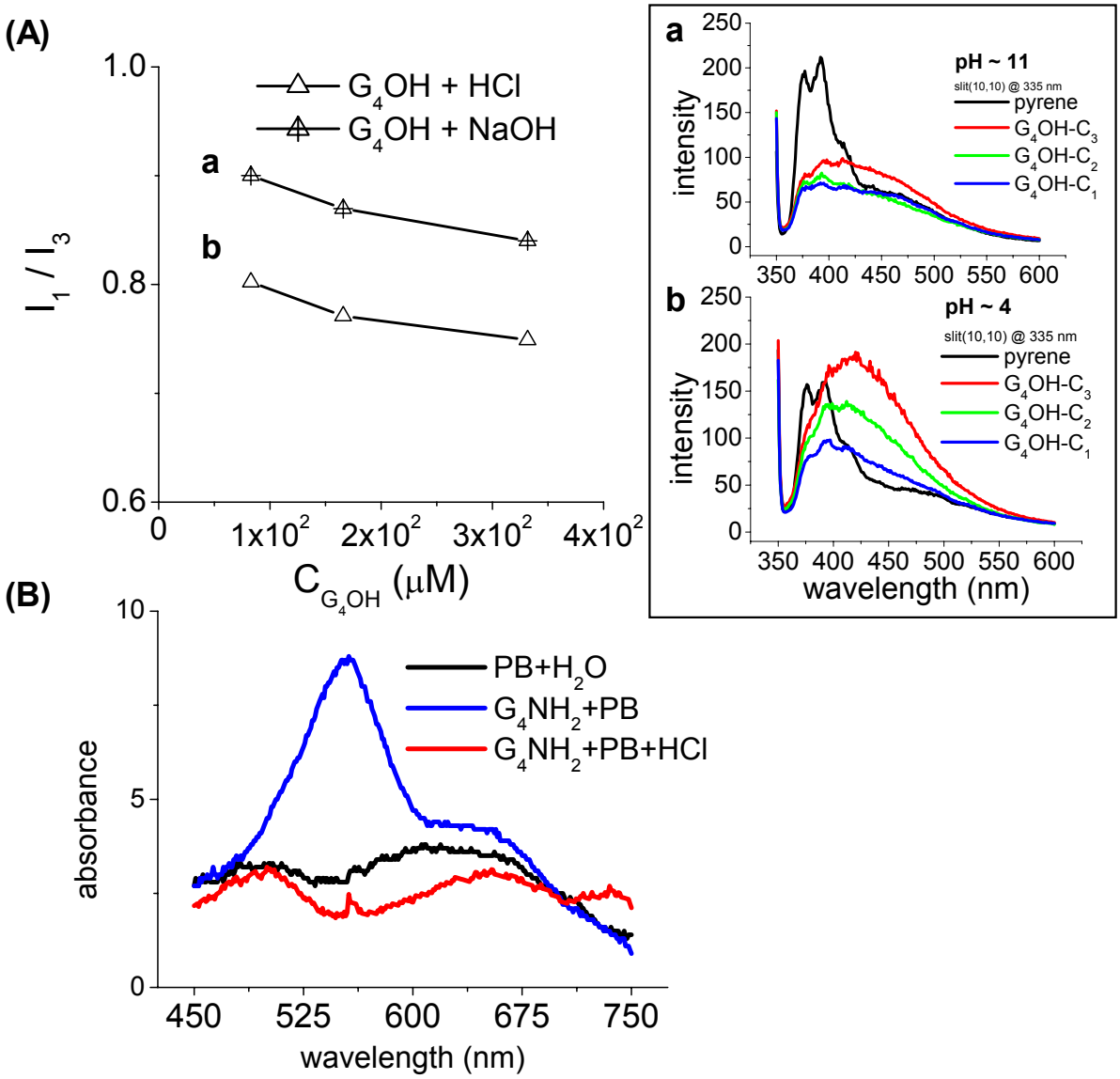

Figure S2. Polarities of G_4OH- and G_4NH_2-cavity were measured by two types of probes, pyrene and phenol blue (PB, also termed N, N-dimethylindoaniline).[1-3] (A) Variation of the intensity ratio of pyrene fluorescence peaks response to various G_4OH concentrations. The y-axis is the ratio of I_1/I_3; I_1 and I_3 are intensities at 372 nm and 383 nm, respectively. The insets a and b in panel A represent two fluorescence spectra of pyrene (5×10^{-4} M) that exhibit very obvious differences at two pH conditions. (B) Representative absorption spectra of PB (1×10^{-6} M) in aqueous G_4NH_2 (1×10^{-4} M). Two absorption bands centered at 560 nm and 650 nm, respectively, are contributed from PB in the hydrophobic and hydrophilic environments.

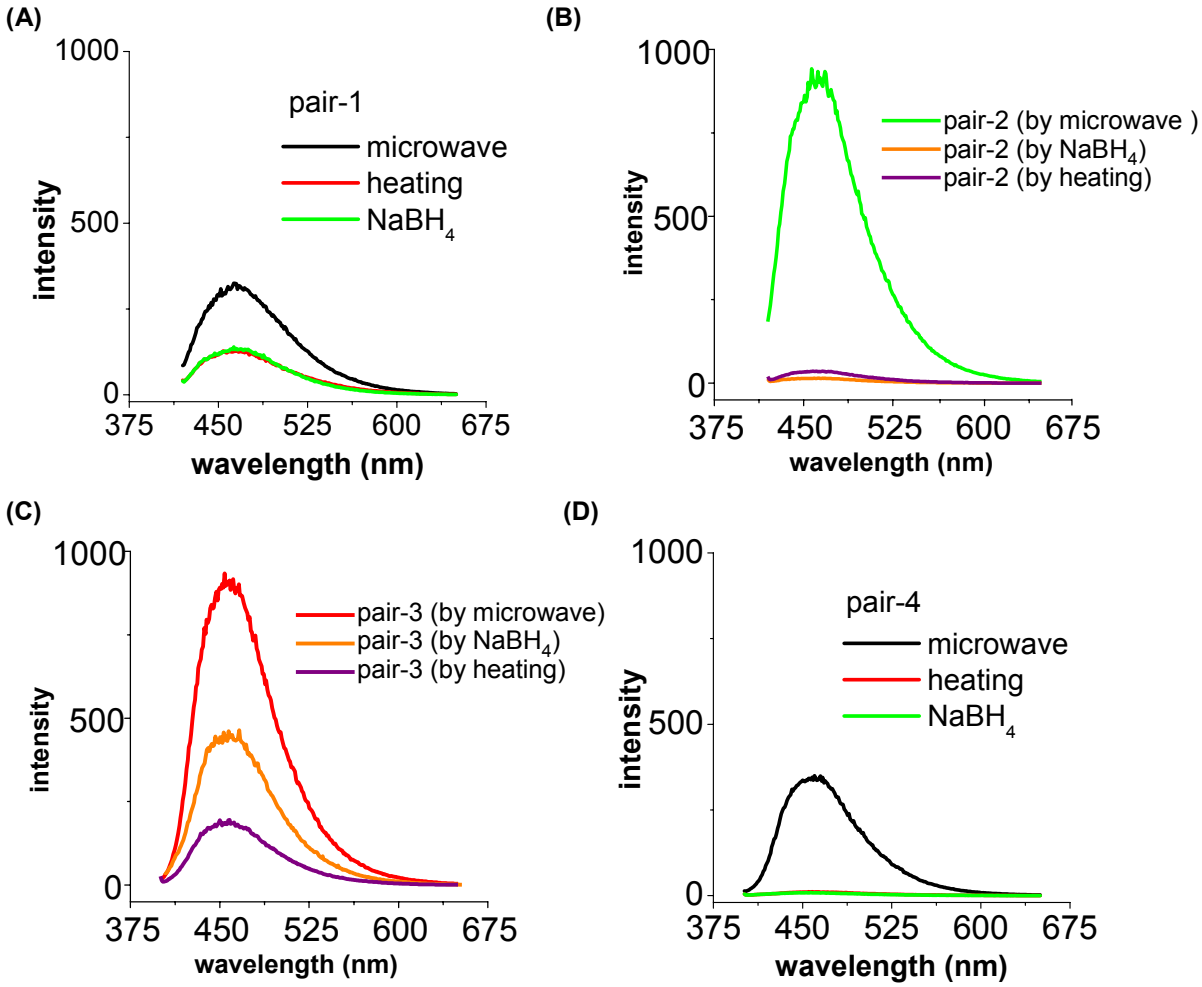

Figure S3. Emission spectra of (A) pair-1, (B) pair-2, (C) pair-3, and (D) pair-4 by treating with three reduction methods including microwave irradiation, $NaBH_4$, and heating.

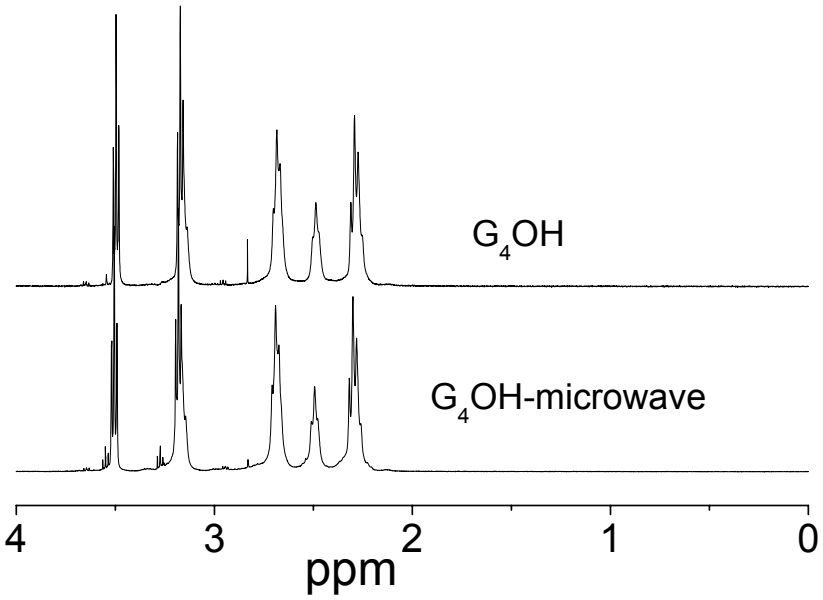

Figure S4. ^{1}H NMR spectra of HO-terminated G4 PAMAM were measured in D_2O to compare their changes in structure by microwave irradiation (300W/120^{o}C) after 45 min.

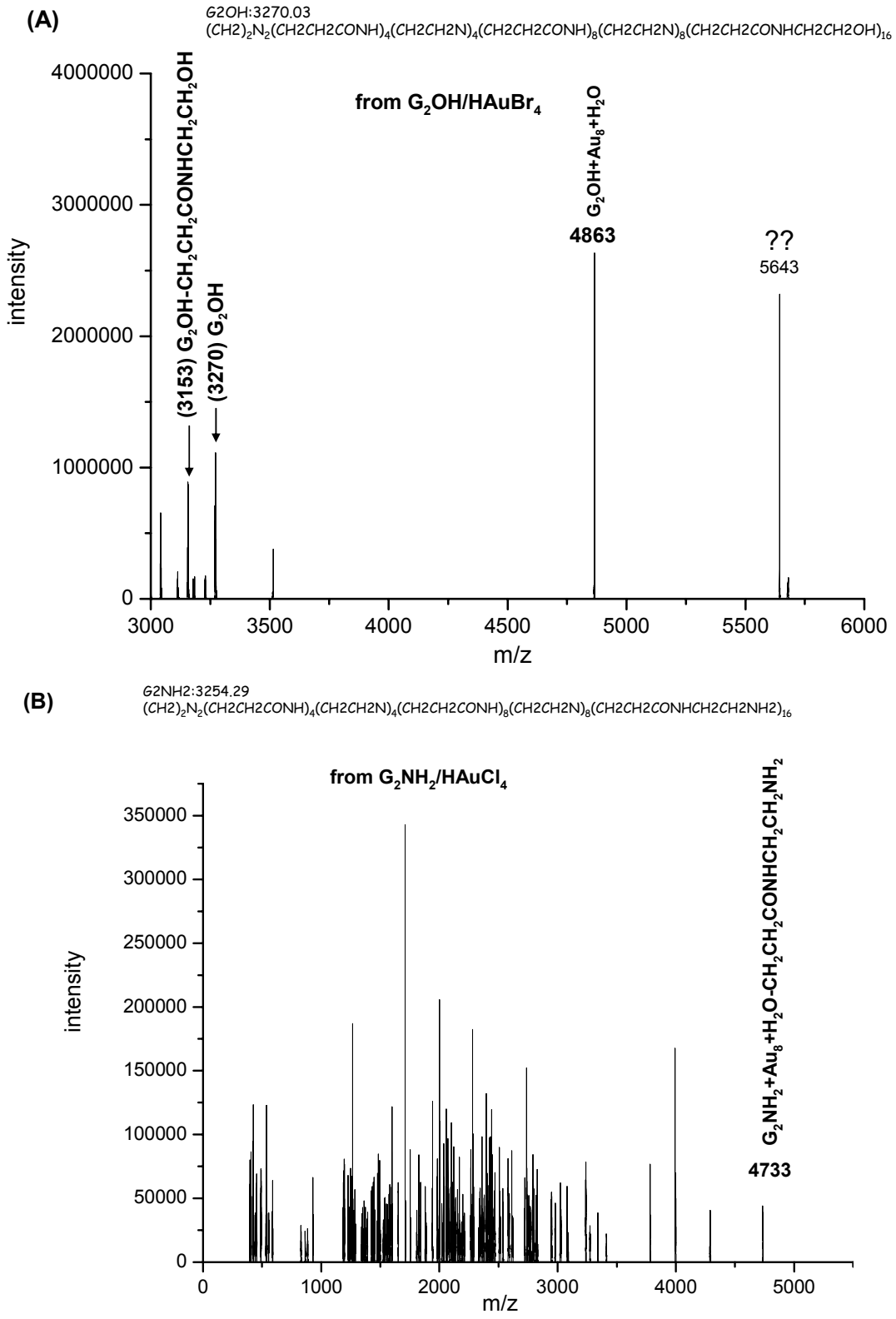

Figure S5. ESI-mass spectra of G_2OH/G_2NH_2-encapusulated Au_8 (lower generation dendrimers) from (A) $AuBr_4^-/G_2OH$-pair and (B) $AuCl_4^-/G_2NH_2$-pair, respectively.

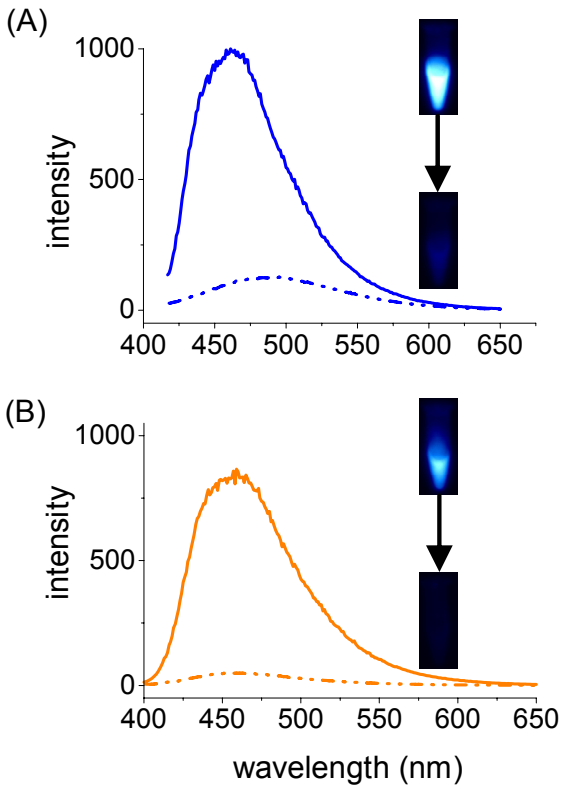

Figure S6. Emission spectra and photographs of Au_8 in response to two typical competition ions including Cl^- for (A) pair-2 ($AuCl_4^-/G_4NH_2$-pair) and Br^- for (B) pair-3 ($AuBr_4^-/G_4OH$-pair), respectively. The measurements were performed 15 min after microwave irradiation, and HCl and HBr were added into the mixture as competition ions.

Cellular Uptake. HeLa cells were cultured in a humidified atmosphere with 5% CO_2. The cell culture medium was minimum essential medium (MEM; Gibco) supplemented with 10% fetal bovine serum (FBS; Hyclone). For the imaging by confocal microscopy, cells were plated 24 h before the experiment. After incubation with Au_8-b and Au_8-d for 1.5 h, the cell image was captured by an Olympus (FV10i) confocal spectral microscope using a 63 x oil immersion objective.

references in supporting information:

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