

Supporting Information

Room Temperature Size Evolution of Thiol-Protected Gold Nanoparticles assisted by Proton Acids and Halogen Anions

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Experimental

Size evolution of thiol-protected Au NPs: In a typical synthesis, purified seed DT-Au NPs synthesized by Jana's method (about 2 nm, 20 mM as Au atom) and TOAB (80 mM) were dissolved in dry toluene (5 mL). Then TFA dry toluene solution was added to be 20 mM and the solution was immediately frozen in liquid N₂ and evacuated repeatedly. The solution was then stirred at room temperature or 55 °C under N₂ atmosphere. Since the reaction is relatively slow at room temperature, a reaction quenching is unnecessary for the room temperature reaction. At the relatively high temperature, the reaction was

quenched by adding amines such as triethylamine to neutralize the TFA. Repeated centrifugal purification using methanol or ethanol afforded pure DT-Au nanoparticles. (Note: Dry toluene, freeze evacuation, and N₂ atmosphere are not necessary for the reaction, although the trace amount of water or oxygen slightly changes the reaction rate.)

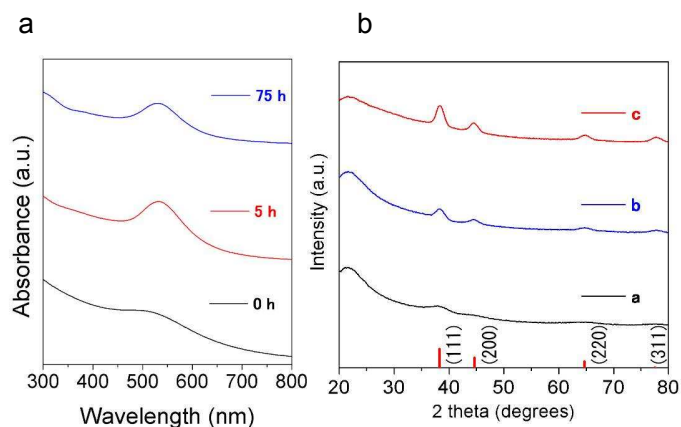


Figure S1. (a) UV-vis spectra of DT-Au NPs (2 mM as Au atoms) with TOAB (20 mM) and TFA (40 mM) at room temperature. (b) XRD patterns of seed DT-Au nanoparticles (a, 2 nm) and TFA treated DT-Au nanoparticles (b: 3.9 nm and c: 5.0 nm).

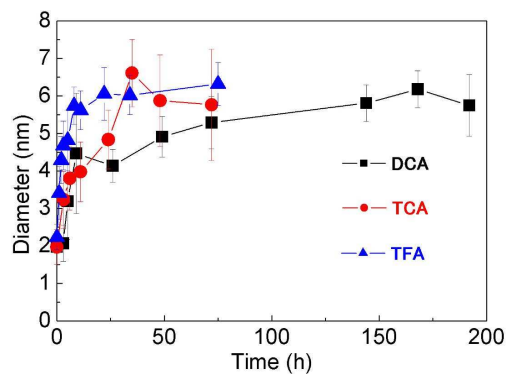


Figure S2. Size and size distribution changes of DT-Au NPs (5 mM as Au atom) with TOAB (50 mM) and either TFA, trichloroacetic acid (TCA) or dichloroacetic acid (DCA, 100 mM for all acids) at room temperature.

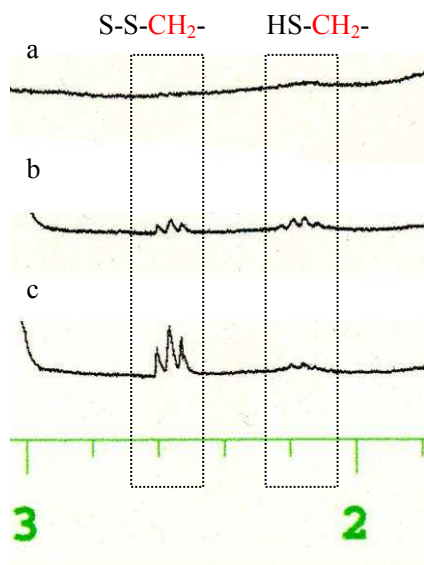


Figure S3. ^1H -NMR spectra of DT-Au NPs (0.6 M as Au atom), TOAB (30 mM) and TFA (60 mM) in benzene- d_6 at room temperature for (a) 0 h, (b) 48 h and (c) 312 h. The chemical shifts of 2.58 ppm and 2.18 ppm were assigned to α -proton (neighboring methylene proton to sulfur atom) of di-*n*-dodecyl disulfide and *n*-dodecanethiol, respectively.

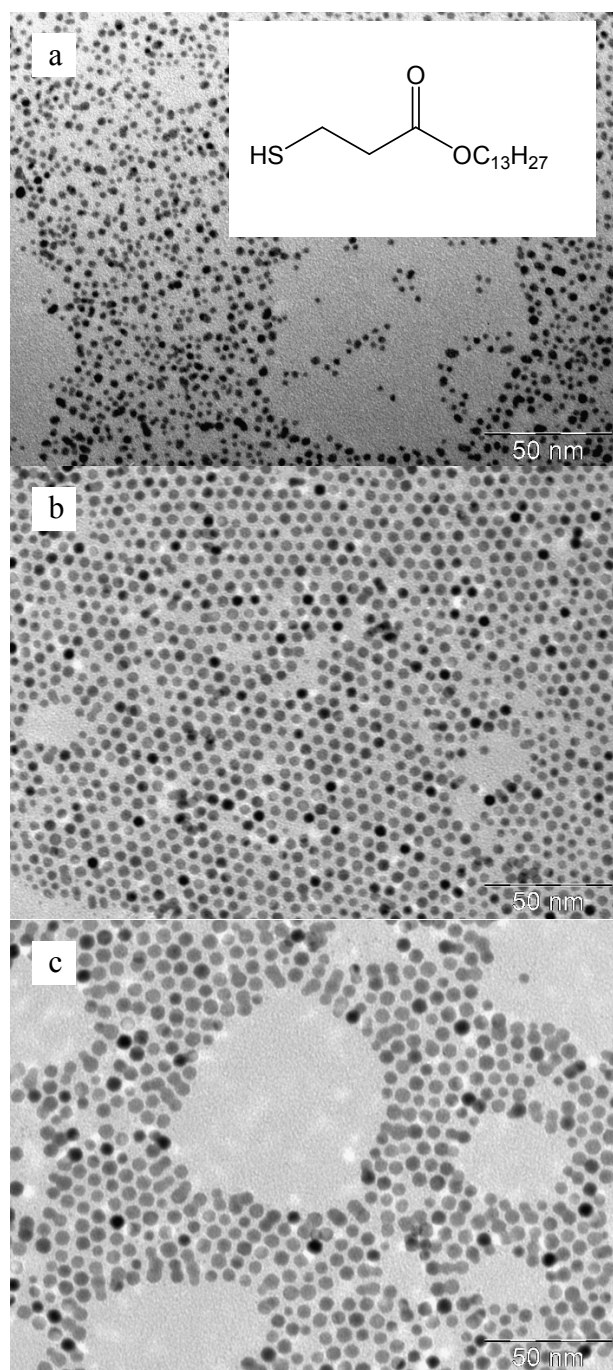


Figure S4. TEM images of (a) tridecyl 3-mercaptopropanate (TDMP)-protected Au seed NPs (2.5 ± 0.5 nm), (b) TDMP-Au NPs (5 mM as Au atoms) reacted with TFA (100 mM) and TOAB (50 mM) at r.t. for 44 h (4.3 ± 0.5 nm) and (c) 267 h (5.4 ± 0.7 nm). Inset in Figure S3a shows chemical structure of TDMP.

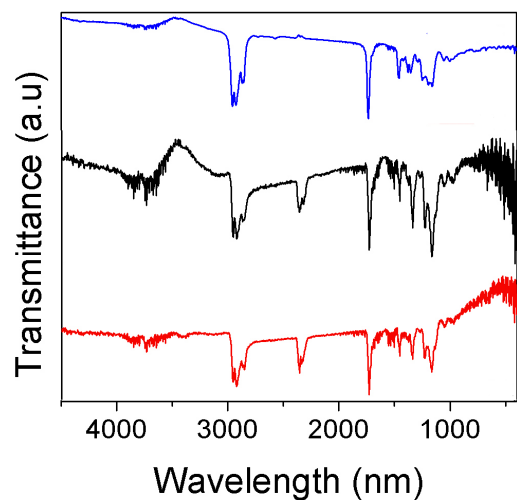


Figure S5. IR spectra of (a) TDMP, (b) seed TDMP-Au NPs, and (c) TDMP-Au NPs (5 mM as Au atoms) reacted with TFA (100 mM) and TOAB (50 mM) at r.t. for 29 h.

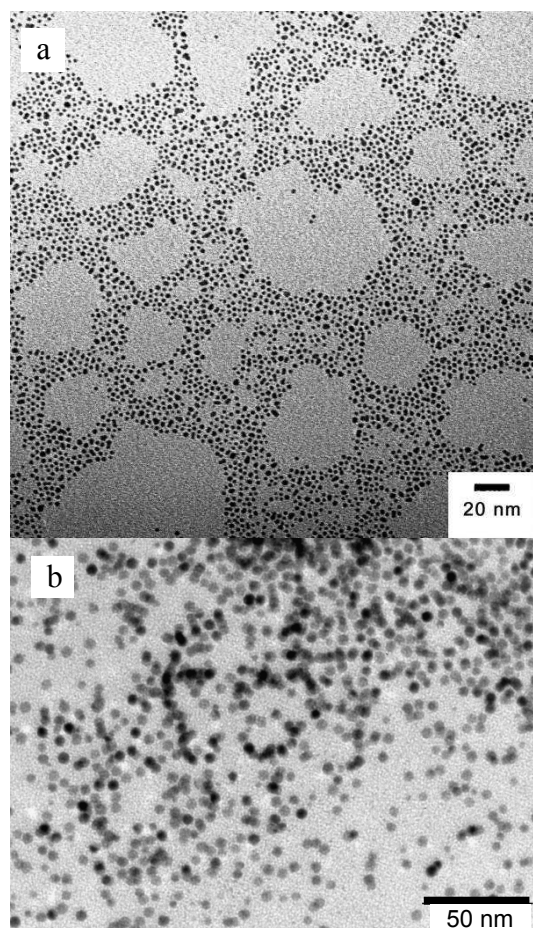


Figure S6. TEM images of (a) hexanethiol protected Au seed NPs (2.2 ± 0.4 nm) and (b) hexanethiol protected Au NPs (5 mM as Au atoms) reacted with TFA (100 mM) and TOAB (50 mM) at 10 °C for 13 h (4.8 ± 0.5 nm).