Electronic Supplementary Information

**Synthesis and Supramolecular Assembly of Clicked Anionic Dendritic Polymers into Polyion Complex Micelles**
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**General Methods.** CH2Cl2, Et3N, pyridine, and i-Pr2EtN were distilled from CaH2. DMSO was dried under 4Å molecular sieves. Column chromatography was performed with 70-230 and 230-400 mesh silica gel. Thin-layer chromatography (TLC) was done on silica aluminium-backed plates. Ultrafiltration was performed on stirred cells with Amicon® YM1 membranes. NMR chemical shifts are reported in ppm (δ units) downfield from internal tetramethylsilane (CDCl3), or the HOD signal (D2O and CD3OD).

**Dynamic Light Scattering.** DLS measurements were carried out on a Malvern Nano ZS (Malvern Instruments, U.K.) operating at 633 nm with a 170° scattering angle. PIC micelles were aged for at least 24 h before measurements.

**Gel Permeation Chromatography.** GPC experiments were performed using a PSS Suprema Lux precolumn (10μm, 8 x 50 mm) and a PSS Suprema Lux column (10μm, 100 Å, 8 x 300 mm) with a refractive index detector. A mixture CH3CN-H2O (1:1) was used as eluent. Dendrimer solutions were filtered through 0.45 μm before injection. Dendrimer concentration was set at 0.25 mg/mL.

**Atomic Force Microscopy.** Samples for AFM imaging were prepared by depositing the PBS aqueous solution of micelles onto Si wafers. The AFM imaging was performed in air using a Multimode NanoScope V system (Veeco, Santa Barbara, CA) operated in tapping mode. Tip Characteristics: 1-10 OHm-cm Phosphorus (n) dopped Si. Cantilever T: 3.5 - 4.5 μm. Frequency: 257-342 KHz. Tip ROC < 10 nm. Tip ROC MAX: 12.5 nm.
Sodium 3-butyn-1-sulfate (1). ClSO₃H (0.47 mL, 7.13 mmol) was added dropwise to a solution of pyridine (1.27 mL, 15.68 mmol) in CCl₄ (6.5 mL) at 0 ºC. After 30 min of stirring, 3-butyn-1-ol (0.54 mL, 7.13 mmol) was added, and the reaction was left at 0 ºC for 4 h. Then, reaction was allowed to reach rt, and after 12 h of stirring, it was extracted with H₂O (3 x 15 mL). The combined aqueous phase was evaporated to half volume, and then saturated Na₂CO₃ added till no CO₂ evolution was observed. The resulting mixture was concentrated, and then triturated with hot EtOH (80 mL), and filtered. The filtrate was evaporated to give 1 as a white powder (1.22 g, 100%). ¹H NMR (250 MHz, D₂O) δ: 4.14 (t, J = 6.3 Hz, 2H), 2.63 (dt, J = 2.3 Hz, J = 6.3 Hz, 2H), 2.40 (t, J = 2.6 Hz, 1H); ¹³C NMR (63 MHz, D₂O) δ: 80.8, 70.2, 66.5, 18.6.

Sodium 4-((prop-2-ynyl carbamoyl)methoxy)naphthalene-2,7-disulfonate (2). Et₃N (0.68 mL, 4.95 mmol) was added to a solution of bromoacetyl bromide (1.00 g, 4.95 mmol) in CH₂Cl₂ (50 mL) at -50 ºC. Then, propargyl amine (0.32 mL, 4.95 mmol) was added dropwise, and the resulting solution was allowed to reach rt and stir overnight. A white precipitate appeared, and was filtered off washing with CH₂Cl₂. The filtrate was evaporated to give a crude product that was purified by column chromatography (silica gel, 10% MeOH/CH₂Cl₂) to give 2-bromo-N-(prop-2-ynyl)acetamide (633 mg, 73%): ¹H NMR (250 MHz, CDCl₃) δ: 6.68 (br s, 1H), 4.09 (dd, J = 2.5 Hz, J = 5.3 Hz, 2H), 3.90 (s, 2H), 2.29 (dt, J = 0.8 Hz, J = 2.6 Hz, 1H); ¹³C NMR (63 MHz, CDCl₃) δ: 165.7, 78.6, 72.4, 30.1, 28.8. i-Pr₂EtN (94 μL, 0.57 mmol) and 2-bromo-N-(prop-2-ynyl)acetamide (100 mg, 0.57 mmol) were added to a solution of 1-naphthol-3,6-disulfonic acid disodium salt hydrate (157 mg, 0.28 mmol, 63% purity) in DMSO (0.40 mL). The resulting mixture was stirred at rt overnight. Then, it was poured into EtOAc (4 mL), and was triturated to give a solid that was collected by filtration washing with acetone. This solid crude product was dissolved in H₂O (25 mL), and was extracted with CH₂Cl₂ (3 x 25 mL). The aqueous phase was evaporated to give 2 as an off-white solid (157 mg, 70% conversion) that was directly used without further purification.
General procedure for the anionic functionalization of [Gn]-N₃ and PEG-[Gn]-N₃:

Dendrimers [Gn]-N₃ and PEG-dendritic block copolymers PEG-[Gn]-N₃ were dissolved in t-BuOH-H₂O (1:1) to give a 0.1M final concentration of terminal azides. Then, 1, 2, or 3 (200 mol% per terminal N₃), and freshly prepared aqueous solutions of CuSO₄ (5 mol% per N₃) and sodium ascorbate (25 mol% per N₃) were added. The resulting solutions were stirred at rt for 24-48 h, and then purified by ultrafiltration [Amicon® YM1, H₂O (3 x 30 mL), aqueous 1M NaCl (30 mL)], and evaporated or freeze-dried. For the synthesis of [Gn]-3 and PEG-[Gn]-3, NaHCO₃ (110 mol% per carboxylic acid group) was added.

[G1]-1: From [G1]-N₃ (35 mg, 0.051 mmol), 1 (53 mg, 0.307 mmol), sodium ascorbate (7.61 mg, 38.4 µmol) and CuSO₄ (1.92 mg, 7.7 µmol) dissolved in t-BuOH (0.85 mL)-H₂O (0.85 mL), and after 24 h of reaction time following the general procedure described above, [G1]-1 (34 mg, 80%) was obtained as a white powder. IR (CsI, cm⁻¹) 2933, 1647, 1223; ¹H NMR (400 MHz, D₂O) δ: 7.90 (s, 1H), 7.80 (s, 2H), 7.14 (s, 2H), 4.56 (t, J = 4.9 Hz, 6H), 4.28-4.15 (m, 12H), 3.94-3.47 (m, 24H), 3.35 (t, J = 7.0 Hz, 2H), 3.04 (t, J = 6.3 Hz, 2H), 3.0 (t, J = 6.1 Hz, 4H), 1.63-1.60 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, D₂O) δ: 172.4, 154.6, 142.7, 133.2, 127.3, 109.4, 75.1, 73.2, 72.8, 72.7, 72.6, 74.2, 72.1, 71.8, 71.7, 71.4, 70.3, 65.5, 52.9, 44.8, 28.1, 25.0, 13.6.

[G2]-1: From [G2]-N₃ (20 mg, 8.1 µmol), 1 (25 mg, 0.145 mmol), sodium ascorbate (3.60 mg, 18.2 µmol), and CuSO₄ (0.91 mg, 3.6 µmol) dissolved in t-BuOH (0.36 mL)-H₂O (0.36 mL), and after 48 h of reaction time following the general procedure described above, [G2]-1 (32 mg, 92%) was obtained as a white foam. IR (CsI, cm⁻¹) 2932, 1648, 1220; ¹H NMR (250 MHz, D₂O) δ: 7.90 (s, 3H), 7.80 (s, 6H), 7.14-7.04 (m, 8H), 4.61-4.48 (m, 18H), 4.31-3.47 (m, 144H), 3.27 (t, J = 7.0 Hz, 2H), 3.10-2.94 (m, 18H), 1.63-1.60 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, D₂O) δ: 176.6, 154.8, 142.5, 133.3, 127.4, 109.0, 75.1, 73.2, 72.8, 72.7, 72.6, 72.4, 72.1, 71.6, 71.3, 70.1, 63.6, 53.1, 44.8, 28.4, 25.2, 13.8.
[G3]-1: From [G3]-N₃ (40 mg, 5.1 µmol), 1 (47 mg, 0.275 mmol), sodium ascorbate (6.81 mg, 34.4 µmol), and CuSO₄ (2.03 mg, 6.9 µmol) dissolved in t-BuOH (0.68 mL)-H₂O (0.68 mL), and after 48 h of reaction time following the general procedure described above, [G3]-1 (58 mg, 91%) was obtained as a white foam. IR (KBr, cm⁻¹) 2927, 1648, 1226; ¹H NMR (300 MHz, D₂O) δ: 8.19-7.83 (m, 27H), 7.10 (s, 26H), 4.63-4.46 (m, 54H), 4.34-3.43 (m, 468H), 3.35 (m, 2H), 3.16-2.83 (m, 54H), 1.63-1.60 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H); ¹³C NMR (100 MHz, CD₃OD) δ: 169.2, 153.7, 140.7, 130.8, 125.6, 107.8, 73.6, 73.2, 71.5, 71.2, 70.5, 70.3, 69.8, 67.6, 51.8, 51.4, 40.9, 27.1, 12.0.

[G3]-2: From [G3]-N₃ (25 mg, 3.2 µmol), 2 (127 mg, 0.171 mmol), sodium ascorbate (47.3 mg, 0.275 mmol), and CuSO₄ (1.07 mg, 4.3 µmol) dissolved in t-BuOH (0.15 mL)-H₂O (0.15 mL), and after 48 h of reaction time following the general procedure described above, [G3]-2 (57 mg, 91%) was obtained as a white foam. ¹H NMR (300 MHz, D₂O) δ: 8.40-8.33 (m, 27H), 8.29 (d, J = 4.6 Hz, 27H), 8.06-8.00 (m, 27H), 7.91-7.83 (m, 54H), 7.18 (s, 26H), 6.60 (s, 27H), 4.62-4.30 (m, 54H), 4.20-3.47 (m, 468H), 3.35 (m, 2H), 1.63-1.59 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).

[G3]-3: From [G3]-N₃ (37 mg, 4.7 µmol), 3 (25 mg, 0.254 mmol), NaHCO₃ (22 mg, 0.280 mmol), sodium ascorbate (6.30 mg, 31.8 µmol), and CuSO₄ (1.58 mg, 6.4 µmol) dissolved in t-BuOH (0.65 mL)-H₂O (0.65 mL), and after 48 h of reaction time following the general procedure described above, [G3]-3 (51 mg, 98%) was obtained as a white foam. ¹H NMR (300 MHz, D₂O) δ: 7.95-7.60 (m, 27H), 7.13 (s, 26H), 4.59-4.52 (m, 54H), 4.22-4.14 (m, 78H), 3.94-3.46 (m, 380H), 3.35 (m, 2H), 2.95-2.84 (m, 54H), 2.56-2.47 (m, 54H), 1.62-1.59 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H).

PEG-[G1]-1: From PEG-[G1]-N₃ (50 mg, 8.6 µmol), 1 (8.86 mg, 0.052 mmol), sodium ascorbate (1.28 mg, 6.4 µmol), and CuSO₄ (0.32 mg, 1.3 µmol), dissolved in t-BuOH (0.130 mL)-H₂O (0.130 mL), and after 48 h of reaction time according to the general procedure, PEG-[G1]-1 (54 mg, 100%) was obtained as a white foam. IR (KBr, cm⁻¹) 2887, 1467, 1344, 1115; ¹H NMR (750 MHz, D₂O)
δ: 7.92 (s, 1H), 7.90 (s, 2H), 7.19 (s, 2H), 4.64-4.50 (m, 6H), 4.35-4.12 (m, 14H), 4.03-3.44 (m, 542H), 3.41 (s, 3H), 3.29 (t, J = 4.9 Hz, 2H), 3.04 (t, J = 6.0 Hz, 2H), 3.01 (t, J = 5.8 Hz, 4H).

**PEG-[G1]-2:** From PEG-[G1]-N3 (20 mg, 3.4 µmol), 2 (25.1 mg, 20.6 µmol), sodium ascorbate (0.51 mg, 2.6 µmol), and CuSO4 (0.13 mg, 0.51 µmol) dissolved in t-BuOH (55 µL)-H2O (55 µL), and after 24 h of reaction time following the general procedure described above, PEG-[G1]-2 (22 mg, 90%) was obtained as a white foam. IR (KBr, cm⁻¹) 2879, 1466, 1034; ¹H NMR (400 MHz, D2O) δ: 8.40-8.33 (m, 3H), 8.29 (d, J = 4.6 Hz, 3H), 8.06-8.00 (m, 3H), 7.91-7.83 (m, 6H), 7.18 (s, 2H), 6.60 (s, 3H), 4.60-4.46 (m, 6H), 4.16-4.04 (m, 8H), 4.00-3.47 (m, 548H), 3.41 (s, 3H), 3.25 (m, 2H).

**PEG-[G1]-3:** From PEG-[G1]-N3 (20 mg, 3.4 µmol), 3 (2.68 mg, 20.1 µmol), NaHCO3 (1.90 mg, 20.6 µmol), sodium ascorbate (0.51 mg, 2.6 µmol), and CuSO4 (0.13 mg, 0.51 µmol) dissolved in t-BuOH (55 µL)-H2O (55 µL), and after 48 h of reaction time following the general procedure described above, PEG-[G1]-3 (19 mg, 91%) was obtained as a white foam. ¹H RMN (400 MHz, D2O) δ: 7.79 (s, 1H), 7.77 (s, 2H), 7.18 (s, 2H), 4.59-4.51 (m, 6H), 4.31-4.00 (m, 44H), 4.00-3.50 (m, 620H), 3.41 (s, 3H), 3.28 (t, J = 4.89 Hz, 2H), 2.94-2.84 (m, 6H), 2.57-2.45 (m, 6H).

**PEG-[G2]-1:** From PEG-[G2]-N3 (25 mg, 3.3 µmol), 1 (10.17 mg, 0.059 mmol), sodium ascorbate (1.46 mg, 7.4 µmol), and CuSO4 (0.37 mg, 1.5 µmol) dissolved in t-BuOH (0.150 mL)-H2O (0.150 mL), and after 48 h of reaction time according to the general procedure, PEG-[G2]-1 (28 mg, 92%) was obtained as a white foam. IR (KBr, cm⁻¹) 2887, 1467, 1344, 1115; ¹H NMR (400 MHz, D2O) δ: 7.87 (br s, 9H), 7.09 (s, 8H), 4.60-4.51 (m, 18H), 4.31-4.00 (m, 44H), 4.00-3.50 (m, 620H), 3.41 (s, 3H), 3.26 (t, J = 4.9 Hz, 2H), 3.04-3.01 (m, 18H).

**PEG-[G3]-1:** From PEG-[G3]-N3 (20 mg, 1.5 µmol), 1 (14 mg, 0.083 mmol), sodium ascorbate (1.03 mg, 5.2 µmol), and CuSO4 (0.26 mg, 1.0 µmol) dissolved in t-BuOH (0.21 mL)-H2O (0.21 mL), and after 48 h of reaction time according to the general procedure, PEG-[G3]-1 (27 mg, 100%)
was obtained as a white foam. IR (KBr, cm⁻¹) 2877, 1458, 13343, 1107; ¹H NMR (400 MHz, D₂O) δ: 7.85 (br s, 27H), 7.10 (s, 26H), 4.61-4.47 (m, 54H), 4.30-4.00 (m, 134H), 4.00-3.49 (m, ~966H), 3.42-3.35 (m, 5H), 3.09-2.97 (m, 54H).

**PEG-[G3]-2:** From PEG-[G3]-N₃ (12 mg, 0.9 μmol), 2 (61 mg, 0.050 mmol), sodium ascorbate (1.23 mg, 6.2 µmol), and CuSO₄ (0.31 mg, 1.2 µmol), dissolved in t-BuOH (0.125 mL)-H₂O (0.125 mL), and after 48 h of reaction time according to the general procedure, **PEG-[G3]-2** (23 mg, 100%) was obtained as a white foam. ¹H NMR (400 MHz, D₂O ) δ: 8.45-8.33 (m, 27H), 8.29 (m, 27H), 8.06-8.00 (m, 27H), 7.91-7.83 (m 54H), 7.18 (s, 26H), 6.60 (s, 27H), 4.63-4.34 (m, 110H), 4.01-3.48 (m, ~1023H), 3.41 (m, 5H).

**PEG-[G3]-3:** From PEG-[G3]-N₃ (34 mg, 2.6 μmol), 3 (14 mg, 0.141 mmol), NaHCO₃ (13 mg, 0.155 mmol), sodium ascorbate (3.49 mg, 17.6 µmol), and CuSO₄ (0.88 mg, 3.5 µmol), dissolved in t-BuOH (0.35 mL)-H₂O (0.35 mL), and after 48 h of reaction time according to the general procedure, **PEG-[G3]-3** (41 mg, 98%) was obtained as a white foam. ¹H NMR (400 MHz, D₂O) δ: 7.87-7.71 (m, 27H), 7.10 (s, 26H), 4.59-4.43 (m, 54H), 4.30-4.12 (m, 80H), 4.00-3.47 (m, ~966H), 3.41 (m, 5H), 2.95-2.83 (m, 54H), 2.63-2.40 (m, 54H).

**Preparation of PIC micelles.** PEG-[G3]-1 and PLL (Mₙ 12400, Mₘ 16100, DP = 77, by LALLS) were separately dissolved in either H₂O or 10 mM PBS pH 7.4, and filtered through 0.45 μm nylon filters. PIC micelles were prepared by mixing these solutions at an equal ratio of L-lysine repetition units and sulfate residues (total concentration: 0.98 mg/mL). Solutions were aged for at least 24 h, and filtered (0.45 μm) before any measurement being performed.