# Supplementary data

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#### **General methods for synthesis**

Unless specified, solvents and reagents were used as received. Pentadecanoyl chloride and heptadecanoyl chloride were synthesized via a reaction of the corresponding carboxylic acid in refluxing thionyl chloride and a few drops of DMF for 24 h. The products were purified by bulbto-bulb distillation until a clear, colourless liquid was obtained. Weisocyanate<sup>TM</sup> was prepared as described previously.<sup>1</sup> Analytical thin layer chromatography was performed on aluminumcoated silica gel 60 Å and detected by dipping in a solution of 10% ethanolic phosphomolybdic acid reagent (20 wt % solution in ethanol) and then heated with a heat gun. The R<sub>f</sub> for 3ECbn in hexane/THF (6:1, v/v) was 0.32–0.41. Flash column chromatography was carried out on silica gel (60 Å). The samples were introduced as concentrated solutions in hexane/THF (6:1, v/v). After eluting the solvent mixture (100 mL), fractions (25 mL) were collected. The flow rate (~64 mL/min) was controlled by compressed air. The product appeared in fractions 3 to 12. Solutions were concentrated by rotary evaporation. Melting points were determined in open capillary tubes at 1°C/min and uncorrected. NMR spectra of 3CCbn series were recorded at 400 and 100 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively, and reported in ppm. References in <sup>1</sup>H and <sup>13</sup>C spectra were TMS and DMSO-d<sub>6</sub>, respectively. NMR spectra of 3CAm14 and 3CAm16 were recorded at 500 and 125 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively, and reported in ppm. References in <sup>1</sup>H and <sup>13</sup>C spectra were CD<sub>3</sub>OD and DMSO- $d_6$ , respectively. IR spectra were recorded on neat samples with an FTIR equipped with a diamond ATR system, and reported in cm<sup>-1</sup>. HRMS data were obtained on a dual-sector mass spectrometer in FAB mode with 2-nitrobenzylalcohol as the proton donor. Elemental analyses were performed by a commercial vendor.

#### Di-tert-butyl 4-(2-(tert-butoxycarbonyl)ethyl)-4-(3-

## tetradecoxycarbonylamino)heptanedioate, 3ECb14

Following the general procedure described in the manuscript, tetradecan-1-ol (0.73 g, 3.40 mmol), Weisocyanate<sup>TM</sup> (1.42 g, 3.22 mmol) gave, after flash column chromatography with 6:1 hexane/EtOAc, a white solid (1.77 g, 84% yield); mp 54.3–54.9 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H), 1.25 (m, 22H), 1.42 (s, 27H), 1.57 (broad p, 2H), 1.91 (t, 6H), 2.21 (t, 6H), 3.96 (broad t, 2H), 4.69 (broad s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.1, 22.7, 25.9, 28.08, 28.99, 29.35, 29.37, 29.58, 29.62, 29.67, 29.69, 29.72, 30.2, 31.9, 56.4, 64.6, 80.6, 154.6, 172.6; IR 3371, 2916, 1727, 1703, 1363, 1142, 1075; HRMS (FAB+) calcd for C<sub>37</sub>H<sub>69</sub>NO<sub>8</sub> (MH<sup>+</sup>) 656.5101, found 656.5105. Anal. Calcd. for C<sub>37</sub>H<sub>69</sub>NO<sub>8</sub>: C, 67.75; H, 10.60; N, 2.14. Found: C, 67.75; H, 10.84; N, 2.27.

# Di-tert-butyl 4-(2-(tert-butoxycarbonyl)ethyl)-4-(3-

## hexadecoxycarbonylamino)heptanedioate, 3ECb16

Following the general procedure described in the manuscript, hexadecan-1-ol (0.789 g, 3.25 mmol) and Weisocyanate<sup>TM</sup> (1.44 g, 3.26 mmol) gave, after flash column chromatography with 6:1 hexane/EtOAc, a white solid (1.8781 g, 84%); mp 60.8–61.4 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.89 (t, 3H), 1.27 (m, 26H), 1.45 (s, 27H), 1.59 (broad p, 2H), 1.92 (t, 3H), 2.23 (t, 3H), 3.99 (broad t, 2H), 4.70 (broad s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.1, 22.7, 25.9, 28.08, 28.99, 29.33, 29.37, 29.56, 29.62, 29.66, 29.70, 30.2, 31.9, 56.4, 64.6, 80.6, 154.6, 172.6; IR 3357, 2921, 1727, 1708, 1530, 1363, 1257, 1142; HRMS (FAB+) calcd for C<sub>39</sub>H<sub>73</sub>NO<sub>8</sub> (MH<sup>+</sup>) 684.5414, found 684.5427. Anal. Calcd for C<sub>39</sub>H<sub>73</sub>NO<sub>8</sub>: C, 68.48; H, 10.76; N, 2.05. Found: C, 68.37; H, 10.83; N, 2.18.

#### Di-tert-butyl 4-(2-(tert-butoxycarbonyl)ethyl)-4-(3-

## octadecoxycarbonylamino)heptanedioate, 3ECb18

Following the general procedure described in the manuscript, octadecan-1-ol (0.907 g, 3.35 mmol) and Weisocyanate<sup>TM</sup> (1.41 g, 3.20 mmol) gave, after flash column chromatography with 6:1 hexane/EtOAc, a white solid (1.80 g, 79%); mp 58.6–59.1 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H), 1.26 (m, 30H), 1.44 (s, 27H), 1.58 (broad p, 2H), 1.91 (t, 3H), 2.22 (t, 3H), 3.98 (broad t, 2H), 4.70 (broad s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.1, 22.7, 25.9, 28.1, 28.99, 29.34, 29.36, 29.57, 29.61, 29.67, 29.71, 30.2, 31.9, 56.4, 64.6, 80.6, 154.6, 172.6; IR 3357, 2921, 1727, 1708, 1531, 1363, 1253, 1142; HRMS (FAB+) calcd for C<sub>41</sub>H<sub>77</sub>NO<sub>8</sub> (MH<sup>+</sup>) 712.5727, found 712.5710. Anal. Calcd for C<sub>41</sub>H<sub>77</sub>NO<sub>8</sub>: C, 69.16; H, 10.90; N, 1.97. Found: C, 69.10; H, 11.10; N, 2.13.

# Di-tert-butyl 4-(2-(tert-butoxycarbonyl)ethyl)-4-(3-

## eicosadecoxycarbonylamino)heptanedioate, 3ECb20

Following the general procedure described in the manuscript, icosan-1-ol (1.02 g, 3.40 mmol) and Weisocyanate<sup>TM</sup> (1.51 g, 3.21 mmol) gave, after flash column chromatography with 6:1 hexane/EtOAc, a white solid (1.51 g, 63%); mp 59.0–59.6 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H), 1.25 (m, 34H), 1.44 (s, 27H), 1.57 (broad p, 2H), 1.90 (t, 3H), 2.21 (t, 3H), 3.97 (broad t, 2H), 4.69 (broad s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.2, 22.8, 26.0, 28.2, 29.11, 29.46, 29.48, 29.69, 29.75, 29.83, 30.3, 32.0, 56.5, 64.7, 80.7, 154.7, 172.7; IR 3338, 2916, 1727, 1703, 1526, 1363, 1142; HRMS (FAB+) calcd for C<sub>43</sub>H<sub>81</sub>NO<sub>8</sub> (MH<sup>+</sup>) 740.6040, found 740.6021. Anal. Calcd for C<sub>43</sub>H<sub>81</sub>NO<sub>8</sub>: C, 69.78; H, 11.03; N, 1.89. Found: C, 69.73; H, 11.27; N, 2.05.

#### Di-tert-butyl 4-(2-(tert-butoxycarbonyl)ethyl)-4-(3-

## docosadecoxycarbonylamino)heptanedioate, 3ECb22

Following the general procedure described in the manuscript, docosan-1-ol (1.11 g, 3.39 mmol) and Weisocyanate<sup>TM</sup> (1.42 g, 3.22 mmol) gave, after flash column chromatography with 6:1 hexane/EtOAc, a white solid (1.70 g, 69%); mp 65.8–66.3 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.88 (t, 3H), 1.25 (m, 38H), 1.44 (s, 27H), 1.59 (broad p, 2H), 1.90 (t, 3H), 2.21 (t, 3H), 3.98 (broad t, 2H), 4.69 (broad s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.3, 22.9, 26.1, 28.3, 29.17, 29.51, 29.54, 29.75, 29.80, 29.89, 30.3, 32.1, 56.5, 64.8, 80.8, 154.8, 172.8; IR 3338, 2916, 1727, 1703, 1531, 1464, 1363, 1142, HRMS (FAB+) calcd for C<sub>45</sub>H<sub>85</sub>NO<sub>8</sub> (MH<sup>+</sup>) 768.6353, found 768.6356; Anal. Calcd for C<sub>45</sub>H<sub>85</sub>NO<sub>8</sub>: C, 70.36; H, 11.15; N, 1.82. Found: C, 70.33; H, 11.25; N, 1.89.

# 4-(2-Carboxyethyl)-4-(3-tetradecoxycarbonylamino)heptanedioic acid, 3CCb14

Following the general procedure described in the manuscript, 3ECb14 (3.42 g, 5.21 mmol) gave upon recrystallization from acetonitrile a white powder (1.96 g, 77%); mp 121.4–121.9 °C; <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  0.80 (t, 3H), 1.19 (broad m, 22H), 1.43 (broad p, 2H), 1.65 (t, 6H), 2.05 (t, 6H), 3.81 (t, 2H), 6.62 (broad s, 1H), 11.98 (broad s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  13.9, 22.1, 25.3, 28.1, 28.68, 28.69, 28.96, 28.98, 29.02, 29.20, 31.3, 55.6, 63.1, 154.5, 174.3; IR 3429, 3165, 2916, 1725, 1678, 1570, 1237, 1090; HRMS (FAB+) calcd for C<sub>25</sub>H<sub>45</sub>NO<sub>8</sub> (MH<sup>+</sup>) 488.3223, found 488.3234 Anal. Calcd for C<sub>25</sub>H<sub>45</sub>NO<sub>8</sub>: C, 61.58; H, 9.30; N, 2.87. Found: C, 61.58; H, 9.51; N, 2.84.

#### 4-(2-Carboxyethyl)-4-(3-hexadecoxycarbonylamino)heptanedioic acid, 3CCb16

Following the general procedure described in the manuscript, 3ECb16 (4.11 g, 6.01 mmol) gave upon recrystallization from acetonitrile a white powder(2.79 g, 90%); mp 123.9–124.7 °C; <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  0.85 (t, 3H), 1.23 (broad m, 26H), 1.50 (broad p, 2H), 1.76 (t, 6H), 2.10 (t, 6H), 3.88 (t, 2H), 6.72 (broad s, 1H), 11.98 (broad s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  13.9, 22.1, 25.4, 28.07, 28.70, 28.71, 28.98, 28.99, 29.03, 29.19, 31.3, 55.6, 63.1, 154.5, 174.3; IR 3429, 3156, 2916, 1723, 1675, 1521, 1234, 1090; HRMS (FAB+) calcd for C<sub>27</sub>H<sub>49</sub>NO<sub>8</sub> (MH<sup>+</sup>) 516.3536, found 516.3521. Anal. Calcd for C<sub>27</sub>H<sub>49</sub>NO<sub>8</sub>: C, 62.89; H, 9.58; N, 2.72. Found: C, 62.67; H, 9.79; N, 2.76.

## 4-(2-Carboxyethyl)-4-(3-octadecoxycarbonylamino)heptanedioic acid, 3CCb18

Following the general procedure described in the manuscript, 3ECb18 (2.93 g, 4.11 mmol) gave upon recrystallization from acetonitrile as a white powder( 1.68 g, 75%); mp 125.3–126.3 °C; <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  0.85 (t, 3H), 1.23 (broad m, 30H), 1.50 (broad p, 2H), 1.76 (t, 6H), 2.10 (t, 6H), 3.88 (t, 2H), 6.71 (broad s, 1H), 12.05 (broad s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  13.9, 22.1, 25.4, 28.05, 28.69, 28.71, 29.02, 29.17, 31.3, 55.5, 63.1, 154.5, 174.3; IR 3431, 3159, 2918, 1725, 1677, 1523, 1236, 1030; HRMS (FAB+) calcd for C<sub>29</sub>H<sub>53</sub>NO<sub>8</sub> (MH<sup>+</sup>) 544.3849, found 544.3855. Anal. Calcd for C<sub>29</sub>H<sub>53</sub>NO<sub>8</sub>: C, 64.06; H, 9.82; N, 2.58. Found: C, 64.02; H, 10.06; N, 2.54.

#### 4-(2-Carboxyethyl)-4-(3-eicosadecoxycarbonylamino)heptanedioic acid, 3CCb20

Following the general procedure described in the manuscript, 3ECb20 (2.68 g, 3.62 mmol) gave upon recrystallization from MeOH/water a white powder (2.00 g, 96%); mp 124.1–124.8 °C; <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  0.85 (t, 3H), 1.23 (broad m, 34H), 1.50 (broad p, 2H), 1.76 (t, 6H), 2.10 (t, 6H), 3.87 (t, 2H), 6.71 (broad s, 1H), 12.06 (broad s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  13.9, 22.1, 25.4, 28.06, 28.68, 28.71, 29.00, 29.17, 31.3, 55.6, 63.1, 154.5, 174.3; IR 3429, 3165, 2916, 1723, 1675, 1521, 1238, 1028; HRMS (FAB+) calcd for C<sub>31</sub>H<sub>57</sub>NO<sub>8</sub> (MH<sup>+</sup>) 572.4162, found 572.4153. Anal. Calcd for C<sub>31</sub>H<sub>57</sub>NO<sub>8</sub>: C, 65.12; H, 10.05; N, 2.45. Found: C, 64.82; H, 10.16; N, 2.49.

## 4-(2-Carboxyethyl)-4-(3-docosadecoxycarbonylamino)heptanedioic acid, 3CCb22

Following the general procedure described in the manuscript, 3ECb22 (1.52 g, 1.98 mmol) gave upon recrystallization from MeOH/water a white powder (1.17, 86%); mp 125.9–126.6 °C; <sup>1</sup>H NMR (DMSO- $d_6$ )  $\delta$  0.85 (t, 3H), 1.23 (broad m, 38H), 1.50 (broad p, 2H), 1.76 (t, 6H), 2.10 (t, 6H), 3.87 (t, 2H), 6.71 (broad s, 1H), 12.06 (broad s, 3H); <sup>13</sup>C NMR (DMSO- $d_6$ )  $\delta$  13.9, 22.1, 25.4, 28.07, 28.71, 28.74, 29.01, 29.18, 31.3, 55.6, 63.1, 154.5, 174.3; IR 3429, 3161, 2916, 1723, 1680, 1521, 1239, 1028; HRMS (FAB+) calcd for C<sub>33</sub>H<sub>61</sub>NO<sub>8</sub> (MH<sup>+</sup>) 600.4475, found 600.4476. Anal. Calcd for C<sub>33</sub>H<sub>61</sub>NO<sub>8</sub>: C, 66.08; H, 10.25; N, 2.34. Found: C, 65.96; H, 10.49; N, 2.37.

**Di***tert*-**butyl 4-(2***-tert*-**butoxycarbonyl-ethyl)-4-pentadecanoylaminoheptanedioate, 3EAm14** The general procedure described in the manuscript afforded a white solid (5.94 g, 76%) ; mp  $66.4-67.2^{\circ}$ C; <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, 3H), 1.24–1.30 (bm, 22H), 1.43 (s, 27H), 1.58 (bm, 2H), 1.96 (m, 6H), 2.08 (t, 2H), 2.21 (m, 6H), 5.77 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.2, 22.7, 25.9, 28.1, 29.39, 29.42, 29.44, 29.58, 29.71, 29.76, 29.89, 30.06, 37.7, 57.3, 80.7, 172.7, 173.0; IR 3362, 2918, 2851, 1718, 1708, 1676, 1536, 1149 cm<sup>-1</sup>; HRMS: for C<sub>37</sub>H<sub>69</sub>NO<sub>7</sub> calcd 640.5152, found 640.5160. Anal. Calcd for C<sub>37</sub>H<sub>69</sub>NO<sub>7</sub>: C, 69.44; H, 10.87; N, 2.19. Found: C, 69.42; H, 10.87; N, 2.21.

# Di-tert-butyl 4-(2-tert-butoxycarbonylethyl)-4-heptadecanoylamino-heptanedioate, 3EAm16

The general procedure described in the manuscript afforded a yellow solid (7.47 g). During the recrystallization of the yellow solid in EtOH/water, a yellow solid formed. The clear, colourless liquid was decanted and left sitting at room temperature. The resulting white solid, 2.74 g, was removed via filtration. The filtrate was placed in a fridge overnight, which yielded a yellow solid (3.76 g). Additional material could possibly be attained from this yellow solid by further purification. The white solid was recrystallized again in EtOH/water, yielding white needles (2.02 g, 25%). This material was used in the subsequent formolysis reactions; mp 64.5–65.3°C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.87 (t, 3H), 1.25–1.28 (bm, 26H), 1.43 (s, 27H), 1.96 (m, 6H), 2.09 (m, 2H), 2.21 (m, 6H), 5.78 (s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  14.2, 22.7, 25.9, 28,1, 29.37, 29.42, 29.57, 29.71, 29.75, 29.87, 30.0, 32.0, 37.7, 57.3, 80.7, 172.7, 173.0; IR 3381, 2915, 1729, 1727, 1712, 1671, 1529, 1146 cm<sup>-1</sup>; HRMS: for C<sub>39</sub>H<sub>73</sub>NO<sub>7</sub> calcd 668.5465, found 668.5461. Anal. Calcd for C<sub>39</sub>H<sub>73</sub>NO<sub>7</sub>: C, 70.12; H, 11.01; N, 2.10. Found: C, 69.77; H, 10.92; N, 2.09.

## 4-(2-Carboxyethyl)-4-pentadecanoylaminoheptanedioic acid, 3CAm14

The general procedure described in the manuscript afforded a white solid (0.42 g, 74%); mp 164.5–164.8°C; <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.89 (t, 3H), 1.28–1.32 (bm, 22H), 1.58 (bm, 2H), 2.02 (m, 6H), 2.16 (m, 2H), 2.26 (m, 6H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  14.5, 22.7, 26.0, 28.6, 29.16, 29.28, 29.36, 29.54, 29.58, 29.61, 31.9, 36.4, 56.8, 172.6, 175.0; IR 3413, 3070, 2915, 2847, 1725, 1694, 1628, 1517, 1175 cm<sup>-1</sup>; HRMS: for C<sub>25</sub>H<sub>45</sub>NO<sub>7</sub> calcd 472.3274, found 472.3247. Anal. Calcd for C<sub>25</sub>H<sub>45</sub>NO<sub>7</sub>: C, 63.67; H, 9.62; N, 2.97. Found: C, 63.68; H, 9.67; N, 2.98.

## 4-(2-Carboxyethyl)-4-heptadecanoylaminoheptanedioic acid, 3CAm16

The general procedure described above afforded a white solid (0.57 g, 80%); mp 168.1–168.7 °C; <sup>1</sup>H NMR (CD<sub>3</sub>OD)  $\delta$  0.89 (t, 3H), 1.28–1.32 (bm, 26H), 1.58 (bm, 2H), 2.01 (m, 6H), 2.16 (t, 2H), 2.26 (m, 6H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>)  $\delta$  14.5, 22.7, 26.0, 28.59, 29.16, 29.27, 29.36, 29.54, 29.61, 31.9, 36.4, 56.8, 172.6, 175.0; IR 3412, 3103, 2915, 1724, 1694, 1628, 1518, 1175 cm<sup>-1</sup>; HRMS: calcd for C<sub>27</sub>H<sub>49</sub>NO<sub>7</sub> 500.3587, found 500.3583. Anal. Calcd for C<sub>27</sub>H<sub>49</sub>NO<sub>7</sub>: C, 64.90; H, 9.88; N, 2.80. Found: C, 64.65; H, 9.71; N, 2.80.

# Reference

**1.** Newkome GR, Weis CD, Childs BJ. Syntheses of  $1 \rightarrow 3$  branched isocyanate monomers for dendritic construction. *Des Monomers Polym* 1998; **1**: 3–14.