Supporting Information

Dually Functionalized Dendrimers by Temperature-Sensitive Surface Modification and Gold Nanoparticle Loading for Biomedical Application

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Synthesis of 4-Nitrophenyl chloroformate functionalized propoxy diethylene glycol (PDEG)

4-Nitrophenyl chloroformate functionalized propoxy diethylene glycol (PDEG-NPC) was synthesized as follows. Propoxy di(ethylene glycol) (3.1 g, 13.7 mmol) and Triethylamine (4.64 ml, 33.3 mmol) were dissolved in 30 ml dry THF, then 4-Nitrophenyl chloroformate (NPC) (5.0 g, 25 mmol) was added. The mixed solution was stirred at room temperature overnight. Then the compound was purified by silica gel (ethyl acetate/hexane = 1/1) and dried in vacuum to afford the final product (PDEG-NPC) (2.3 g, yield 45%). The structure of PDEG was confirmed by ^{1}H NMR (Figure S1). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 0.92 (t, Ha), 1.62 (m, Hb), 3.44 (t, Hc), 3.62 (t,Hd), 3.70 (t,), 3.83 (t, Hf), 4.46 (t, Hg), 7.39 (d, Hh), 8.28 (d,Hi).

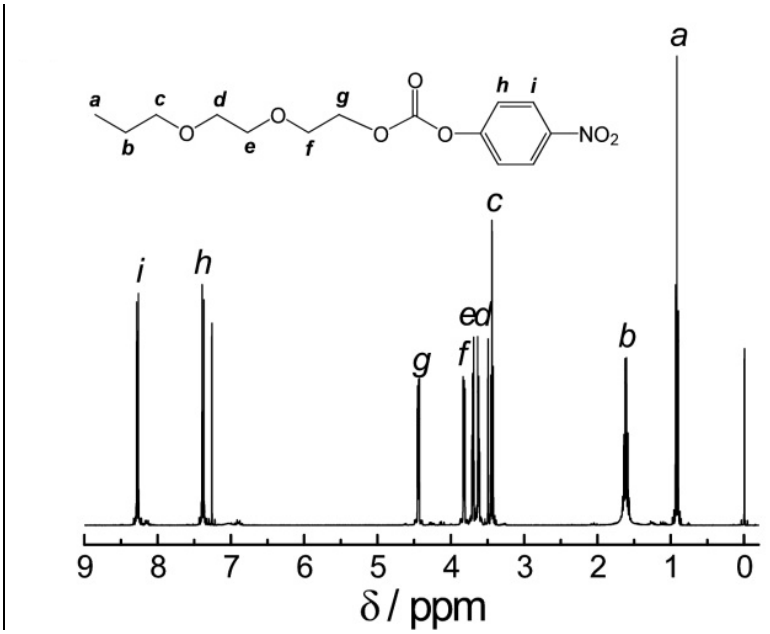

Figure S1. ^{1}H NMR spectrum of PDEG-4-nitrophenyl carbonate in $CDCl_3$.

Synthesis of PDEG-modified PAMAM G5 dendrimer

The PAMAM G5 dendrimer (172 mg, 6.0 μmol) was dissolved in 5 ml dry DMSO. PDEG-NPC (479mg, 1.53 mmol) was dissolved in 3 ml dry DMSO and then was added to the dendrimer solution. The mixed solution was stirred at room temperature for 5 days. The synthesized dendrimer was purified by Sephadex LH20 column with methanol as elution solvent. The eluting dendrimers were detected using an UV detector at a fixed wavelength of 220 nm. The dendrimer solution was dried in vacuum to afford the final product PDEG-G4-PAMAM (262.9 mg, yield 88%). The structure of PDEG-modified PAMAM G5 dendrimer was confirmed by ^{1}H NMR (Figure S2) and ^{13}C NMR (Figure S3). ^{1}H NMR (400 MHz, CD_3OD) : δ 0.91 (t, Ha), 1.57 (q, Hb), 2.39 (br, Hj), 2.64 (br, Hl), 2.84 (br, Hk), 3.26 (br, Hh, Hi, Hm), 3.41 (t, Hc), 3.61 (t, Hd,He,Hf), 4.15 (br, Hg). ^{13}C NMR (400 MHz, CD_3OD) : δ 13.0, 25.9, 36.3, 40.4, 42.4, 43.3, 53.1, 55.5, 67.1, 72.5, 73.1, 73.5, 75.9,160.7, 176.7.

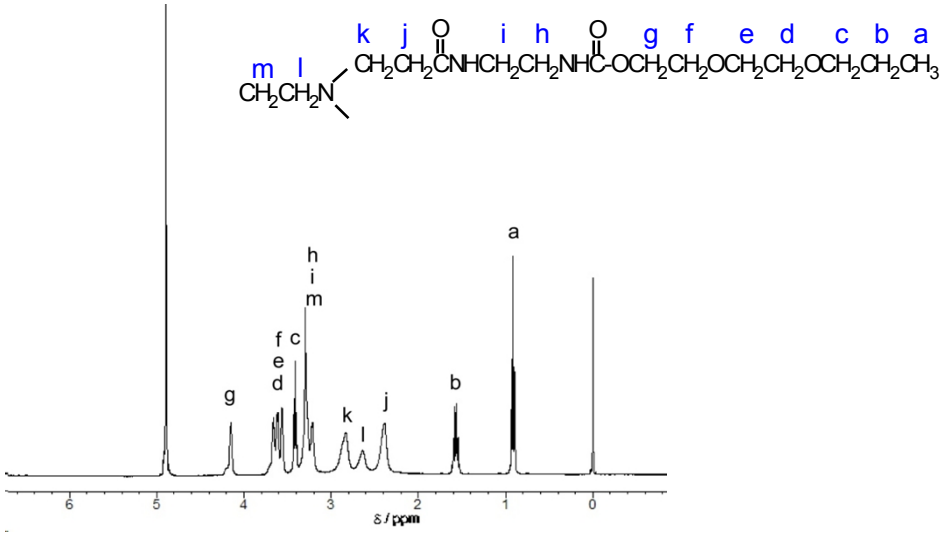

Figure S2. ^{1}H NMR spectrum of PDEG-G5 in CD_3OD (400 MHz).

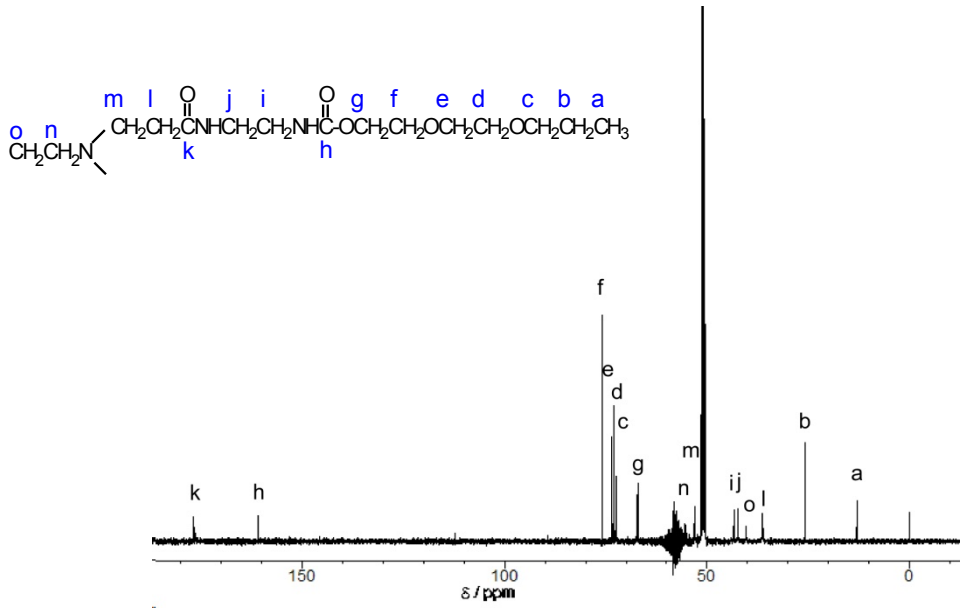

Figure S3. ^{13}C NMR spectrum of PDEG-G5 in D_2O (400 MHz).

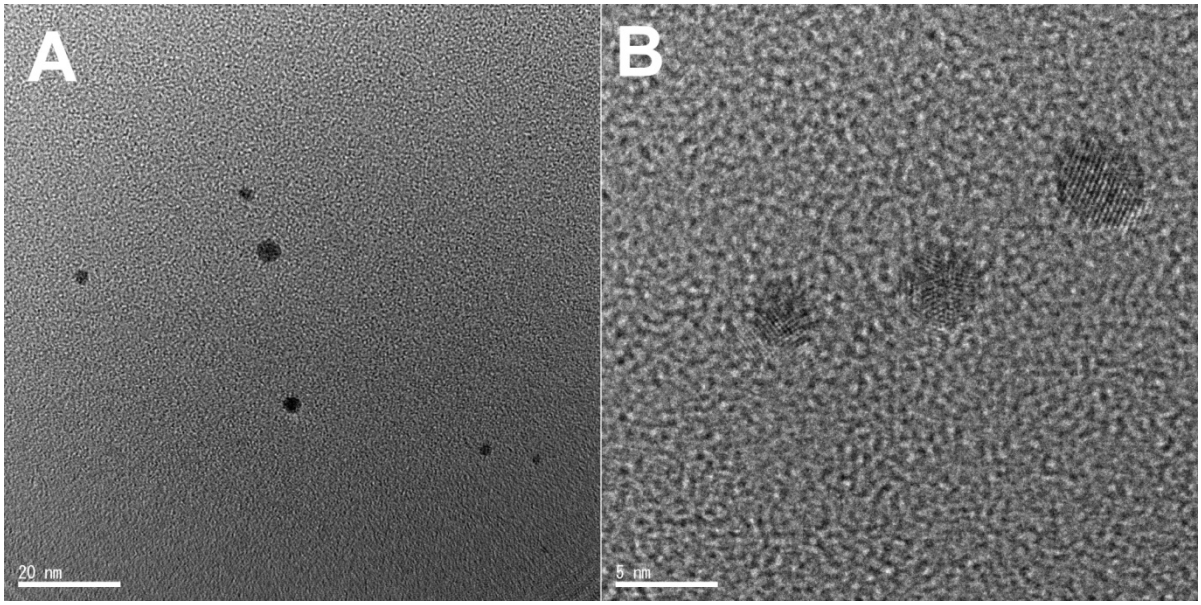

Figure S4. High resolution TEM images for PDEG-G5-Au_{10} with lower (A) and higher (B) magnifications. Bars in (A) and (B) represent 20 nm and 5 nm, respectively.

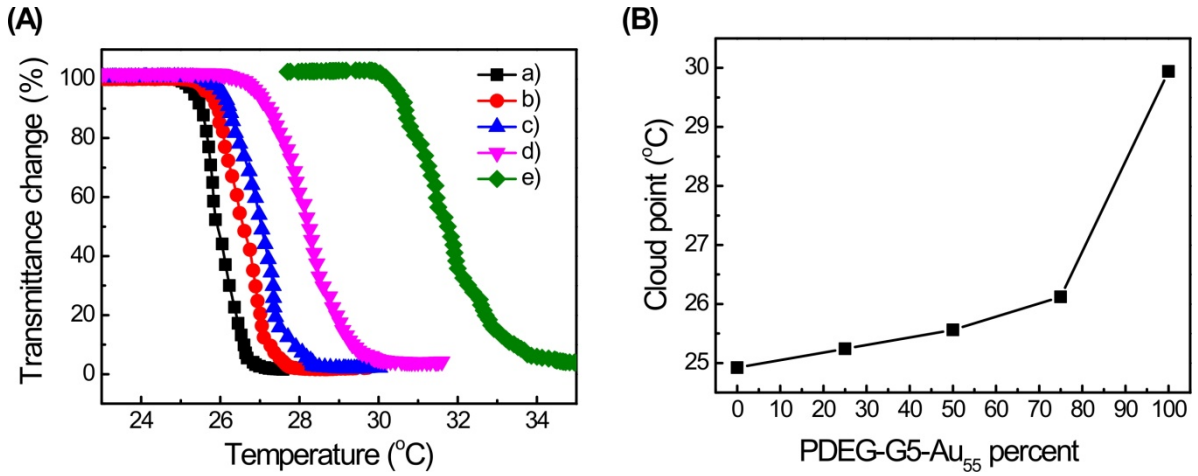

Figure S5. (A) Effect of temperature on transmittance for solutions of (a) PDEG-G5, (b) 75% PDEG-G5 + 25% PDEG-G5-Au_{55}, (c) 50% PDEG-G5 + 50% PDEG-G5-Au_{55}, (d) 25% PDEG-G5 + 75% PDEG-G5-Au_{55}, and (e) PDEG-G5-Au_{55}. (B) Cloud point of mixed PDEG-G5 and PDEG-G5-Au_{55} solutions as a function of PDEG-G5-Au_{55} content. All samples were dissolved in 50 mM phosphate buffer solution (pH 7.0). [dendrimer] = 1.5 mg/mL.

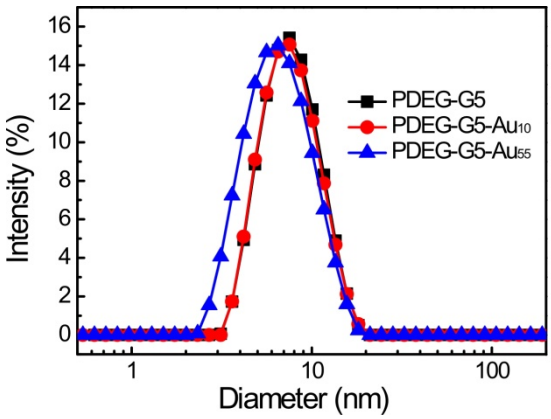

Figure S6. Size distribution of dendrimers in phosphate buffered saline (pH 7.4) were measured using a Zetasizer Nano ZS90 (Malvern Instruments) with a standard He−Ne 633 nm laser and 173° back scatter. Mean diameters and standard deviations for PEDG-G5, PDEG-G5-Au_{10}, and PDEG-G5-Au_{55} dendrimers were estimated as 8.0±2.8 nm, 8.0±2.9 nm, and 7.0±3.0 nm, respectively.