Macromolecular Structure Evolution toward Giant Molecules of Complex Structure: Tandem Synthesis of Asymmetric Giant Gemini Surfactants

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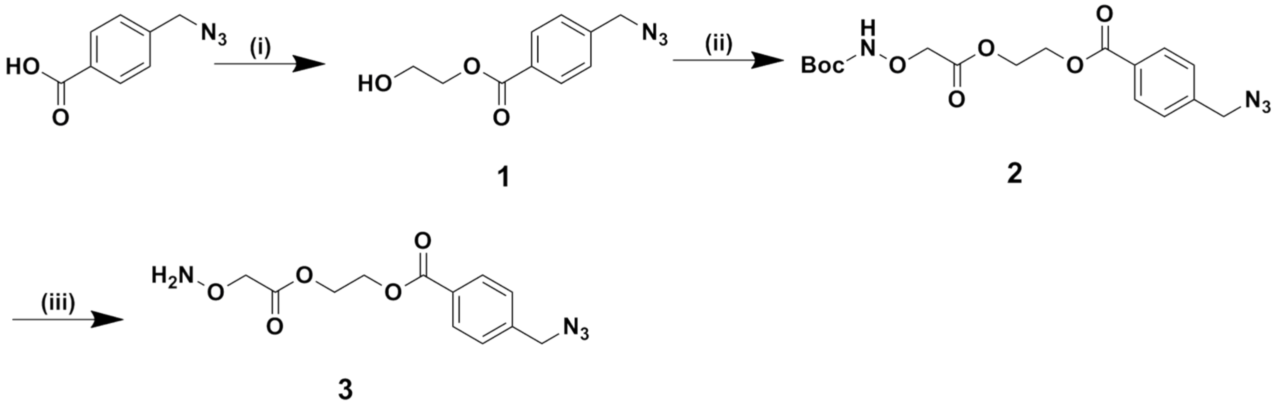
Synthetic Procedures



Scheme S1. Synthetic Approach for compound 3 as the "click" adaptor: (i) ethylene glycol, DPTS, DIPC, dry CH_2Cl_2, 0 °C, 68%; (ii) (boc-aminooxy) acetic acid, DPTS, DIPC, dry CH_2Cl_2, 0 °C, 83%; (iii) hydrogen chloride solution, 25 °C, 84%.

Compound 1. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar was added 4-(azidomethyl)benzoic acid (177 mg, 1.0 mmol), ethylene glycol (620 mg, 10.0 mmol) and DPTS (295 mg, 1.0 mmol), followed by the addition of 30 mL freshly dried CH_2Cl_2 to fully dissolve the solids. The mixture was capped by a rubber septum, cooled to 0 ^{o}C and stirred for 10 min before DIPC (189 mg, 1.5 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hr. The white precipitates were then filtered off and the filtrate was washed with water and brine, dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using CH_2Cl_2 as the eluent to afford the product (150 mg, 68 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.05 (d, 2H, $-OCCC_2\underline{H}_2-$), 7.36 (d, 2H, $-CH_2CC_2\underline{H}_2-$), 4.43 (t, 2H, $-OC\underline{H}_2CH_2OH$), 4.38 (s, 2H, $-C\underline{H}_2N_3$), 3.93 (t, 2H, $-OCH_2C\underline{H}_2OH$), 2.74 (s, 1H, $-OCH_2CH_2O\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 166.48, 140.68, 130.18, 129.74, 127.92, 66.68, 61.06, 54.18.

Compound 2. To a 100 mL round-bottomed flask equipped with a magnetic stirring bar was added compound 1 (221 mg, 1.0 mmol), (boc-aminooxy) acetic acid (201 mg, 1.05 mmol) and DPTS (295 mg, 1.0 mmol), followed by the addition of 30 mL freshly dried CH_2Cl_2 to fully dissolve the solids. The mixture was capped by a rubber septum, cooled to 0 ^{o}C and stirred for 10 min before DIPC (189 mg, 1.5 mmol) was added dropwise via a syringe. The mixture was allowed to warm up to room temperature and stirred for another 12 hr. The white precipitates was then filtered off and the filtrate was washed with water and brine, dried over Na_2SO_4. After solvent removal, the residue was purified by flash chromatography on silica gel using CH_2Cl_2/EtOAc (v/v = 8/1) as the eluent to afford the product (342 mg, 83 %). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 8.07 (d, 2H, $-OCCC_2\underline{H}_2-$), 7.82 (s, 1H, $-CH_2ON\underline{H}-$), 7.39 (d, 2H, $-CH_2CC_2\underline{H}_2-$), 4.56 (m, 4H, $-OC\underline{H}_2C\underline{H}_2O-$), 4.47 (s, 2H, $-C\underline{H}_2ONH-$), 4.42 (s, 2H, $-C\underline{H}_2N_3$), 1.48(s, 9H, $-OOCC(C\underline{H}_3)_3$). ^{13}C NMR (75 MHz, $CDCl_3$, ppm, δ): 169.40, 165.83, 156.25, 140.82, 130.21, 129.46, 127.96, 82.01, 72.47, 62.80, 62.50, 54.17, 28.11.

Compound 3 (the "Click" Adaptor). Compound 2 (300 mg, 0.73 mmol) was dissolved in 10 mL of hydrogen chloride solution. The solution was stirred for 4 h, followed by the addition of excess Et_3N to adjust the pH. The white precipitates were then filtered off and the filtrate was then evaporated under vacuum. The residue was purified by flash chromatography on silica gel using CH_2Cl_2/EtOAc (v/v = 1/3) as the eluent to afford the product as a white powder (180 mg, 84 %). ^{1}H NMR (300 MHz, DMSO-d6, ppm, δ): 8.00 (d, 2H, $-OCCC_2\underline{H}_2-$), 7.53 (d, 2H, $-CH_2CC_2\underline{H}_2-$), 4.79 (s, 2H, $-C\underline{H}_2ONH_2$), 4.58 (s, 2H, $-C\underline{H}_2N_3$), 4.50 (m, 4H, $-OC\underline{H}_2C\underline{H}_2O-$), 3.58 (s, 2H, $-ON\underline{H}_2$). ^{13}C NMR (75 MHz, DMSO-d6, ppm, δ): 168.12, 165.77, 141.77, 130.16, 129.49, 128.94, 70.69, 63.37, 53.49. MS (ESI MS): Calcd. for $C_{12}H_{15}N_4O_5$ 295.10, Found: 294.76 $(M{\cdot}H)^+$.

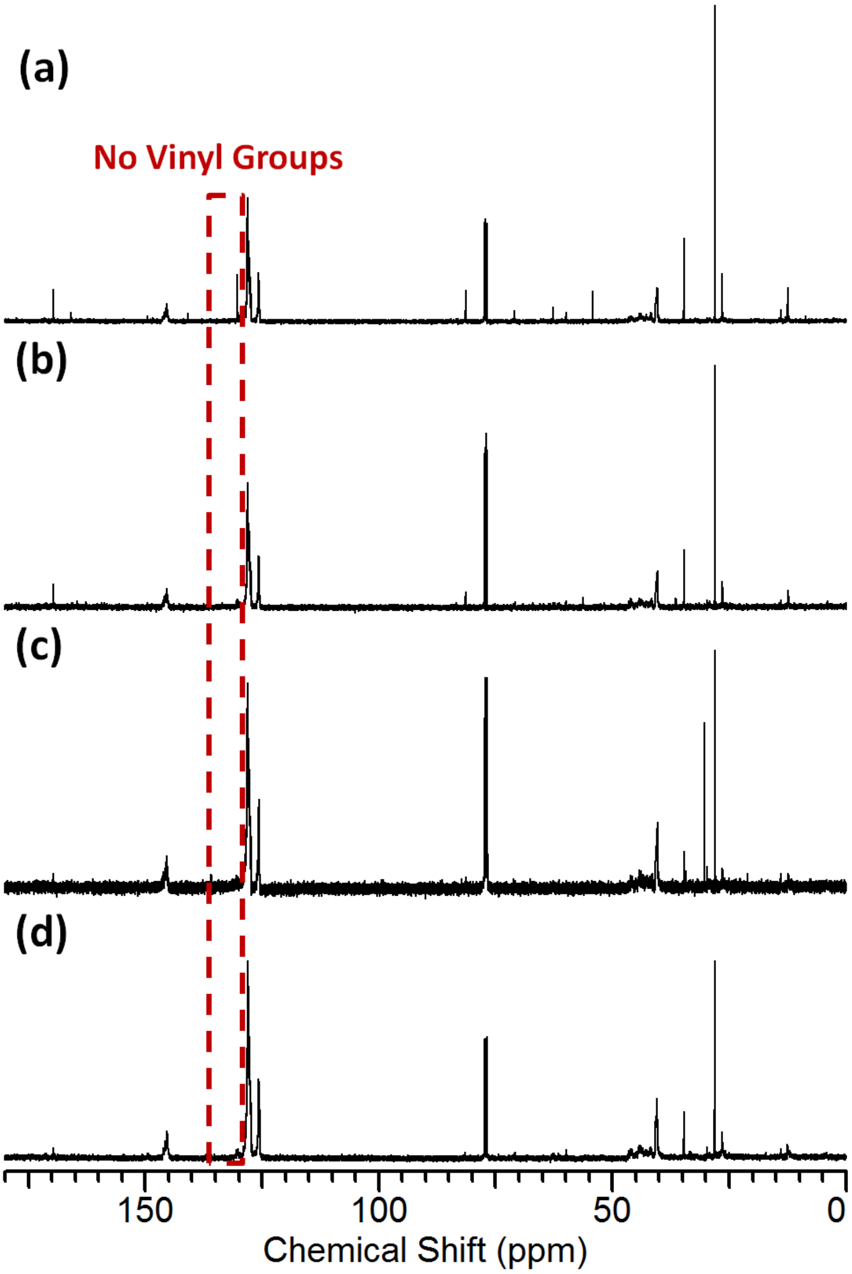


Figure S1. ^{13}C NMR spectra of (a) PS$_{48}$-(*t*BAPOSS)-N$_3$, (b) PS$_{48}$-(*t*BAPOSS)-(*t*BAPOSS)-PS$_{32}$, (c) PS$_{48}$-(*t*BAPOSS)-(APOSS)-PS$_{48}$, and (d) PS$_{48}$-(*t*BAPOSS)-(APOSS)-PS$_{32}$.

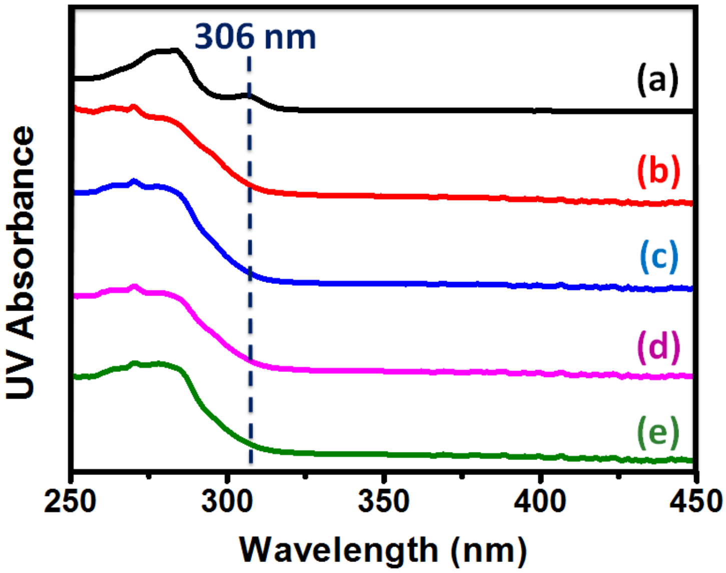


Figure S2. UV spectra of (a) CHO-(VPOSS)-DIBO (black curve), (b) PS_{48}-(*t*BAPOSS)-N_3 (red curve), (c) PS_{48}-(*t*BAPOSS)-(*t*BAPOSS)-PS_{32} (blue curve), (d) PS_{48}-(*t*BAPOSS)-(APOSS)-PS_{48} (purple curve), and (e) PS_{48}-(*t*BAPOSS)-(APOSS)-PS_{32} (green curve).

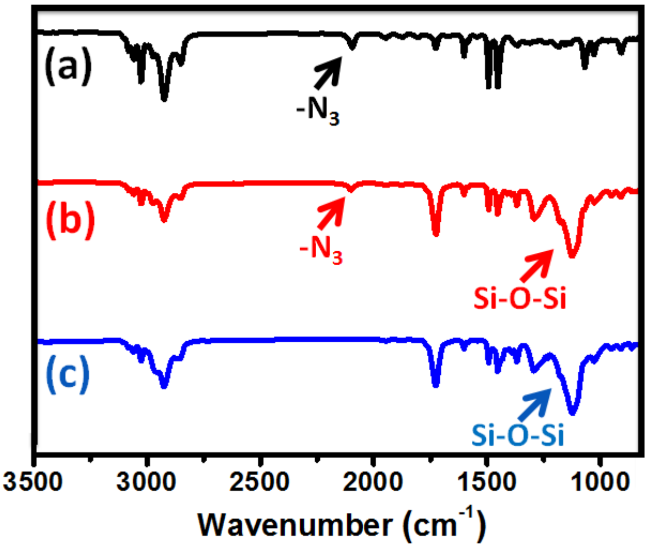


Figure S3. FTIR spectra of (a) PS_{48}-N_3 (black curve), (b) PS_{48}-(*t*BAPOSS)-N_3 (red curve), and (c) PS_{48}-(*t*BAPOSS)-(*t*BAPOSS)-PS_{32} (blue curve).

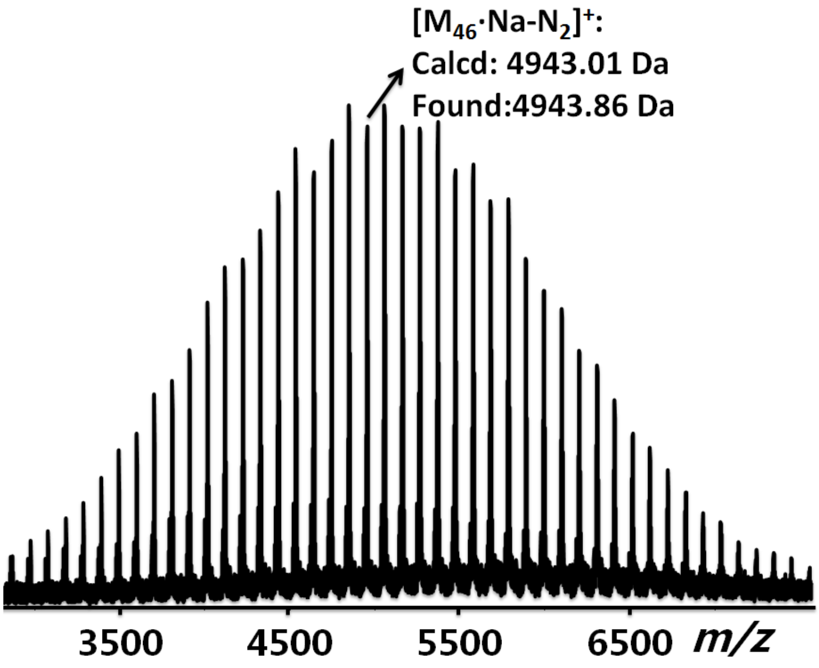


Figure S4. MALDI-TOF mass spectra of PS$_{48}$-N$_3$. The full spectrum was obtained in positive linear mode.

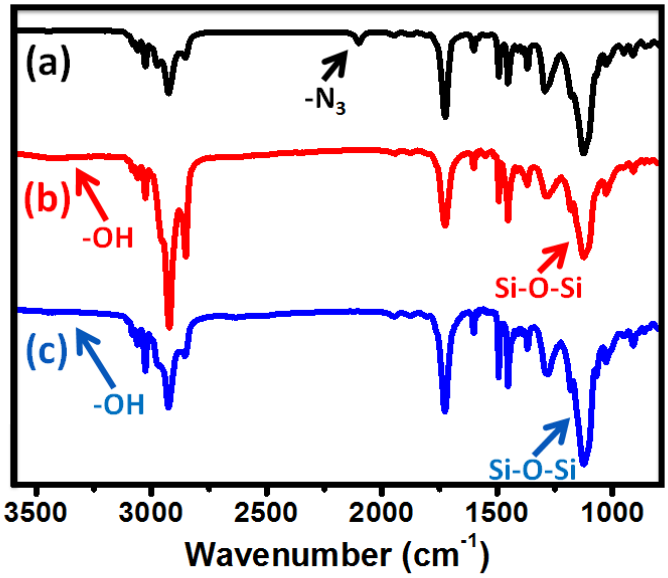


Figure S5. FTIR spectra of (a) PS$_{48}$-(*t*BAPOSS)-N$_3$ (black curve), (b) PS$_{48}$-(*t*BAPOSS)-(APOSS)-PS$_{48}$ (red curve), and (c) PS$_{48}$-(*t*BAPOSS)-(APOSS)-PS$_{32}$ (blue curve).