Dendrimer Ligand Directed Nanoplate Assembly

Katherine C. Elbert,†,# Thi Vo,‡,# Nadia M. Krook,§ William Zygmunt,‡ Jungmi Park,‡ Kevin G. Yager,‖ Russell J. Composto,§ Sharon C. Glotzer,*‡,⊥,¶ Christopher B. Murray*,‡,§

† Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, United States
‡ Department of Chemical Engineering, University of Michigan, Ann Arbor, MI, 48109, United States
§ Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA 19104, United States
‖ Center for Functional Nanomaterials, Brookhaven National Laboratory, Upton, New York, 11973, United States
⊥ Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, United States
¶ Biointerfaces Institute, University of Michigan, Ann Arbor, MI, 48109, United States

Table of Contents

Synthesis of Dendritic Ligands ................................................................. 2
Additional Figures and Microscopy .......................................................... 8
Scaling Theory for Branching Ligand Architecture ..................................... 16
Mapping of Scaling Prediction to Simulation ............................................. 20
References .............................................................................................. 21
NMR Characterization of Ligands ............................................................ 22
Synthesis of Dendritic Ligands

Scheme S1. Synthesis of generation 2 dendrimer ligands.

Methyl 3,5-bis((3,4,5-tris(dodecyloxy)benzyl)oxy)benzoate, 2a. Was synthesized as reported previously.\(^1\) To a reaction flask was added 5-(chloromethyl)-1,2,3-tris(dodecyloxy)benzene (9.34 g, 13.74 mmol), methyl 3,5 dihydroxybenzoate (0.66 g, 3.92 mmol), \(\text{K}_2\text{CO}_3\) (2.17 g, 15.70 mmol), KI (0.20 g, cat), and DMF (100 mL). The reaction mixture was heated to 80 °C for 20 hours and was subsequently cool to room temperature, diluted with \(\text{H}_2\text{O}\) (2 x 50 mL), and 1 M HCl (2 x 50 mL). The resulting organic layers were dried with \(\text{Na}_2\text{SO}_4\), filtered, and concentrated under vacuum. The crude product was purified with column chromatography (hexanes → hexanes:EtOAc 100:5), to afford pure 2a as a white solid (4.33 g, 76 %). \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.31 (d, \(J = 2.3\) Hz, 2H), 6.81 (t, \(J = 2.4\) Hz, 1H), 6.63 (s, 4H), 4.96 (s, 4H), 3.99 (q, \(J = 6.6\) Hz, 12H), 3.91 (s, 3H), 1.84 – 1.75 (m, 12H), 1.50 (q, \(J = 7.6, 7.1\) Hz, 12H), 1.36 – 1.26 (m, 96H), 0.92 – 0.87 (m, 18H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 166.83, 159.96, 153.50, 138.29, 132.16, 131.49, 108.55, 107.39, 106.41, 73.56, 70.85, 69.30, 52.32, 32.14, 32.12, 30.55, 29.95, 29.93, 29.90, 29.85, 29.83, 29.81, 29.62, 29.59, 29.56, 26.34, 26.31, 22.87, 14.26; MALDI-TOF (m/z): [M+Na]\(^+\) calcd. for C\(_{94}\)H\(_{164}\)O\(_{10}\)Na, 1476.22; found 1479.089.
Methyl 3,4,5-tris((3,4,5-tris(dodecyloxy)benzyl)oxy)benzoate, 3a. As for 2a. Methyl 3,4,5-trihydroxybenzoate (0.33 g, 1.81 mmol), 5-(chloromethyl)-1,2,3-tris(dodecyloxy)benzene (4.00 g, 5.89 mmol), K$_2$CO$_3$ (1.0 g, 7.25 mmol), KI (cat), 50 mL DMF. 3a was isolated as an off-white solid (2.79 g, 73 %). $^1$H NMR (CDCl$_3$) $\delta$ 7.38 (s, 2H), 6.63 (s, 4H), 6.60 (s, 2H), 5.04 (d, $J$ = 5.1 Hz, 6H), 3.93 (t, $J$ = 6.6 Hz, 4H), 3.91 – 3.86 (m, 14H), 3.76 (t, $J$ = 6.4 Hz, 3H), 1.77 – 1.69 (m, 18H), 1.49 – 1.40 (m, 18H), 1.32 – 1.26 (m, 144H), 0.88 (t, $J$ = 6.7 Hz, 27H); $^{13}$C NMR (CDCl$_3$) $\delta$ 166.72, 153.50, 153.24, 152.79, 142.78, 138.13, 138.08, 132.60, 131.88, 125.46, 109.88, 106.51, 105.98, 75.37, 73.61, 73.53, 71.91, 69.32, 69.14, 52.38, 32.18, 32.17, 30.66, 30.64, 30.05, 30.01, 30.00, 29.97, 29.94, 29.92, 29.90, 29.86, 29.81, 29.73, 29.69, 29.64, 29.62, 26.45, 26.41, 26.40, 22.92, 14.33; MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{137}$H$_{242}$O$_{14}$Na, 2134.82; found 2140.689.

(3,5-Bis((3,4,5-tris(dodecyloxy)benzyl)oxy)phenyl)methanol, 2b. In a reaction flask was combined LiAlH$_4$ (0.60 g, 15.84 mmol) and THF (100 mL) at 0 °C, followed by slow addition of 2a (5.75 g, 3.96 mmol). The reaction mixture was then heated to 70 °C for 4 hours. Then the reaction mixture was cooled to 0 °C before being quenched slowly with ice water. The solution was then concentrated under reduced pressure, dissolved in CHCl$_3$ (100 mL), and washed with 1 M HCl (2 x 50 mL), followed by being dried with Na$_2$SO$_4$, filtered, and concentrated under pressure. 2b was isolated as a white solid (4.74 g, 84 %). $^1$H NMR (CDCl$_3$) $\delta$ 6.63 – 6.60 (m, 6H), 6.54 (t, $J$ = 2.4 Hz, 1H), 4.90 (s, 4H), 4.62 (s, 2H), 3.97 (q, $J$ = 6.3 Hz, 12H), 1.82 – 1.73 (m, 12H), 1.51 – 1.45 (m, 12H), 1.34 – 1.27 (m, 96H), 0.91 – 0.88 (m, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 160.30, 153.45, 143.77, 138.15, 131.91, 106.37, 105.79, 101.37, 77.43, 73.58, 70.62, 69.30, 65.27, 32.12, 32.11, 30.53, 29.94, 29.92, 29.89, 29.88, 29.84, 29.83, 29.81, 29.62, 29.57, 29.55, 26.33, 26.31, 22.86, 14.26; MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{93}$H$_{164}$O$_9$Na, 1448.23; found 1451.045.
(3,4,5-Tris((3,4,5-tris(dodecyloxy)benzyl)oxy)phenyl)methanol, 3b. As for 2b. 3a (1.00 g, 0.48 mmol), LiAlH₄ (0.06 g, 1.45 mmol), THF (25 mL). Isolated as a white solid (0.88 g, 88%).

**1H NMR** (CDCl₃) δ 6.64 (d, J = 4.5 Hz, 8H), 4.95 (d, J = 9.5 Hz, 6H), 4.53 (s, 2H), 3.97 – 3.90 (m, 7H), 3.87 (t, J = 6.4 Hz, 8H), 3.77 (t, J = 6.3 Hz, 3H), 1.79 – 1.72 (m, 18H), 1.52 – 1.50 (m, 4H), 1.48 – 1.41 (m, 14H), 1.36 – 1.28 (m, 144H), 0.91 (t, J = 6.7 Hz, 27H); **13C NMR** (CDCl₃) δ 153.34, 153.13, 152.96, 137.83, 137.80, 137.62, 137.34, 133.00, 132.31, 106.66, 106.26, 105.67, 75.31, 73.46, 73.37, 71.54, 69.14, 68.95, 67.96, 65.07, 32.10, 30.60, 30.57, 29.98, 29.96, 29.94, 29.92, 29.87, 29.83, 29.79, 29.76, 29.69, 29.64, 29.61, 29.57, 29.56, 26.40, 26.38, 26.35, 26.31, 22.84, 14.20; MALDI-TOF (m/z): [M+Na]⁺ calcd. for C₁₃₆H₂₄₂O₁₃Na, 2106.82; found 2112.689.

5,5'-(((5-(Chloromethyl)-1,3-phenylene)bis(oxy))bis(methylene))bis(1,2,3-tris(dodecyloxy)benzene), 2c. 2b (1.10 g, 0.77 mmol) was combined with 25 mL DCM and cooled to 0 °C before adding 2,6-ditert butyl 4-methyl pyridine (0.47 g, 2.31 mmol), then SOCl₂ (0.17 mL, 2.31 mmol). The reaction was warmed to room temperature and stirred for 3 hours under N₂ atm. The reaction mixture was then concentrated under vacuum, dissolved in CHCl₃ (100 mL) and washed with 1 M HCl (2 x 50 mL). The organic layer was dried with Na₂SO₄ and filtered before being concentrated under vacuum. 2c was isolated as a yellow solid (0.98 g, 88%).

**1H NMR** (CDCl₃) δ 6.65 (s, 2H), 6.61 (s, 4H), 6.58 (s, 1H), 4.92 (s, 4H), 4.52 (s, 2H), 3.97 (q, J = 6.1 Hz, 12H), 1.82 – 1.74 (m, 12H), 1.47 (t, J = 7.5 Hz, 12H), 1.34 – 1.27 (m, 96H), 0.89 (t, J = 6.8 Hz, 18H); **13C NMR** (CDCl₃) δ 160.33, 153.53, 139.73, 138.30, 131.67, 107.86, 106.51, 102.30, 73.64, 70.82, 69.38, 46.51, 32.16, 32.14, 30.56, 29.97, 29.95, 29.92, 29.87, 29.84, 29.65, 29.61, 29.58, 26.36, 26.33, 22.90, 14.31; MALDI-TOF (m/z): [M+Na]⁺ calcd. for C₉₃H₁₅₇ClO₃Na, 1466.19; found 1469.005.
5,5',5''-(((5-(Chloromethyl)benzene-1,2,3-triyl)tris(oxy))tris(methylene))tris(1,2,3-
tris(dodecyloxy)benzene), 3c. As for 2c. 3b (1.15 g, 0.56 mmol), 2,6-ditert butyl 4-methyl
pyridine (0.34 g, 1.69 mmol), SOCl$_2$ (0.13 mL, 1.69 mmol), CH$_2$Cl$_2$ (25 mL). 3c was isolated as
a yellow solid (1.07 g, 91 %). $^1$H NMR (CDCl$_3$) $\delta$ 6.69 (s, 2H), 6.62 (d, $J$ = 5.2 Hz, 6H), 5.00 (s,
4H), 4.97 (s, 2H), 4.47 (s, 2H), 3.95 (t, $J$ = 6.5 Hz, 5H), 3.88 (t, $J$ = 6.3 Hz, 10H), 3.77 (t, $J$ = 6.3
Hz, 3H), 1.78 – 1.71 (m, 18H), 1.50 – 1.43 (m, 18H), 1.33 – 1.27 (m, 144H), 0.89 (t, $J$ = 6.2 Hz,
27H); $^{13}$C NMR (CDCl$_3$) $\delta$ 153.37, 153.12, 153.06, 138.75, 137.97, 137.88, 133.11, 132.77,
132.01, 108.93, 107.16, 106.43, 105.82, 77.43, 75.32, 73.43, 73.36, 71.84, 69.15, 68.96, 58.30,
46.63, 37.45, 32.08, 32.07, 30.57, 30.54, 30.17, 29.95, 29.92, 29.89, 29.87, 29.84, 29.82, 29.79,
29.76, 29.73, 29.71, 29.63, 29.59, 29.54, 29.52, 29.50, 26.36, 26.32, 26.29, 22.81, 15.42, 14.19;
MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{136}$H$_{241}$ClO$_{12}$Na, 2124.78; found 2130.649.

5,5'-(5-(Azidomethyl)-1,3-phenylene)bis(oxy))bis(methylene))bis(1,2,3-
tris(dodecyloxy)benzene), 2d. 2c (1.00 g, 0.69 mmol) was combined with NaN$_3$ (0.13 g, 2.08
mmol), and 30 mL DMF and was heated at 70 °C for 16 hours. The reaction mixture was cooled
to room temperature and diluted in CHCl$_3$ (100 mL) then washed with water (2 x 50 mL). The
organic layers were dried with Na$_2$SO$_4$, filtered, concentrated under vacuum, then the product
was precipitated out of cold MeOH. 2d was isolated as yellow solid (0.92 g, 92 %). $^1$H NMR
(CDC$_3$) $\delta$ 6.61 (s, 4H), 6.59 (d, $J$ = 2.2 Hz, 1H), 6.56 (d, $J$ = 2.2 Hz, 2H), 4.92 (s, 4H), 4.27 (s,
2H), 3.99 – 3.93 (m, 12H), 1.81 – 1.73 (m, 12H), 1.49 – 1.44 (m, 12H), 1.34 – 1.26 (m, 96H),
0.90 – 0.86 (m, 18H); $^{13}$C NMR (CDCl$_3$) $\delta$ 160.51, 153.56, 153.06, 138.33, 137.83, 131.67, 107.41,
106.52, 102.07, 73.66, 70.84, 69.40, 55.09, 32.17, 32.15, 30.58, 29.99, 29.97, 29.93, 29.88,
29.85, 29.84, 29.82, 29.81, 15.42, 14.19; MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{93}$H$_{163}$N$_3$O$_8$Na, 1473.23; found 1476.045.
5,5',5''-(((5-(azidomethyl)benzene-1,2,3-triyl)tris(oxy))tris(methylene))tris(1,2,3-tris(dodecyloxy)benzene), 3d. As for 2d. 3c (1.50 g, 0.713 mmol), NaN₃ (0.14 g, 2.14 mmol), DMF (30 mL). 3d was isolated as a yellow solid (1.44 g, 96 %).

1H NMR (CDCl₃) δ 6.64 (d, J = 2.2 Hz, 6H), 6.62 (s, 2H), 5.02 (s, 4H), 5.00 (s, 2H), 4.22 (s, 2H), 3.96 (t, J = 6.7 Hz, 5H), 3.90 (t, J = 6.4 Hz, 10H), 3.80 (t, J = 6.3 Hz, 3H), 1.79 – 1.73 (m, 18H), 1.51 – 1.43 (m, 18H), 1.35 – 1.29 (m, 144H), 0.90 (t, J = 6.7 Hz, 27H);

13C NMR (CDCl₃) δ 153.47, 153.31, 153.20, 138.68, 138.05, 137.97, 132.86, 132.09, 131.19, 108.52, 106.81, 106.51, 105.82, 75.41, 73.53, 73.46, 71.96, 69.33, 69.25, 69.06, 55.33, 55.09, 32.15, 32.13, 30.60, 30.01, 29.98, 29.96, 29.94, 29.91, 29.88, 29.86, 29.83, 29.80, 29.77, 29.69, 29.65, 29.60, 29.58, 29.56, 26.42, 26.38, 26.35, 22.88, 14.27; MALDI-TOF (m/z): [M+Na]+ calcd. for C₁₃₆H₂₄₁N₃O₁₂Na, 2131.82; found 2137.689.

(9-(1-(3,4,5-Tris(dodecyloxy)benzyl)-1H-1,2,3-triazol-4-yl)nonyl)phosphonic acid, 1. Compound 1 was synthesized as reported previously.² 5-(azidomethyl)-1,2,3-tris(dodecyloxy)benzene (1.7 g, 2.50 mmol), 10-undecenoic phosphonic acid (0.5 g, 2.74 mmol), CuSO₄·5H₂O (cat), sodium ascorbate (cat), THF (3 mL), and H₂O (0.5 mL) were combined and stirred for 12 hours at 75 °C with microwave irradiation. The solution was diluted with CHCl₃ (100 mL) and washed with 4 M HCl (2 x 50 mL) then 1 M HCl (50mL), before being dried with Na₂SO₄, filtered, and concentrated under vacuum. The crude product was diluted in a small amount of CHCl₃ and precipitated out of cold MeOH as pure 1 as a white powder, yield (1.58 g, 69 %).¹H NMR (CDCl₃) δ 10.43 (s, 2H), 7.24 (s, 1H), 6.44 (s, 2H), 5.36 (s, 2H), 3.91 (q, J = 7.0 Hz, 6H), 3.68 (t, J = 7.8 Hz, 2H), 1.79 – 1.71 (m, 8H), 1.65 – 1.59 (m, 4H), 1.49 – 1.41 (m, 8H), 1.33 – 1.25 (m, 54H), 0.87 (t, J = 6.7 Hz, 9H); ¹³C NMR (CDCl₃) δ 153.79, 148.53, 138.74, 129.50, 121.16, 106.94, 73.67, 69.48, 54.85, 32.14, 30.55, 30.35, 30.22, 29.96, 29.95, 29.92, 29.90, 29.88, 29.86, 29.82, 29.65, 29.60, 29.58, 29.40, 29.18, 29.04, 29.00, 28.90, 27.08, 26.33, 26.32, 25.96, 25.46, 22.90, 22.40, 22.36, 14.31; MALDI-TOF (m/z): [M+Na]+ calcd. for C₅₄H₁₀₀N₅O₆PNa, 940.724; found 941.825.
(9-(1-(3,5-Bis((3,4,5-tris(dodecyloxy)benzyl)oxy)benzyl)-1H-1,2,3-triazol-4-yl)nonyl)phosphonic acid, 2. As for 1, 2d (0.50 g, 0.34 mmol), 10-undecenoic phosphonic acid (0.09 g, 0.38 mmol), CuSO$_4$·5H$_2$O (cat), sodium ascorbate (cat), THF (3 mL), H$_2$O (0.5 mL), 16 hours at 75 °C under microwave irradiation. Isolated 2 as a yellow solid (0.35 g, 61 %). $^1$H NMR (CDCl$_3$) δ 7.23 (s, 1H), 6.58 (s, 5H), 6.50 (s, 2H), 5.40 (s, 2H), 4.86 (s, 4H), 3.98 – 3.92 (m, 12H), 2.67 (t, $J$ = 8.1 Hz, 2H), 1.82 – 1.71 (m, 16H), 1.65 – 1.61 (m, 2H), 1.49 – 1.42 (m, 14H), 1.35 – 1.26 (m, 106H), 0.89 – 0.86 (m, 18H); $^{13}$C NMR (CDCl$_3$) δ 160.57, 153.47, 148.62, 138.19, 136.86, 131.39, 121.23, 107.26, 106.37, 102.17, 100.12, 73.58, 70.76, 69.27, 54.47, 32.12, 32.10, 30.53, 29.94, 29.92, 29.89, 29.84, 29.81, 29.62, 29.60, 29.58, 29.55, 29.37, 29.20, 29.04, 28.87, 26.32, 25.44, 22.87, 14.28; MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{104}$H$_{184}$N$_3$O$_{11}$PNa, 1705.36; found 1708.284.

(9-(1-(3,4,5-Tris((3,4,5-tris(dodecyloxy)benzyl)oxy)benzyl)-1H-1,2,3-triazol-4-yl)nonyl)phosphonic acid, 3. As for 1, 3d (0.30 g, 0.14 mmol), 10-undecenoic phosphonic acid (0.04 g, 0.16 mmol), CuSO$_4$·5H$_2$O (cat), sodium ascorbate (cat), THF (3 mL), H$_2$O (0.5 mL), 20 hours at 75 °C under microwave irradiation. Isolated 3 as a yellow solid (0.20 g, 62 %). $^1$H NMR (CDCl$_3$) δ 7.17 (s, 1H), 6.58 (d, $J$ = 13.8 Hz, 8H), 5.35 (s, 2H), 4.95 (s, 6H), 3.92 (t, $J$ = 6.5 Hz, 5H), 3.86 (t, $J$ = 6.4 Hz, 10H), 3.74 (t, $J$ = 6.4 Hz, 3H), 2.68 (s, 2H), 1.74 – 1.63 (m, 21H), 1.48 – 1.39 (m, 21H), 1.31 – 1.24 (m, 154H), 0.88 (t, $J$ = 6.8 Hz, 27H); $^{13}$C NMR (CDCl$_3$) δ 153.54, 153.50, 153.28, 139.31, 138.08, 138.03, 132.75, 131.85, 129.44, 108.77, 106.41, 105.87, 75.44, 73.61, 73.54, 71.96, 69.32, 69.11, 32.17, 32.16, 30.67, 30.66, 30.05, 30.03, 30.01, 29.98, 29.95, 29.92, 29.88, 29.83, 29.75, 29.71, 29.68, 29.63, 29.61, 29.04, 28.92, 28.77, 28.66, 26.48, 26.45, 26.42, 22.92, 14.32; MALDI-TOF (m/z): [M+Na]$^+$ calcd. for C$_{147}$H$_{262}$N$_3$O$_{13}$PNa, 2363.965; found 2369.834.
Additional Figures and Microscopy

![Graph showing weight percent vs. temperature for different ligands]

**Figure S1.** TGA of the NCs functionalized with OA and the dendrimer ligands, highlighting successful ligand exchange, due to change in observed thermal decomposition of ligands from about 190 °C to above 300 °C.
**Figure S2.** TEM images of self-assembled mono or bilayers on various subphases for each dendritic ligand.
**Figure S3.** 2D GISAXS images of self-assembled mono or bilayers on various subphases for each dendritic ligand. Data was converted into reciprocal-space, including correction for Ewald sphere curvature. Data is displayed as the \((q_x, q_z)\) projection (where the \(q_y\) component is ignored for plotting purposes).
Figure S4. Linecuts along the out-of-plane ($q_z$) direction obtained from GISAXS for (a) OA@NC, (b) 1@NC, (c) 2@NC, and (d) 3@NC. The discontinuity at $q_z = 0.08 \text{ Å}^{-1}$ (marked by a star) appears due to the beamstop, which affects the range of pixels used in data averaging.
Figure S5. Angle (azimuthal) linecuts extracted from GISAXS for (a) OA@NC, (b) 1@NC, (c) 2@NC, and (d) 3@NC. Data was extracted along the angular direction at a constant q corresponding to the most intense peak along qz (q of 0.110 Å⁻¹ to 0.130 Å⁻¹, depending on material).
Figure S6. Large area view of bilayer film of 1@NC.
Figure S7. TEM tilt tomography of multilayer film of 3@NC.
Figure S8. TEM tilt tomography of bilayer film of 2@NC.
Scaling Theory for Branching Ligand Architecture

We provide a detailed derivation of a generalized scaling law for branching graft architecture. We start with the scaling relations for the end-to-end distance for non-grafted branching chains in both a good and theta solvent as shown in Eq. I.1 and I.2, respectively.\(^3,4\)

\[
R \sim N^{5/2(d+2)} \Lambda^{-1/2(d+2)} \nu^{1/(d+2)} \\
R \sim N^{7/4(d+1)} \Lambda^{(5-2d)/4(d+1)}
\]

(I.1) \hspace{1cm} (I.2)

where \(R\) is the end-to-end distance, \(N\) is the chain length, \(\Lambda\) is the branching activity, \(\nu\) is the excluded volume of the chain’s statistical segment, and \(d\) is the dimensionality. Here, \(\Lambda\) is defined such that \(N\Lambda = 1\) converges to the linear chain limit. We are interested in the 3D limit to capture our experimental systems. For \(d = 3\), Eq. I.1 and I.2 become:

\[
R \sim N^{1/2} \Lambda^{-1/10} \nu^{1/5} \\
R \sim N^{7/16} \Lambda^{-1/16}
\]

(I.3) \hspace{1cm} (I.4)

As a consistency check, in the limit of a linear chain, \(\Lambda \sim N^{-1}\) and Eq. I.3 and I.4 converge to the well known good and theta scaling behavior for linear chains – \(R \sim N^{3/5} \nu^{1/5}\) and \(R \sim N^{1/2}\), respectively.

Using Eq. I.3 and I.4, we now define a parameter \(\alpha = R_{\text{good}}/R_{\text{theta}}\) that measures how much a chain swells relative to its equilibrium conformation when placed in a good solvent environment.

\[
\alpha^5 \sim N^{1/2} \nu [N\Lambda]^{-3/16}
\]

(I.5)

Again, Eq. I.5 converges to its linear chain analog of \(\alpha \sim N^{1/2} \nu\) when \(N\Lambda = 1\). In general, values for \(N\Lambda\) are always greater than 1 for branching chains. Thus, by inspection, it is immediately clear that branching reduces the amount a chain of length \(N\) can swell relative to its linear counterpart. This is a direct manifestation of junctions along a branching chain’s backbone that place physical constraints on how much a local segment can swell.

The above results are for free chains in solution. To bridge Eq. I.1 - I.5 to the grafting limit, we utilize an analogous scaling argument employed by Vo et al.\(^5\) for linear grafts on the surface of anisotropic particles. Again, we define three relevant regimes for chain behavior as a function of the radial distance \(r\) away from the grafting surface – swollen (semi-dilute), un-swollen (theta), and stretched (flat-brush).

We start with the radial region around the core where chains are swollen. In this limit, the chain swells due to favorable interactions with the solvent and we can apply Eq. I.5 in conjunction with the constraint that local and global monomer volume fraction within a layer \(r\) must be equal to give:

\[
\xi(r) \sim rf^{-1/2} \Omega^{3/2}
\]

(I.6)
where $\xi$ is the correlation blob size, $n$ is the number of monomers, $\psi$ is the volume fraction, $b$ is the kuhn length, and $f$ is the number of grafts and is related to the grafting density $\sigma$ via the relation $\sigma \sim f / r_o^2$ with $r_o$ representing the in-sphere radius of the shape of interest. In order to keep Eq. I.6 - I.9 generalized for an arbitrary core shape, we introduced the parameter $\Omega$ that defines both the shape and specific position on the particle surface.

As we move radially inward, there exists a cross-over value of $r_\theta$ where the local monomer concentration is high enough that no additional solvent can penetrate into the brush layer. At this point, chains can no longer swell due to solvent interaction and must relax back to their theta conformation. The transition value of $r_\theta$ can be directly solved for by setting $\alpha(r) \sim 1$ in Eq. I.7 to give

$$r_\theta \sim b f^{1/2} \nu^{-7/5} \Omega^{-3/2} \Lambda^{1/5} \quad (I.10)$$

Enforcing $\alpha(r) = 1$ also enables us to derive the analog of Eqs. I.6 and I.8 - I.9 for the theta regime:

$$\xi(r) \sim rf^{-1/2} \Omega^{3/2} \quad (I.11)$$

$$n(r) \sim \left(\frac{r}{b}\right)^{16/7} f^{-8/7} \Omega^{24/7} \Lambda^{1/7} \quad (I.12)$$

$$\psi(r) \sim \left(\frac{r}{b}\right)^{-5/7} f^{5/14} \Omega^{15/14} \Lambda^{1/7} \quad (I.13)$$

Moving further radially inward, we will eventually hit another cross-over value of $r_c$ where the chains are so confined that they are forced to fully extend to an all-trans conformation. In this fully-stretched limit, the monomer concentration becomes uniform. Setting $\psi(r) \sim 1$ in Eq. I.13 allows for us to solve for $r_c$ to be

$$r_c \sim b f^{1/2} \Omega^{-3/2} \Lambda^{1/5} \quad (I.14)$$

Knowing $\psi(r) \sim 1$ and $\alpha(r) \sim 1$ trivially makes $\xi(r) \sim b$ and $n(r) \sim 1$ for the stretched regime. Table I.1 and Eq. I.15 provide a summary of the derived scaling behavior in the various regimes along with the cross-over distances.
Table S1 1: Scaling Behavior for Anisotropic Grafting

<table>
<thead>
<tr>
<th></th>
<th>Swollen</th>
<th>Theta</th>
<th>Stretched</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\zeta(r)$</td>
<td>$r \Omega^{3/2} f^{-1/2}$</td>
<td>$r \Omega^{3/2} f^{-1/2}$</td>
<td>$b$</td>
</tr>
<tr>
<td>$n(r)$</td>
<td>$r^2 f^{-1} v^{-2/5} \Omega^{3/2} \Lambda^{1/5} b^{-2}$</td>
<td>$r^{16/7} f^{-8/7} \Omega^{24/7} b^{-16/7}$</td>
<td>$1$</td>
</tr>
<tr>
<td>$\psi(r)$</td>
<td>$r^{-1} f^{1/2} v^{-2/5} \Omega^{-3/2} \Lambda^{1/5} b$</td>
<td>$r^{-5/7} f^{5/4} \Omega^{15/14} \Lambda^{1/7} b^{5/7}$</td>
<td>$1$</td>
</tr>
<tr>
<td>$a(r)$</td>
<td>$r^{1/8} f^{-1/16} v^{7/40} \Omega^{3/16} \Lambda^{-1/40} b^{-1/8}$</td>
<td>$1$</td>
<td>$1$</td>
</tr>
</tbody>
</table>

Swollen: $r > b f^{1/2} \Omega^{-3/2} \Lambda^{1/5}$

Unswollen: $b f^{1/2} \Omega^{-3/2} \Lambda^{1/5} < r < b f^{1/2} \Omega^{-7/5} \Lambda^{-3/2} \Lambda^{1/5}$ (I.15)

Core: $r < b f^{1/2} \Omega^{-3/2} \Lambda^{1/5}$

In order to predict the corona size that results from grafting we integrate the $\psi(r)$ across all relevant regimes as follows

$$N f b^3 \int_0^R \phi(r) d\bar{r}$$

where $N$ is the total chain length, $R$ is the center-to-chain distance of interest, and $d\bar{r} \sim r^2 \Omega^3 dr$.

Expanding over the relevant regimes gives:

$$N f b^3 \sim \int_0^{r_c} r^2 \Omega^3 dr + \int_{r_c}^{r_0} b^{5/7} f^{5/14} \Omega^{57/14} v^{9/7} dr + \int_{r_0}^R b f^{1/2} v^{-2/5} \Omega^{3/2} \Lambda^{1/5} r dr$$  \hspace{1cm} (I.16)

Integrating and grouping terms give

$$R^2 \sim N b^2 f^{1/2} \nu^{2/5} \Omega^{-3/2} \Lambda^{-1/5} + b^2 f^{13/14} \nu^{2/5} \Omega^{-6/7} \Lambda^{9/35} \left( \Omega^{48/7} - \nu^{-16/5} \right) + b^2 f^{2/5} \nu^{-2/5} \Omega^{-3} \Lambda^{-1/5} \left( \nu^{-16/5} - 1 \right)$$  \hspace{1cm} (I.17)

We are interested only in the dominant term in $N$. Dropping all other terms gives

$$R \sim N^{1/2} b f^{1/4} \nu^{1/5} \Omega^{-3/4} \Lambda^{-1/10}$$  \hspace{1cm} (I.18)

In its current form, Eq. I.18 is hard to directly compare with the linear grafting result. To better facilitate comparison, we can rewrite it as:

$$R \sim r_o \sigma^{1/5} \nu^{1/5} b^{2/5} \left[ \frac{N b}{\Omega r_o} \right]^{3/5} \left[ \frac{r_o \sigma^{1/2}}{N \Lambda \Omega^{3/2}} \right]^{1/10}$$  \hspace{1cm} (I.19)
For a linear chain, the corona size is:

$$ R \sim r_o \sigma^{1/5} \nu^{1/5} b^{2/5} \left[ \frac{N}{\Omega} \frac{b}{r_o} \right]^{3/5} $$  \hspace{1cm} (I.20)

By inspection, we gain a factor of \( \left[ \frac{r_o \sigma^{1/2}}{N \Lambda \Omega^{3/2}} \right]^{1/10} \) in the branching result. Note here that convergence to the linear limit is now convoluted by both the effect of grafting ( \( r_o \sigma^{1/2} \)) and of the core shape ( \( \Omega^{3/2} \)). As a result, rather than \( N \Lambda \sim 1 \) resulting in a linear chain in the free chain limit, we get \( N \Lambda \sim r_o \sigma^{1/2} \Omega^{-3/2} \). Eq. I.19 gives us a way to directly compare the effect of branching versus linear chains. From Eq. I.5, we noted that branching alters the degree of swelling a chain experiences. This is analogous to rescaling the kuhn length \( b \) of the chain. Thus, we can group the extra factor together with the \( b^{2/5} \) dependency in both Eq. I.19 and I.20 to give

$$ b_{\text{branch}} \sim b_{\text{linear}} \left[ \frac{r_o \sigma^{1/2}}{N \Lambda \Omega^{3/2}} \right]^{1/4} $$  \hspace{1cm} (I.21)

Setting \( \Omega \sim 1 \) to remove the effect of core shape gives the kuhn length rescaling employed in the main text. Lastly, we can define the free energy for the chain

$$ \frac{F}{kT} \sim \frac{R^2}{N^{7/16} \Lambda^{-1/16}} + \nu \frac{N^2 f}{(\Omega R)^3} $$  \hspace{1cm} (I.22)

This free energy can then be used as a Boltzmann weighting factor to determine the probability \( P \) of grafting to various locations on the surface of any arbitrarily defined anisotropic particle. Eq. I.23 defines the partitioning probability and will be heavily utilized to understand how corona morphology drives self-assembly as well as for mapping our theoretical predictions to simulation.

$$ P \sim \frac{\exp(-F/kT)}{\iiint \exp(-F/kT) d\vec{r}} $$  \hspace{1cm} (I.23)
Mapping of Scaling Prediction to Simulation

Here, we provide an example of how we mapped the theoretical scaling results from the previous section to a set of parameters for use in simulation. We first compute the partitioning probability of ligands on the surface of the nanoplate. This is performed via generating grid points on the particle surface and computing $P$ from Eq. I.23 at each point. A set of potential mean forces was then computed between two grafted particles using $P$ as an additional weighting probability of interactions between each point on the particles’ surface. While exact, creating a unique bead type for each point on the particle surface becomes prohibitively expensive for a molecular dynamics simulations (Fig. S9a). In order to reduce the complexity of the simulation model, we categorize the continuous probability distribution into 3 distinct group based on the value, $P$, of the scaled grafting probabilities: low for $P \in [0,0.33)$, medium for $P \in [0.33,0.5)$, and high for $P \in [0.5,1]$ (Fig. S9b). Potential mean forces for surface points falling within each probability range are then averaged together to give an effective potential of interaction that can be readily employed in simulation (Fig. S9c). We then create a rigid body of smaller surface beads that sit on the nanoplate and attribute interaction strengths to each bead based on the bead type (red, blue, or green) for use in simulation. Standard mixing rules apply for cross interactions between particle types.

Figure S9. Mapping of Scaling Theory to Simulation. a). Original partitioning probabilities for ligand to surface nanoplate. b). Categorization of surface points based on bracketing range for partitioning probabilities (low: red, medium: blue, and high: green). c). Averaged potential mean force computed from surface point interactions for each bracketing range used simulation.
References


Copies of $^1$H and $^{13}$C spectra