Supporting Information

Solid Phase Synthesis of Soluble Nanoparticles with Anchored, Recyclable Dendrimer Templates

John D. Gilbertson,[A] Ganesh Vijayaraghavan,[B] Keith J. Stevenson,[B] and Bert D. Chandler[*,A]

[A]Department of Chemistry, Trinity University, San Antonio, TX 78212-7200, and

[B]Department of Chemistry, University of Texas at Austin, 1 University Station A5300,

Austin, Texas 78712-0165

[*]Bert.chandler@trinity.edu

Table of Contents

Determination of the reaction yield of 1,2-epoxydodecane with $G5NH_{2anch}$. To a freshly prepared solution (5 mL DMF-d_6 + 3 mL CD_3OD) of 2.0 g (1.2 μmol) $G5NH_{2anch}$, 75 μmol toluene was also added as an internal standard and allowed to shake at 50 rpm in a sealed vessel at 45 ˚C for 2 hours (to account for any loss due to swelling of the beads). After two hours, 30.0 mg (163 μmol) 1,2-epoxydodecane was added and an aliquot was immediately analyzed by ^{1}H NMR. The solution was then shaken at 50 rpm in a sealed vessel at 45 ˚C for 48 hours and analyzed by ^{1}H NMR every 24 hours. The resonances at 2.6 ppm (1,2-epoxydodecane) and 7.2 ppm (toluene) were integrated and compared to determine ~ 50% coverage of $G5NH_{2anch}$ by 1,2-epoxydodecane to produce $G5C12_{anch}$ after 48 hours.

UV-Vis titration plot of Co^{II} complexation by G5C12 in solution. In a quartz UV-Vis cuvette, 5 mL of a 2.2 μM solution of G5C12 in toluene was stirred. To that solution, 17 μL of an 8.4 mM solution of $CoCl_2 \cdot 6H_2O$ in EtOH was added every 5 minutes with stirring. A UV-Vis spectrum of the solution was collected after each aliquot (up to 400 equivalents Co^{II}) was added.

$G0NH_2$ anchoring and alkylation. 500 mg Mp-anhydride resin (3.70 mmol anhydride) was swelled in 5 mL DMF for one hour, followed by addition of 6 mg $G0NH_2$ PAMAM dendrimer (0.122 μmol) dissolved in 3 mL CH_3OH. The vessel was sealed, placed in a shaker at 50 rpm, and heated at 45 ˚C for 12 hours. The anchored amine terminated dendrimer is denoted $G0NH2_{anch}$.

To the above solution 12.0 mg (65.1 μmol) 1,2-epoxydodecane was added. The solution was shaken at 50 rpm in a sealed vessel at 45 ˚C for 48 hours. After reaction, the

beads were filtered, rinsed with MeOH, and allowed to dry in a vacuum oven at 40 °C overnight. The alkylated $G0NH2_{anch}$ is denoted $G0C12_{anch}$.

Encapsulation and reduction of Au^{III} with $G0C12_{anch}$. 200 mg of alkylated anchored dendrimer beads ($G0C12_{anch}$) containing an average dendrimer loading of 4.65 μmol were stirred in 20 mL toluene for one hour. To that mixture, 3 mg of $HAuCl_4$ in 1 mL of EtOH was added to the solution to simulate a 55:1 Au:dendrimer molar ratio, respectively. This simulated ratio is based on the # of primary amines present (which is the same as in the $G5C12_{anch}$) allowing comparison of the respective templating ability of the two different generation of dendrimers. The beads and $HAuCl_4$ were allowed to stir for one hour and then were filtered, rinsed with 10 mL (3x) toluene, and redispersed in 20 mL fresh toluene. 2000 μL of a freshly prepared 50 mM $NaBH_4$ in MeOH was then added to the stirring beads, instantly changing their color from yellow to purple.

Extraction of Au nanoparticles from the $G0C12_{anch}$. The above mixture was decanted and 10 mL of toluene containing 3000 μL decanethiol was added to the beads with vigorous stirring. The solution remained colorless, and the beads remained purple, after stirring for 24 hours. No extraction was observed.

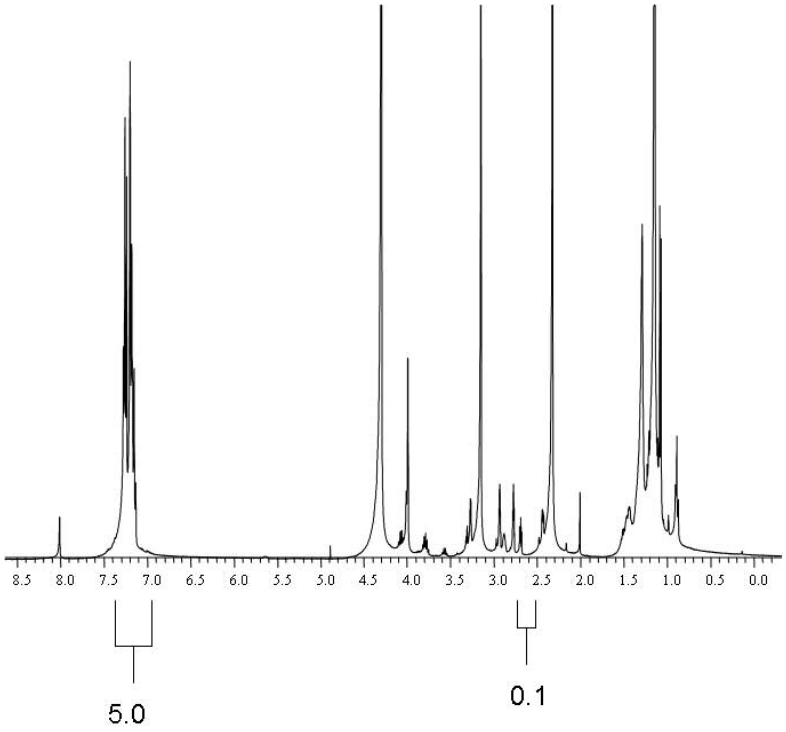

Figure S1. ^{1}H NMR spectrum of the reaction mixture between G5NH$_{2anch}$ and 1,2-epoxydodecane after 48 hours. The resonance at 7.2 ppm corresponds to an internal standard of 75 μmol toluene. The resonance at 2.6 ppm is attributed to one proton on the unreacted 1,2-epoxydodecane.

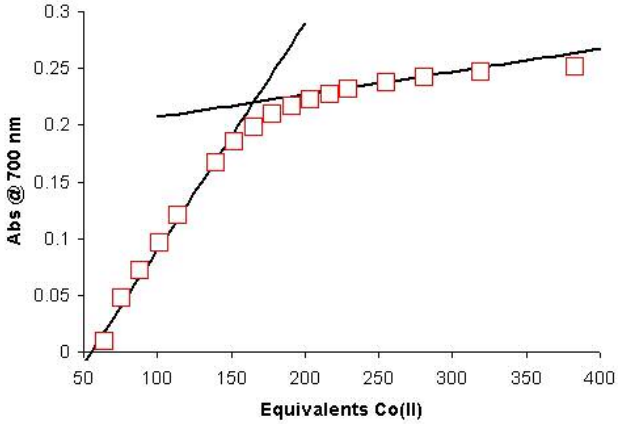

Figure S2. Titration plot of Co^{II} uptake by 2.2 μM G5C12 with in solution. The intersection point corresponds to ~165 equivalents of Co^{II} per dendrimer.

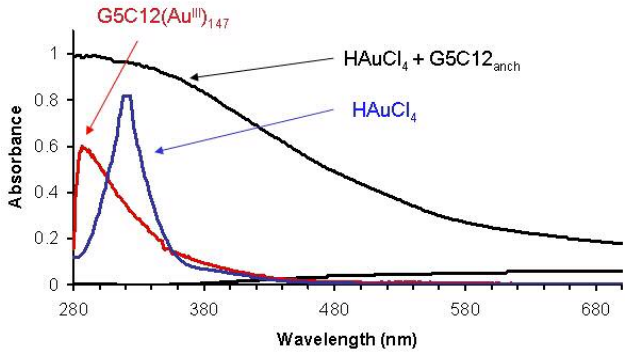

Figure S3. UV-visible spectra of solutions of 200 µM $HAuCl_4$ (blue line) and $G5C12(Au^{III})_{147}$ (red line) in EtOH/toluene. The black line is a UV-visible reflectance spectrum of filtered and dried $HAuCl_4$ and $G5C12_{anch}$.

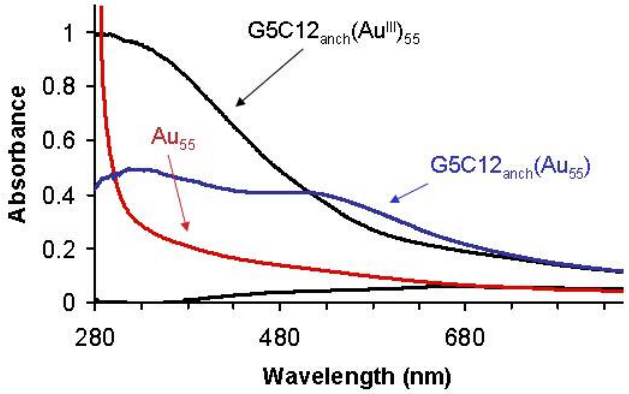

Figure S4. UV-Vis reflectance spectra of $G5C12_{anch}(Au^{III})_{55}$ (black) and $G5C12_{anch}(Au_{55})$ DENs (blue), as well as a solution UV-Vis spectrum of $(C_{10}SH)$ Au_{55} MPCs (red). The black line with no absorbance is a UV-Vis reflectance spectrum of filtered and dried resin beads that were stirred with $HAuCl_4$ (no Au^{III} uptake).

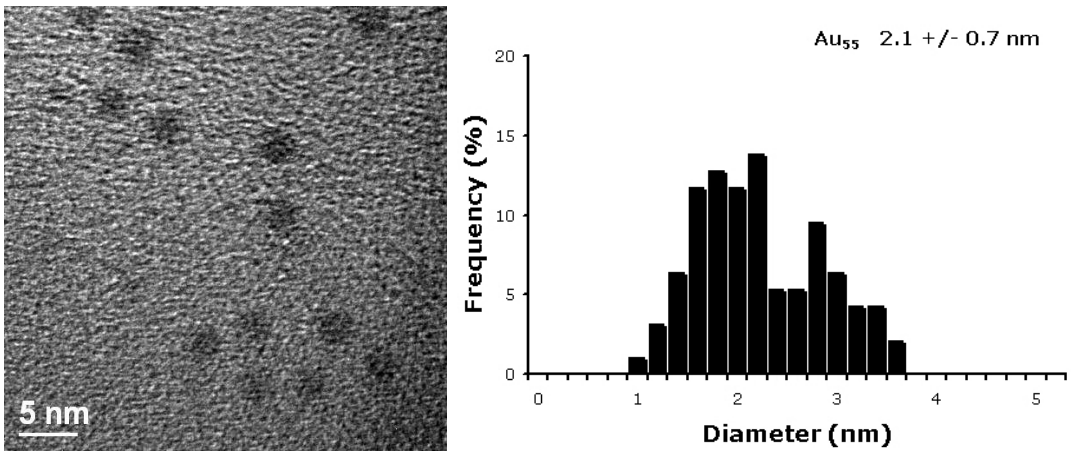

Figure S5. TEM image of ($C_{10}SH$) Au_{55} MPCs synthesized from $G5C12_{anch}$. The corresponding particle size distribution (100 particles) is also shown. Note: the larger and somewhat bimodal particle size distribution may indicate that the anchored dendrimers are less effective at templating smaller particles, or that the extraction is less effective for the smaller metal:dendrimer ratio.

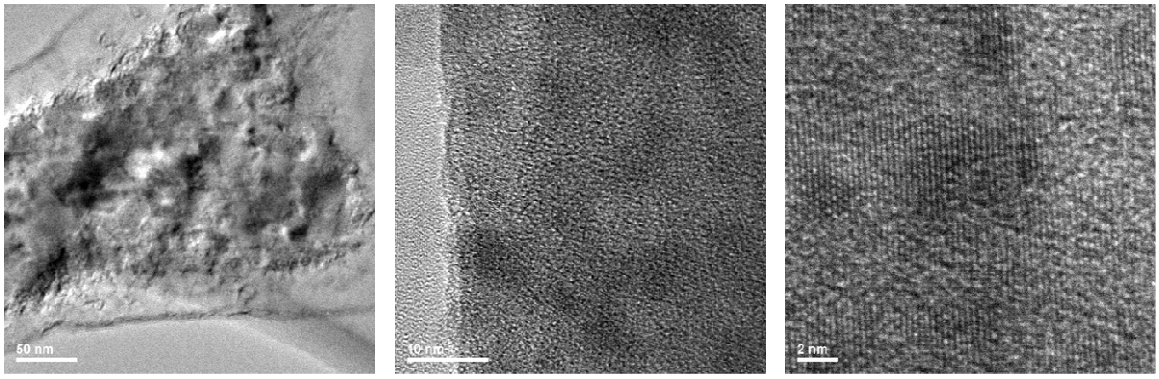

Figure S6. TEM images of $G5C12_{anch}(Au_{147})$ pre extraction. Note the presence of dark spots approximately ~2-3 nm in size.