

## **The Effect of Structural Tuning on the Folding-Unfolding and Dimer-Chain Equilibria of Bifunctional H-Bonding Unimers**

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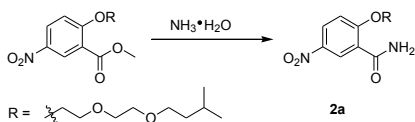
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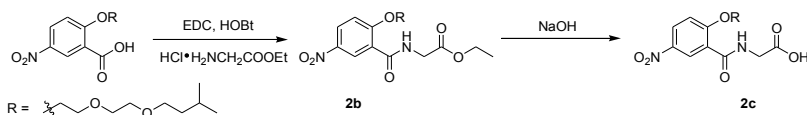
## 1. Materials and Methods

All reagents were purchased from commercial sources (Fisher Scientific, Acros, Alfa Aesar and Aldrich) and were used as received unless otherwise noted. Silica gel column chromatography was carried out with silica gel 60 (mesh 230-400) and products were detected as single spots by thin-layer chromatography (precoated 0.25 mm silica plates from Sorbent). All  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data were recorded on Varian Inova 500 (or 400) Spectrometers (500 MHz or 400 MHz) and Varian Mercury 300 Spectrometer (300 MHz). NMR chemical shifts are reported in ppm relative to internal standard TMS, and coupling constant,  $J$ , is reported in Hertz (Hz). For the  $^1\text{H}$  NMR experiments,  $\text{CDCl}_3$  (99.8% D),  $\text{DMF-d}_7$  (99.5%) and  $\text{DMSO-d}_6$  (99.8% D) were purchased from Cambridge Isotope Laboratory and used without further purification. Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH, Bremen, Germany) equipped with an ESI interface and an ion trap analyzer.

## 2. Syntheses

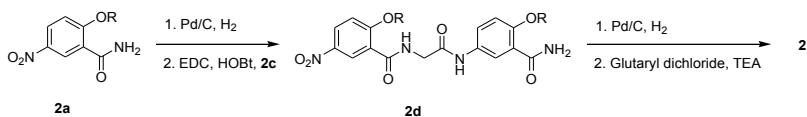


Compound **2a**: Ammonium hydroxide (18 mL) was added to a methanol solution (9 mL) of methyl 2-(2-(2-(isopentyloxy)ethoxy)ethoxy)-5-nitrobenzoate <sup>1</sup>(1.62 g, 4.56 mmol). The reaction mixture was allowed to react at 40°C overnight. Most of the solvent is removed in a reduced pressure. Water and dichloromethane were added. The aqueous layer was extracted with dichloromethane three times. Organic layer was combined and solvent was removed in vacuum. White powder was obtained as the product (1.24g, 80%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ 8.61 (d, *J* = 3.0 Hz, 1H), 8.34 (dd, *J* = 9.1, 3.0 Hz, 1H), 7.89 (s, 1H), 7.71 (s, 1H), 7.40 (d, *J* = 9.2 Hz, 1H), 4.43 – 4.37 (m, 2H), 3.87 – 3.81 (m, 2H), 3.59 (m, 2H), 3.47 (m, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.57 (m, 1H), 1.32 (m, 2H), 0.90 – 0.71 (m, 6H). <sup>13</sup>C NMR (126 MHz, DMSO-*d*<sub>6</sub>) δ 164.55, 161.78, 141.21, 128.30, 126.93, 123.96, 114.88, 70.21, 69.95, 69.53, 69.16, 68.68, 38.46, 25.00, 22.91. ESI MS: calculated 363.4, found 363.3 (M + Na)<sup>+</sup>.



Compound **2b**: **2b** was prepared following a reported method.<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.05 (d, *J* = 2.8 Hz, 1H), 8.49 (s, 1H), 8.29 (dd, *J* = 9.1, 2.8 Hz, 1H), 7.07 (d, *J* = 9.1 Hz, 1H), 4.39 (m, 2H), 4.29 – 4.15 (m, 4H), 4.07 – 3.91 (m, 2H), 3.75 – 3.61 (m, 2H), 3.59 – 3.48 (m, 2H), 3.43 (t, *J* = 6.9 Hz, 2H), 1.61 (m, 1H), 1.42 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.85 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 169.81, 163.01, 161.28, 141.92, 128.45, 128.10, 122.19, 112.96, 70.75, 70.02, 69.92, 69.32, 68.69, 61.39, 42.08, 38.29, 25.05, 22.58, 14.17. ESI MS: calculated 449.5, found 449.3 (M + Na)<sup>+</sup>.

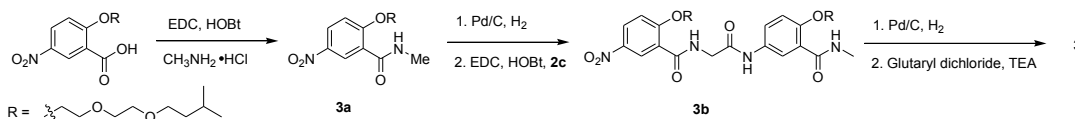
Compound **2c**: **2c** was prepared following a reported method.<sup>2</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.09 (d, *J* = 2.9 Hz, 1H), 8.61 (t, *J* = 4.5 Hz, 1H), 8.35 (dd, *J* = 9.1, 2.9 Hz, 1H), 7.09 (d, *J* = 9.1 Hz, 1H), 4.49 – 4.38 (m, 2H), 4.32 (m, 2H), 4.03 – 3.95 (m, 2H), 3.79 – 3.69 (m, 2H), 3.69 – 3.62 (m, 2H), 3.55 (t, *J* = 7.1 Hz, 2H), 1.77 – 1.57 (m, 1H), 1.52 (m, 2H), 1.01 – 0.81 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 172.05, 163.51, 161.30, 141.91, 128.34, 121.81, 112.99, 70.71, 70.12, 70.03, 69.36, 68.71, 42.23, 38.01, 25.03, 22.56. ESI MS: calculated 399.4, found 399.1(M + H)<sup>+</sup>.



Compound **2d**: A solution of **2a** (0.60 g, 1.76 mmol) in dichloromethane /methanol was shaken in the presence of Pd/C (10%) under a hydrogen atmosphere for 2 hours, and then catalyst was filtered. The filtrate was evaporated in vacuum, yielding the corresponding amine. To a solution **2c** (0.70 g, 1.76 mmol), EDC (0.38 g, 2.47 mmol) and HOBT (0.26 g, 1.94 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL), the CH<sub>2</sub>Cl<sub>2</sub> solution (6 mL) of freshly prepared amine was added. The reaction was allowed to proceed for 4 hours at room temperature. The mixture was then washed with diluted HCl and solvent was removed in vacuum. Purification was accomplished by chromatography on silica gel using chloroform/methanol to afford **2d** (0.64 g, 78%) as a light yellow solid. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ 10.13 (s, 1H), 8.71 – 8.64 (m, 2H), 8.36 (dd, *J* = 9.1, 2.9 Hz, 1H), 8.05 (d, *J* = 2.8 Hz, 1H), 7.79 (dd, *J* = 8.7, 2.8 Hz, 1H), 7.74 (s, 1H), 7.53 (s, 1H), 7.44 (d, *J* = 9.1 Hz, 1H), 7.12 (d, *J* = 8.9 Hz, 1H), 4.49 – 4.41 (m, 2H), 4.24 – 4.18 (m, 2H), 4.16 (m, 2H), 3.93 – 3.87 (m, 2H), 3.80 – 3.74 (m, 2H), 3.63 – 3.58 (m, 2H), 3.58 – 3.55 (m, 2H), 3.50 – 3.45 (m, 2H), 3.46 – 3.41 (m, 2H), 3.38 (t, *J* = 6.8 Hz, 2H), 3.32 – 3.26 (m, 2H), 1.64 – 1.55 (m, 1H), 1.55 – 1.46 (m, 1H), 1.34 (q, *J* = 6.9 Hz, 2H), 1.27 (q, *J* = 6.7 Hz, 2H), 0.82 (d, *J* = 6.6 Hz, 6H), 0.76 (d, *J* = 6.6 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ 167.16, 165.96, 163.15, 161.90, 153.02, 141.28, 132.74, 128.53, 126.99, 123.93, 122.96, 122.91, 122.60, 115.03, 114.60, 70.34, 70.17, 70.12, 69.93, 69.89, 69.16, 69.09, 69.00, 68.80, 68.72, 48.70, 48.68, 43.88, 38.48, 38.43, 25.01, 24.97, 22.93, 22.87. ESI MS: calculated 713.8, found 713.5 (M + Na)<sup>+</sup>.

Compound **2**: A solution of **2d** (0.28 g, 0.41 mmol) in dichloromethane /methanol was shaken in the presence of Pd/C (10%) under a hydrogen atmosphere for 2 hours, and catalyst was then filtered. The filtrate was evaporated in vacuum, yielding the corresponding amine. The amine and triethylamine (0.05 g, 0.49 mmol) were dissolved in dry dichloromethane (10 mL), followed by a solution of glutaryl dichloride (34.8 mg, 0.20 mmol) in dichloromethane (5 mL). The resulting mixture was allowed to react overnight at room temperature. The crude was washed with diluted HCl and then solvent was removed in vacuum. Purification was accomplished by chromatography on silica gel using chloroform/methanol to afford **2** (0.21 g, 71%) as a pale yellow solid. <sup>1</sup>H NMR (300 MHz, DMF-d<sub>7</sub>) δ 10.15 (s, 2H), 10.02 (s, 2H), 8.88 (t, *J* = 5.0 Hz, 2H), 8.30 (dd, *J* = 9.3, 2.4 Hz, 4H), 7.99 – 7.91 (m, 8H), 7.44 (s, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 9.0 Hz, 2H), 4.32 (m, 12H), 4.00 – 3.93 (m, 4H), 3.93 – 3.85 (m, 4H), 3.76 – 3.58 (m, 8H), 3.58 – 3.51 (m, 8H), 3.45 (t, *J* = 6.7 Hz, 4H), 3.39 (t, *J* = 6.8 Hz, 4H), 2.47 (t, *J* = 7.2 Hz,

4H), 2.10 – 1.96 (m, 2H), 1.75 – 1.49 (m, 4H), 1.37 (m, 8H), 0.86 (d,  $J = 6.7$  Hz, 12H), 0.81 (d,  $J = 6.6$  Hz, 12H).  $^{13}\text{C}$  NMR (75 MHz, DMF- $d_7$ )  $\delta$  170.86, 167.59, 165.75, 164.60, 153.19, 153.01, 133.72, 133.05, 123.87, 123.75, 122.89, 122.79, 122.32, 122.07, 114.23, 114.19, 70.38, 70.23, 69.97, 69.32, 69.17, 69.14, 69.07, 69.02, 68.83, 43.75, 38.49, 38.45, 35.84, 24.93, 22.20, 21.46. ESI MS: calculated 1418.7, found 1418.5 ( $\text{M} + \text{H}$ ) $^+$ .



Compound **3a**: The product was prepared following the procedure reported previously.<sup>2</sup>  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.56 (d,  $J = 3.0$  Hz, 1H), 8.30 (dd,  $J = 9.0, 2.5$  Hz, 1H), 8.29 – 8.09 (m, 1H), 7.38 (d,  $J = 9.1$  Hz, 1H), 4.47 – 4.35 (m, 2H), 3.92 – 3.80 (m, 2H), 3.69 – 3.58 (m, 2H), 3.55 – 3.44 (m, 2H), 3.36 (t,  $J = 6.7$  Hz, 2H), 2.83 (d,  $J = 4.6$  Hz, 3H), 1.55 (m, 1H), 1.31 (m, 2H), 0.84 – 0.77 (m, 6H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  164.29, 162.20, 141.89, 128.68, 127.26, 124.67, 115.49, 71.04, 70.68, 70.28, 69.82, 69.33, 39.12, 27.45, 25.63, 23.50. ESI MS: calculated 355.5, found 355.3 ( $\text{M} + \text{H}$ ) $^+$ .

Compound **3b**: The product was prepared following the procedure reported previously.<sup>2</sup>  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.16 (s, 1H), 8.68 (s, 2H), 8.37 (d,  $J = 9.1$  Hz, 1H), 8.23 (d,  $J = 3.4$  Hz, 1H), 8.02 (s, 1H), 7.78 (d,  $J = 8.6$  Hz, 1H), 7.45 (d,  $J = 9.1$  Hz, 1H), 7.14 (d,  $J = 9.1$  Hz, 1H), 4.61 – 4.35 (m, 2H), 4.35 – 4.09 (m, 4H), 3.90 (s, 2H), 3.79 (s, 2H), 3.66 – 3.54 (m, 4H), 3.54 – 3.31 (m, 8H), 2.81 (s, 3H), 1.70 – 1.38 (m, 2H), 1.38 – 1.15 (m, 4H), 0.96 – 0.67 (m, 12H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  167.19, 165.06, 163.17, 161.91, 152.69, 141.28, 132.92, 128.55, 126.98, 123.59, 123.10, 122.92, 122.19, 115.04, 114.92, 70.34, 70.12, 70.01, 69.88, 69.15, 69.08, 68.96, 68.71, 43.87, 38.47, 38.42, 26.65, 24.98, 22.91, 22.87. ESI MS: calculated 705.8, found 705.4 ( $\text{M} + \text{H}$ ) $^+$ .

Compound **3**: The product was prepared following the procedure reported previously.<sup>2</sup> The crude product was purified using flash column chromatography to yield a pale powder (0.11g, 62%).  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.12 (s, 2H), 9.93 (s, 1H), 8.70 (s, 2H), 8.23 (m, 2H), 8.13 – 7.93 (m, 3H), 7.80 (m, 3H), 7.68 (s, 1H), 7.24 (s, 3H), 7.12 (d,  $J = 8.5$  Hz, 3H), 4.37 – 4.04 (m, 12H), 3.94 – 3.81 (m, 4H), 3.81 – 3.70 (m, 4H), 3.64 – 3.54 (m, 12H), 3.47 (m, 8H), 3.41 – 3.31 (m, 6H), 2.81 (m, 6H), 2.75 – 2.62 (m, 4H), 2.33 (m, 4H), 2.06 – 1.90 (m, 2H), 1.89 – 1.74 (m, 2H), 1.57 (m, 4H), 1.38 – 1.22 (m, 8H), 0.87 – 0.68 (m, 24H).  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  173.32, 170.74, 167.47, 165.06, 164.37, 156.55, 152.64, 133.60, 133.02, 131.94, 129.47, 123.58,

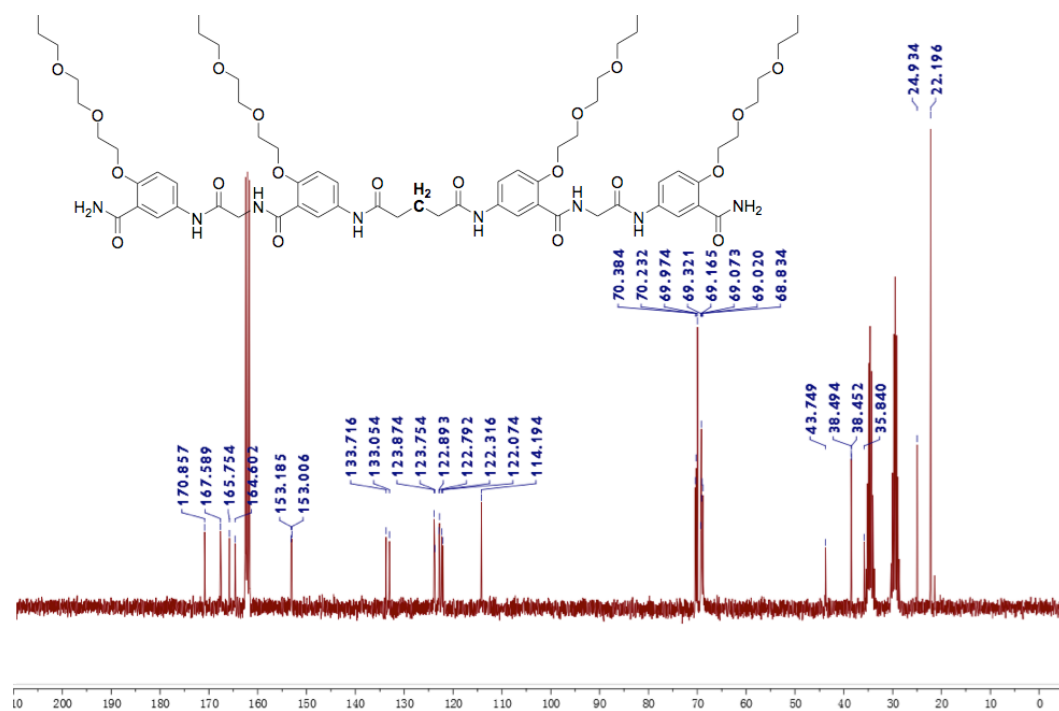
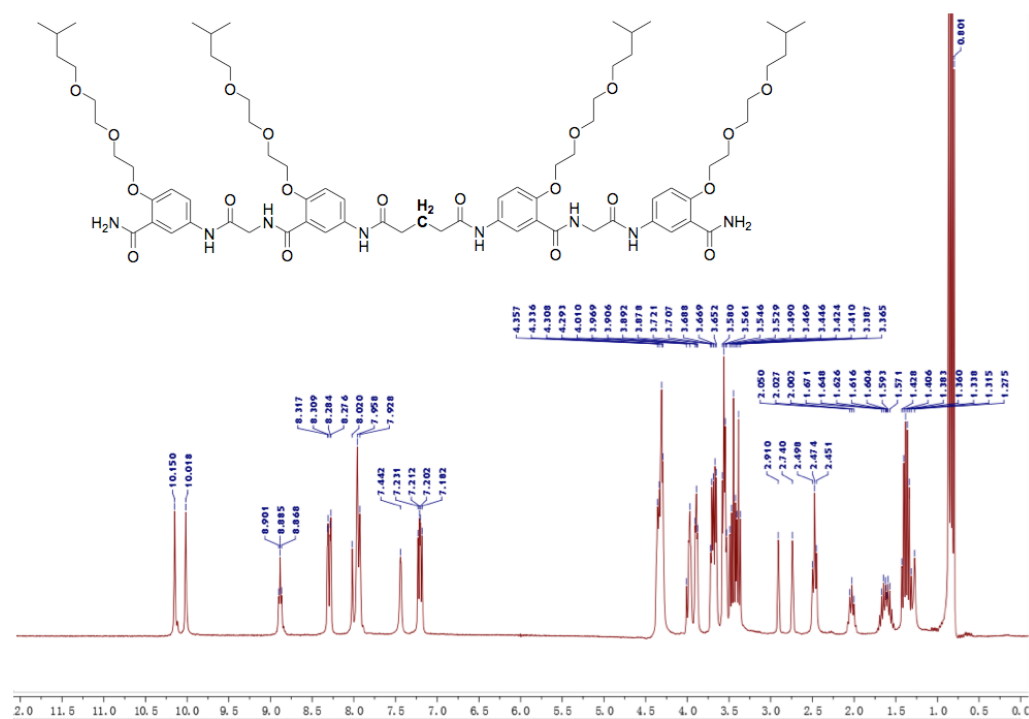
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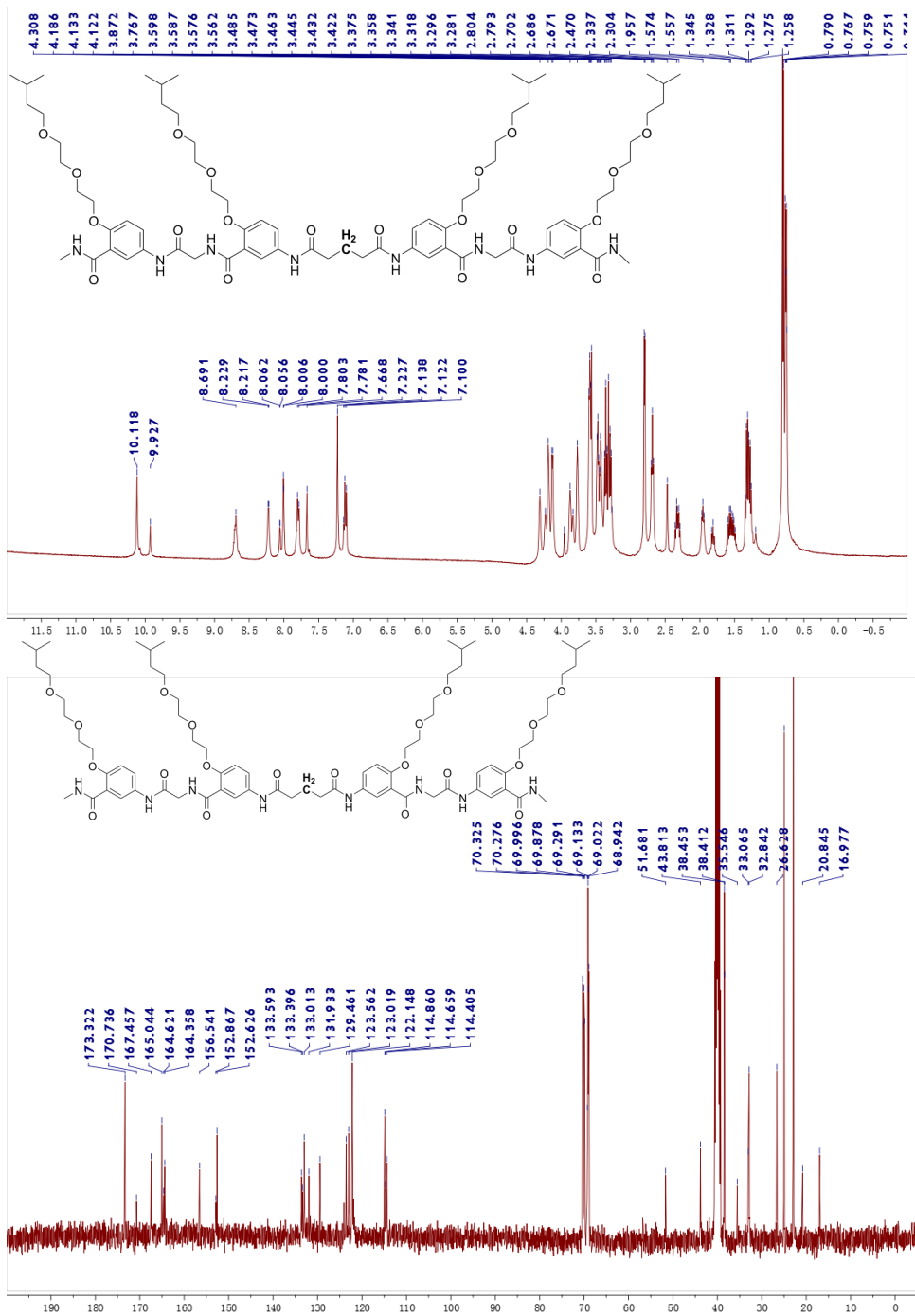
Compound **4b**: A solution of **4a** (1.09 g, 2.84 mmol) in dichloromethane /methanol was shaken in the presence of Pd/C (10%) under a hydrogen atmosphere for 2 hours, and then catalyst was filtered. The filtrate was evaporated in vacuum, yielding the corresponding amine. To a solution of 2-(5-nitro-2-(octyloxy)benzamido)acetic acid <sup>2</sup>(1.0 g, 2.84 mmol), EDC (0.48 g, 3.09 mmol) and HOBt (0.42 g, 3.09 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (45 mL) was added the CH<sub>2</sub>Cl<sub>2</sub> solution (5 mL) of freshly prepared amine. The reaction was allowed to proceed for 4 hours at room temperature. The mixture was then washed with diluted HCl and solvent was removed in vacuum. Purification was accomplished by chromatography on silica gel using chloroform/methanol to afford **4b** (1.44 g, 71%) as a light yellow solid. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>) δ 10.16 (s, 1H), 8.65 (d, *J* = 3.1 Hz, 2H), 8.33 (dd, *J* = 9.2, 3.0 Hz, 1H), 8.21 (t, *J* = 5.6 Hz, 1H), 7.99 (d, *J* = 2.8 Hz, 1H), 7.80 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.39 (d, *J* = 9.3 Hz, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 4.28 (t, *J* = 6.4 Hz, 2H), 4.23 – 4.13 (m, 4H), 3.85 – 3.71 (m, 2H), 3.64 – 3.57 (m, 2H), 3.56 – 3.44 (m, 4H), 3.42 – 3.35 (m, 2H), 3.31 – 3.22 (m, 2H), 3.20 (s, 3H), 1.96 – 1.74 (m, 2H), 1.57 – 1.12 (m, 18H), 0.95 – 0.69 (m, 6H). <sup>13</sup>C NMR (75 MHz, DMSO-d<sub>6</sub>) δ 167.07, 164.35, 163.12, 161.99, 152.62, 140.95, 132.79, 128.48, 126.86, 123.47, 123.09, 122.86, 122.22, 114.48, 114.33, 71.69, 70.79, 70.27,

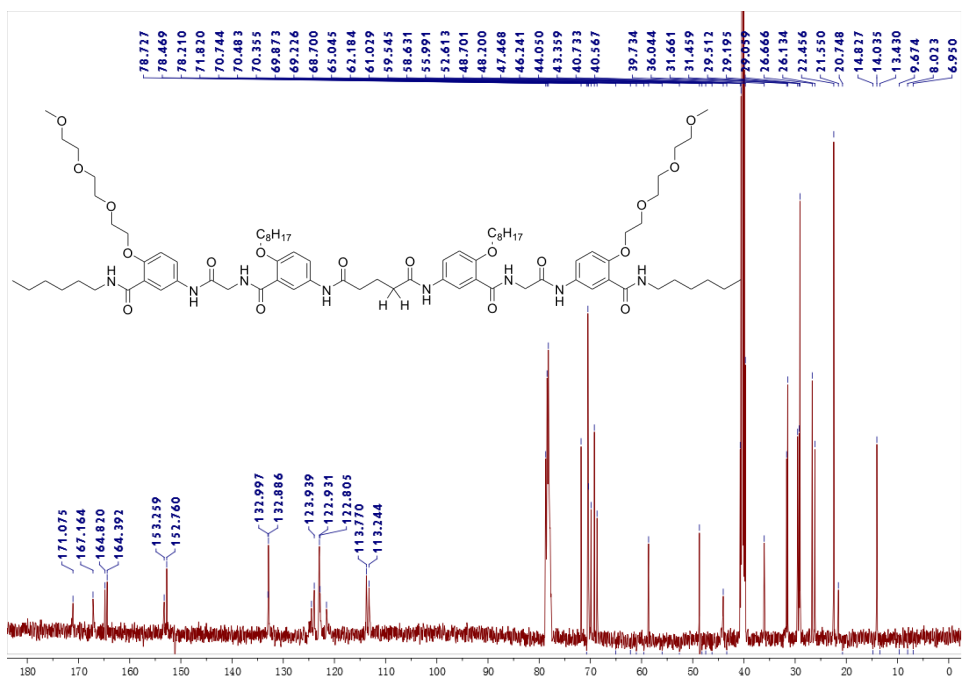
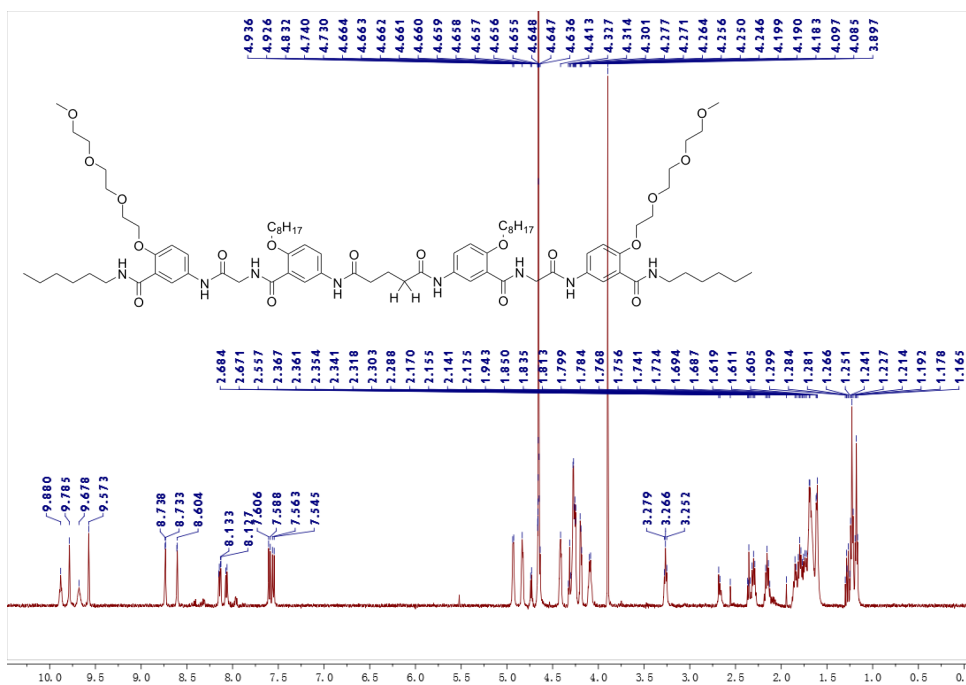
70.09, 69.09, 68.74, 58.48, 43.91, 39.55, 31.69, 31.49, 29.53, 29.20, 29.13, 28.69, 26.63, 26.03, 22.53, 14.36. ESI MS: calculated 739.9, found 739.6 (M + Na)<sup>+</sup>.

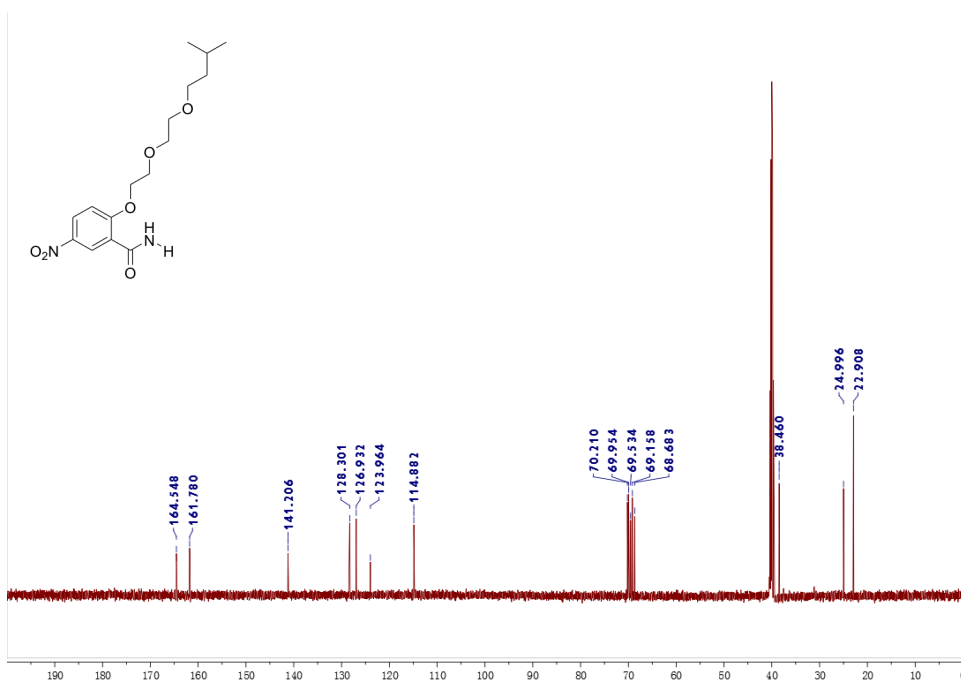
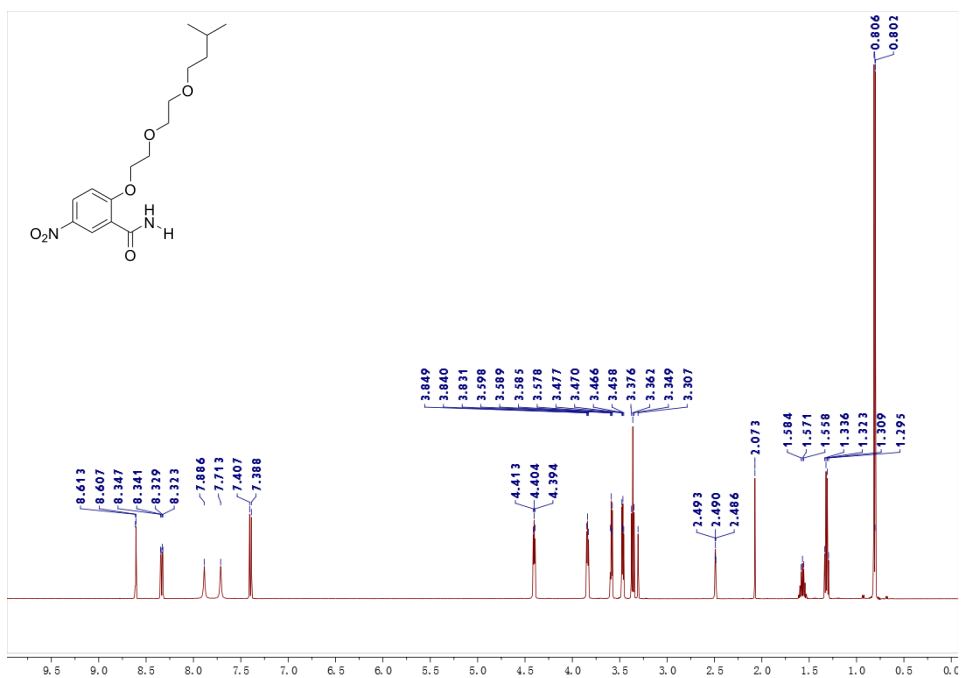
**Compound 1:** A solution of **4b** (0.12 g, 0.17 mmol) in dichloromethane /methanol was shaken in the presence of Pd/C (10%) under a hydrogen atmosphere for 2 hours, and catalyst was then filtered. The filtrate was evaporated in vacuum, yielding the corresponding amine. The amine and triethylamine (0.18 g, 1.8 mmol) were dissolved in dry dichloromethane (20 mL), followed by a solution of glutaryl dichloride (14.8 mg, 0.08 mmol) in dichloromethane (5 mL). The resulting mixture was allowed to react overnight at room temperature. The crude was washed with diluted HCl and then solvent was removed in vacuum. Purification was accomplished by chromatography on silica gel using chloroform/methanol to afford **1** (0.17 g, 66%) as a pale yellow solid. <sup>1</sup>H NMR (500 MHz, CF<sub>3</sub>COOH/D<sub>2</sub>O) δ 9.88 (s, 1H), 9.78 (s, 1H), 9.68 (s, 1H), 9.57 (s, 1H), 8.74 (d, *J* = 2.2 Hz, 1H), 8.61 (d, *J* = 2.4 Hz, 1H), 8.14 (dd, *J* = 9.0, 2.9 Hz, 1H), 8.07 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H), 7.55 (d, *J* = 9.1 Hz, 1H), 4.96 – 4.90 (m, 4H), 4.86 – 4.80 (m, 4H), 4.45 – 4.38 (m, 4H), 4.29 – 4.23 (m, 8H), 4.22 – 4.16 (m, 4H), 4.13 – 4.06 (m, 4H), 3.90 (s, 6H), 3.26 (t, *J* = 6.8 Hz, 4H), 2.73 – 2.61 (m, 2H), 2.35 – 2.26 (m, 2H), 2.21 – 2.10 (m, 2H), 1.90 – 1.53 (m, 36H), 1.28 – 1.13 (m, 12H). <sup>13</sup>C NMR (126 MHz, 30%DMSO-d<sub>6</sub>/70%CDCl<sub>3</sub>) δ 171.08, 167.16, 164.82, 164.39, 153.26, 152.76, 151.17, 132.89, 124.48, 123.94, 123.00, 122.93, 122.80, 121.55, 113.77, 113.24, 71.82, 70.48, 69.87, 69.23, 68.70, 58.63, 48.70, 36.04, 31.66, 31.46, 29.51, 29.19, 29.06, 26.66, 26.13, 22.46, 14.03. MS-MALDI: calculated 1491.9, found 1491.5 (M + Na)<sup>+</sup>.

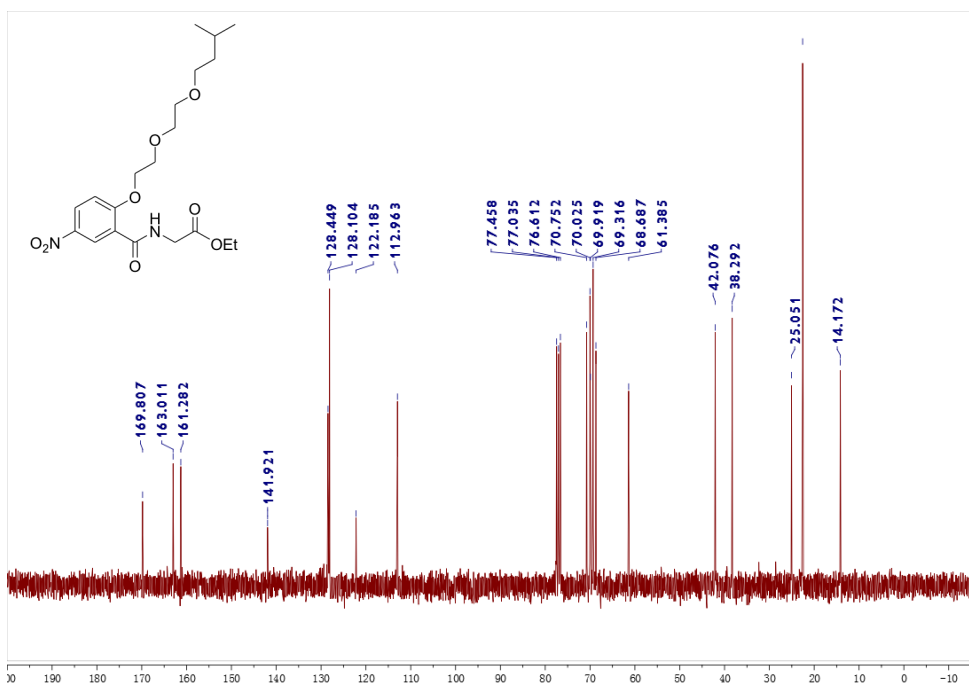
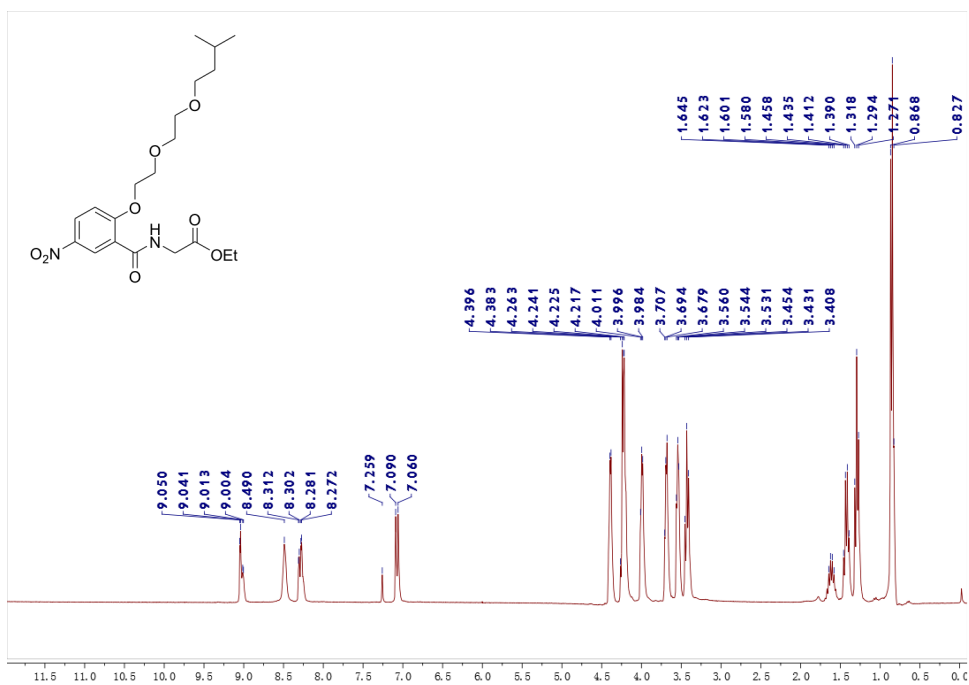
### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

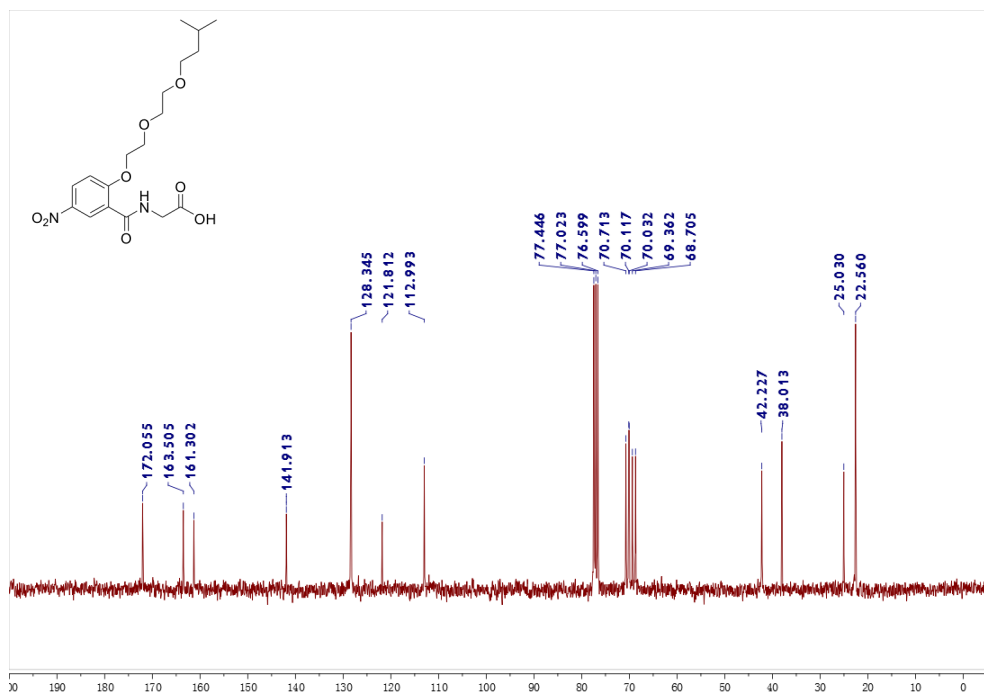
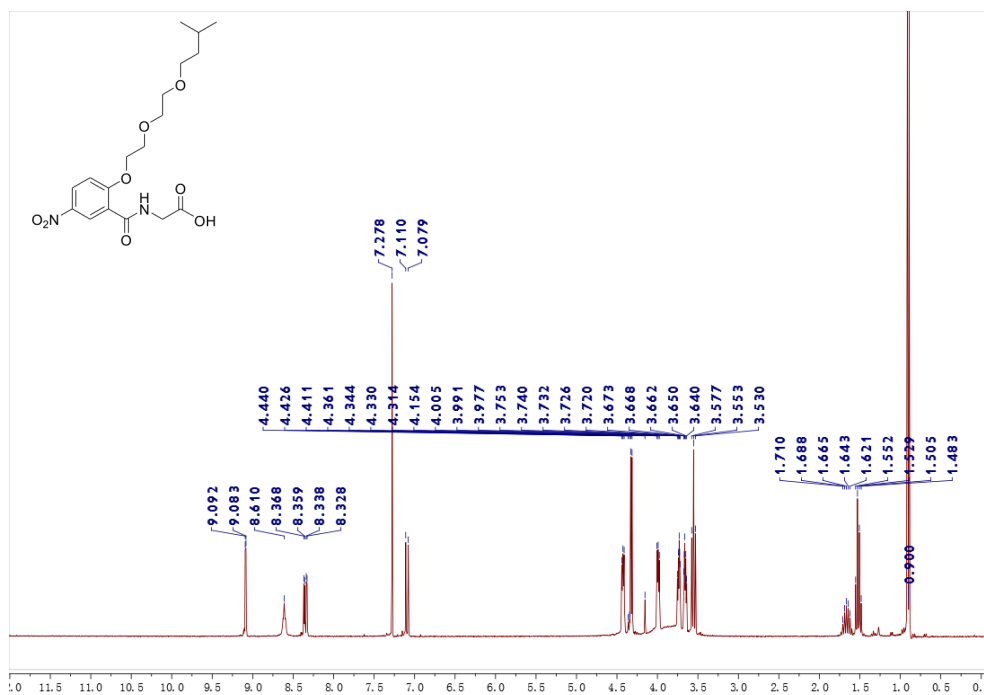


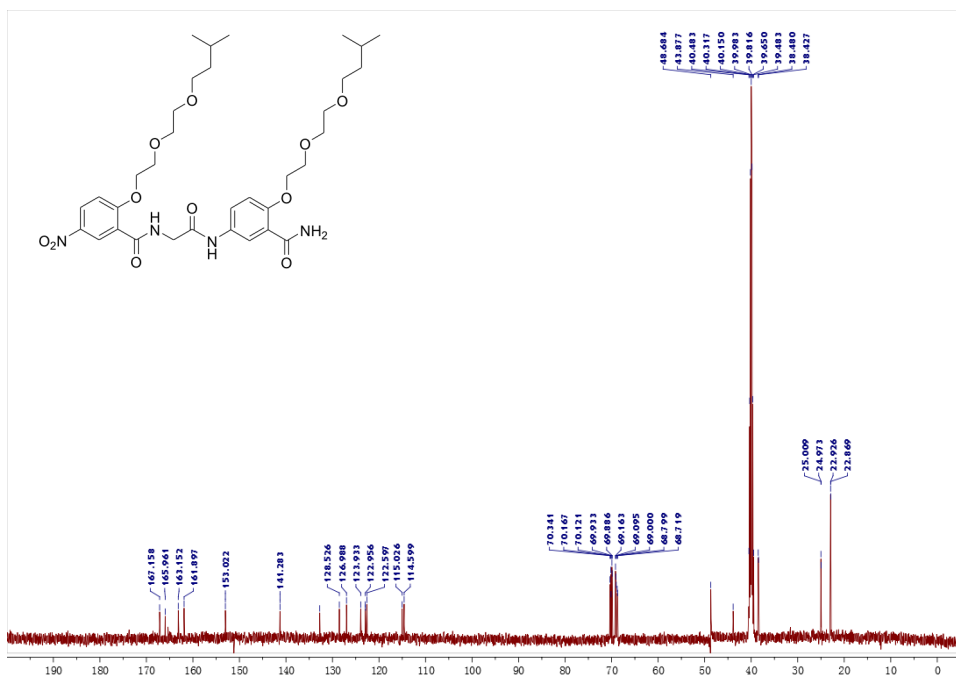
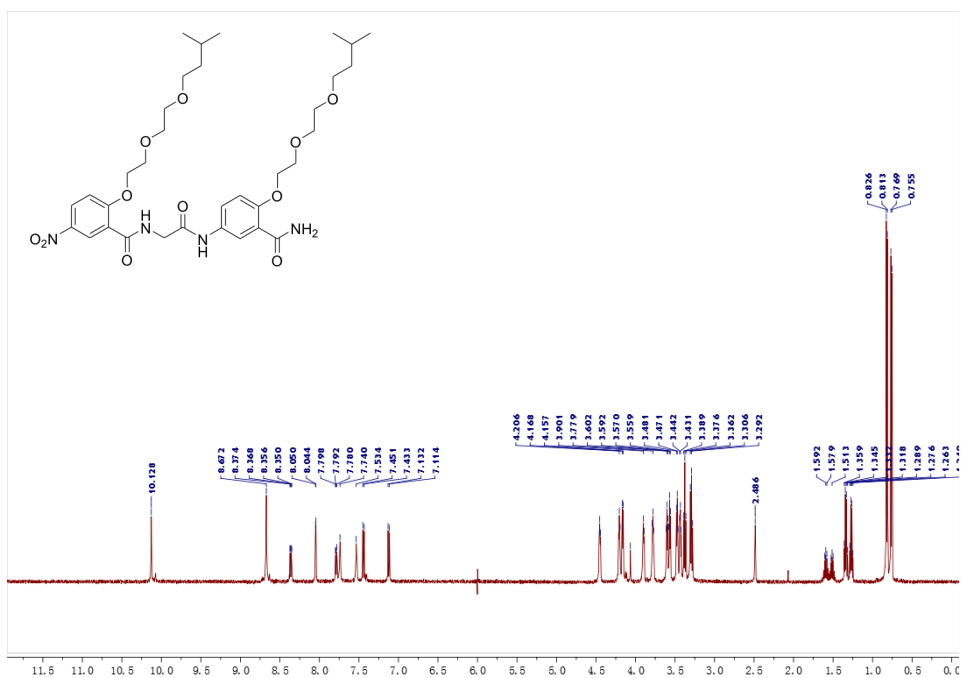


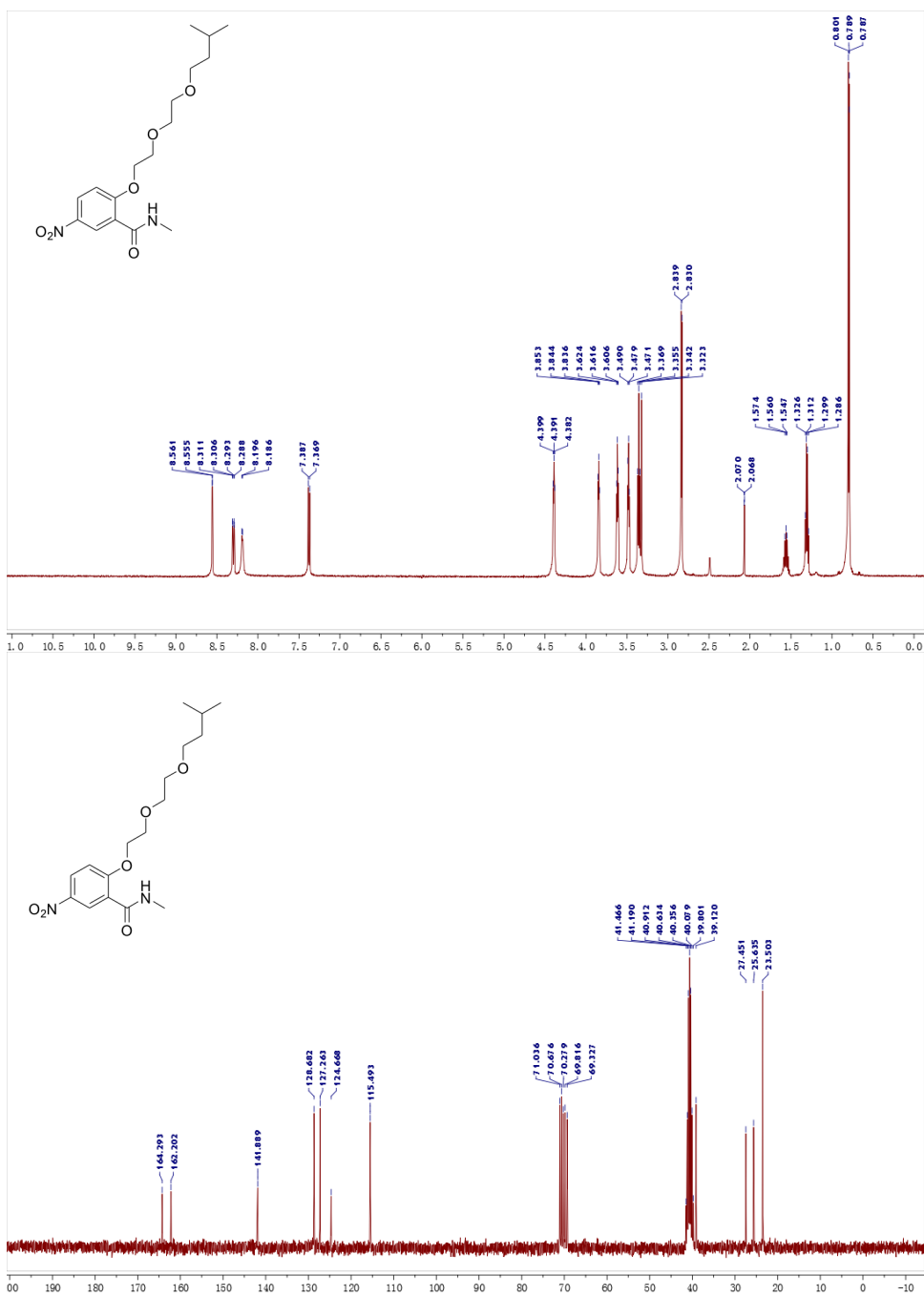


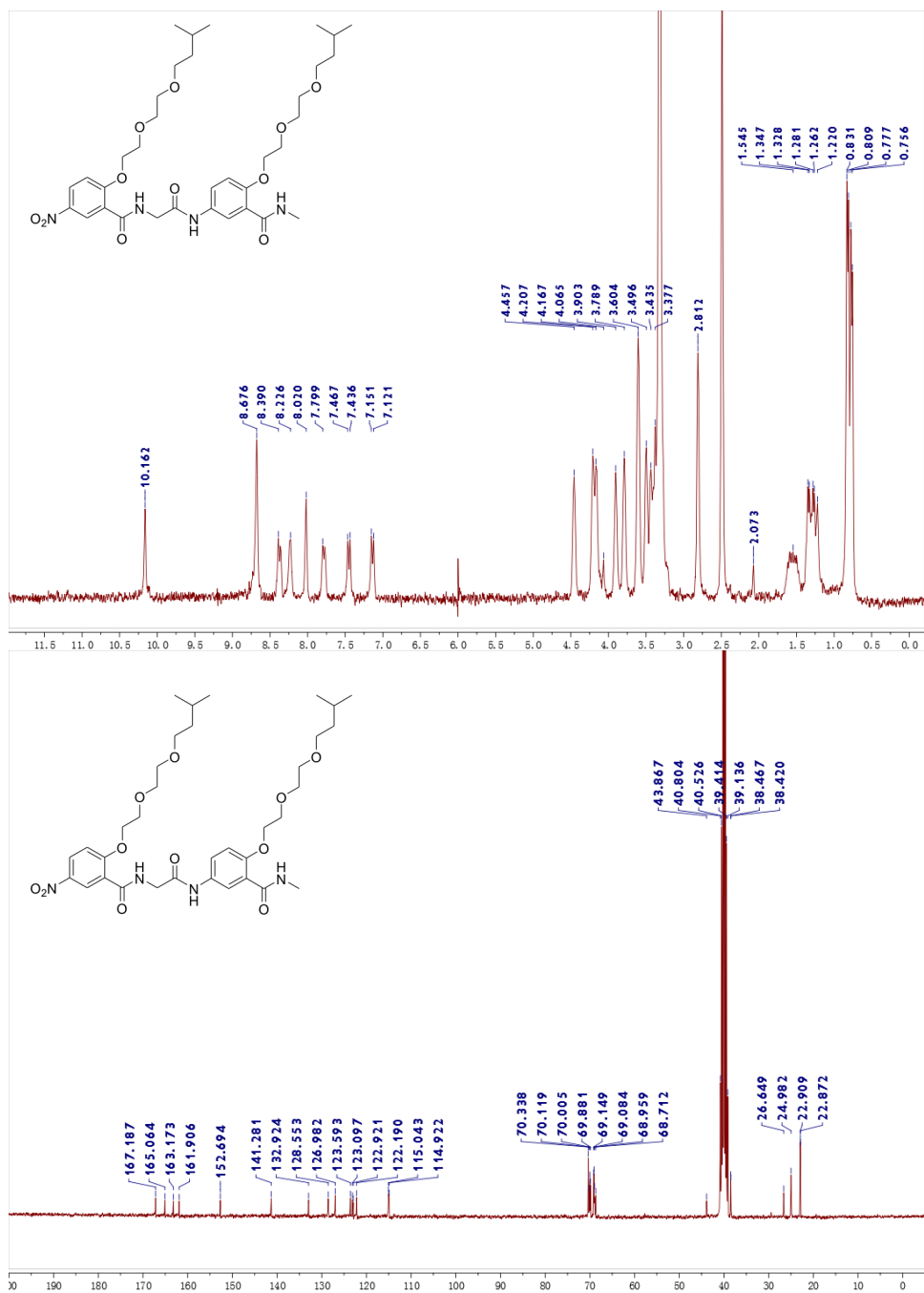


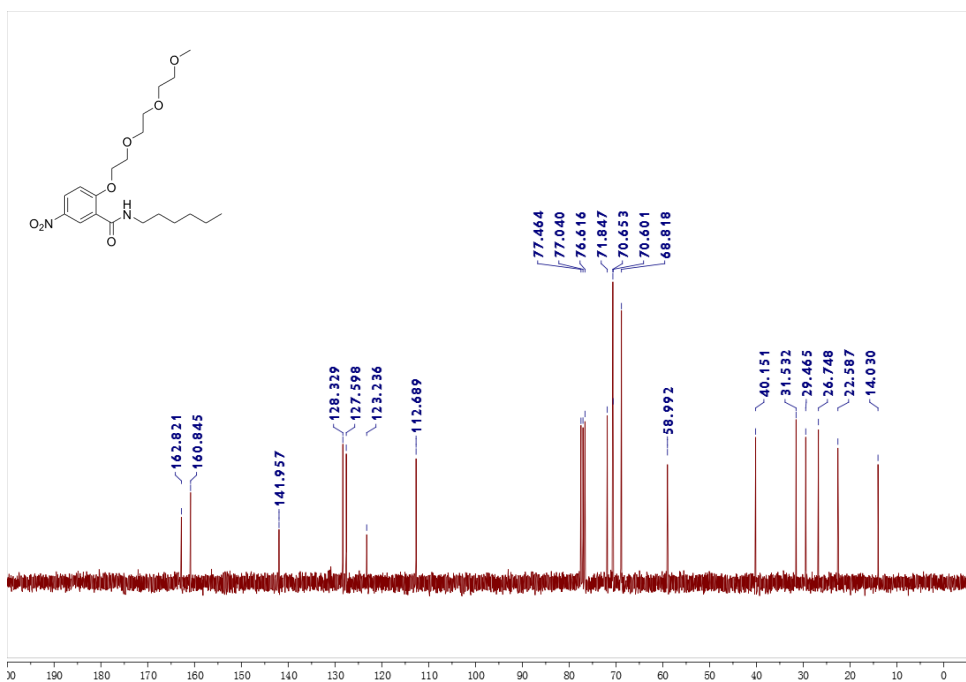
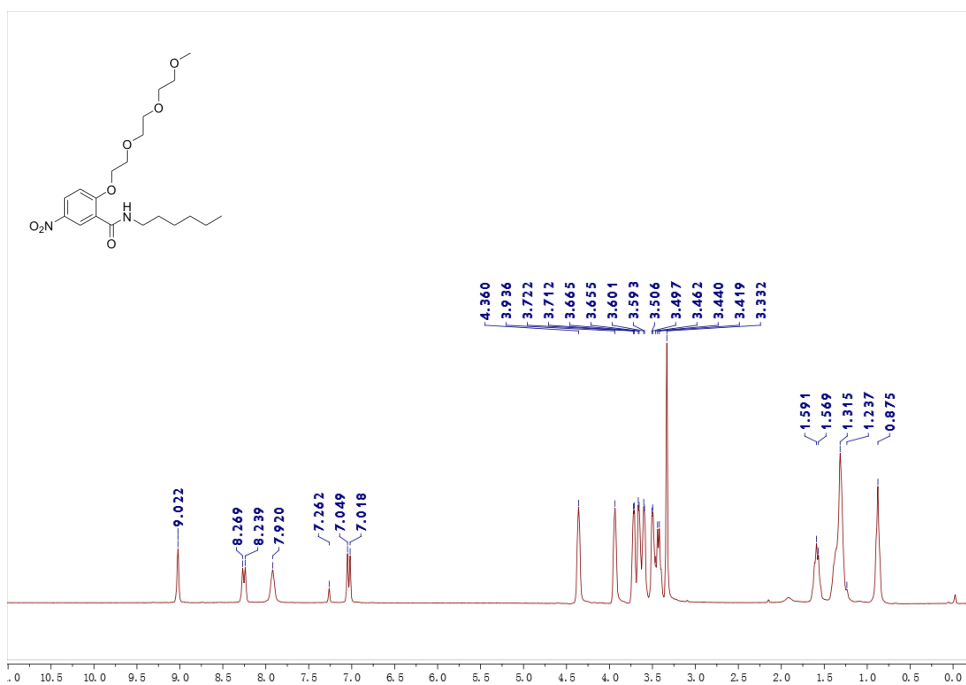


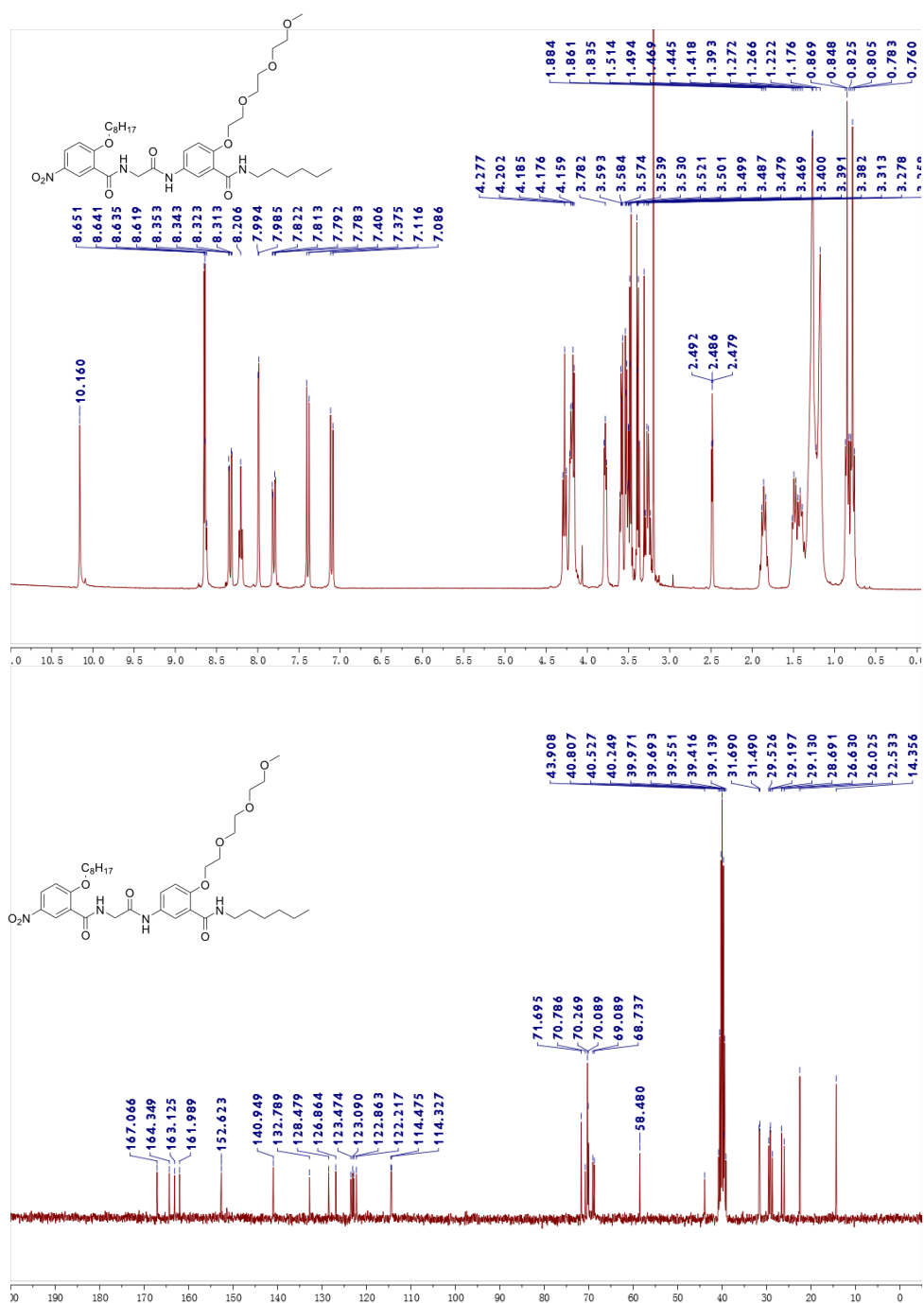




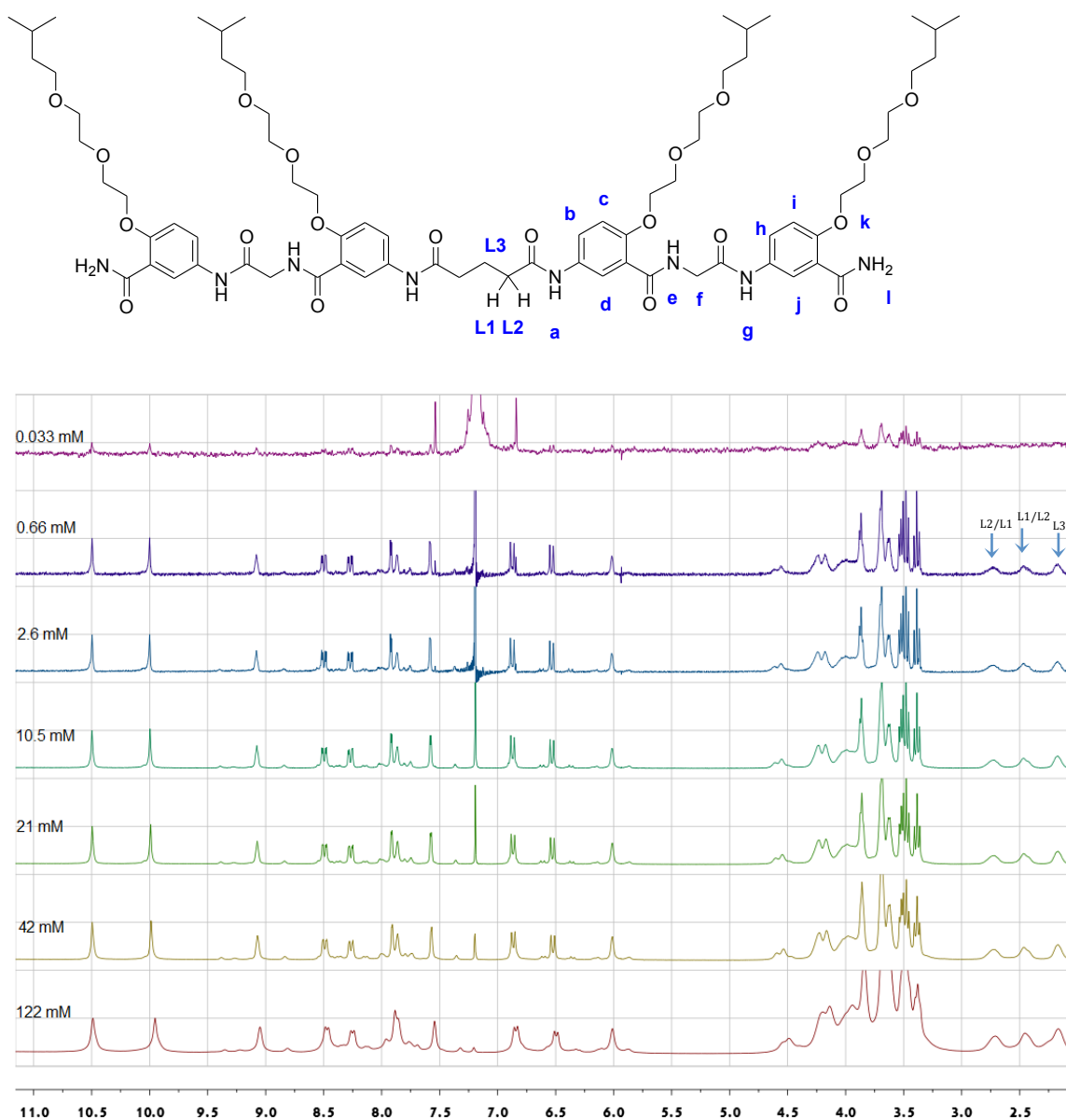




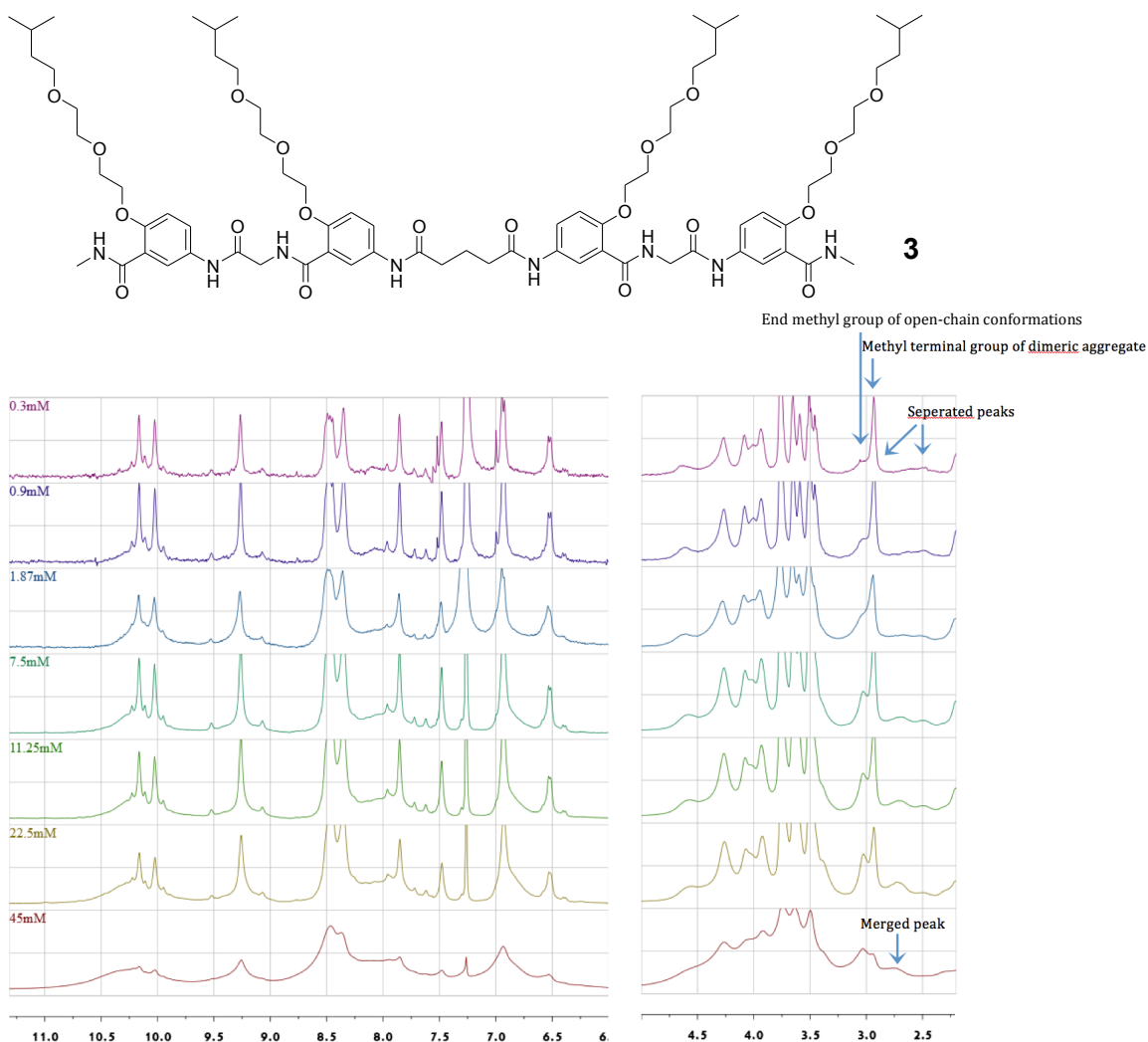




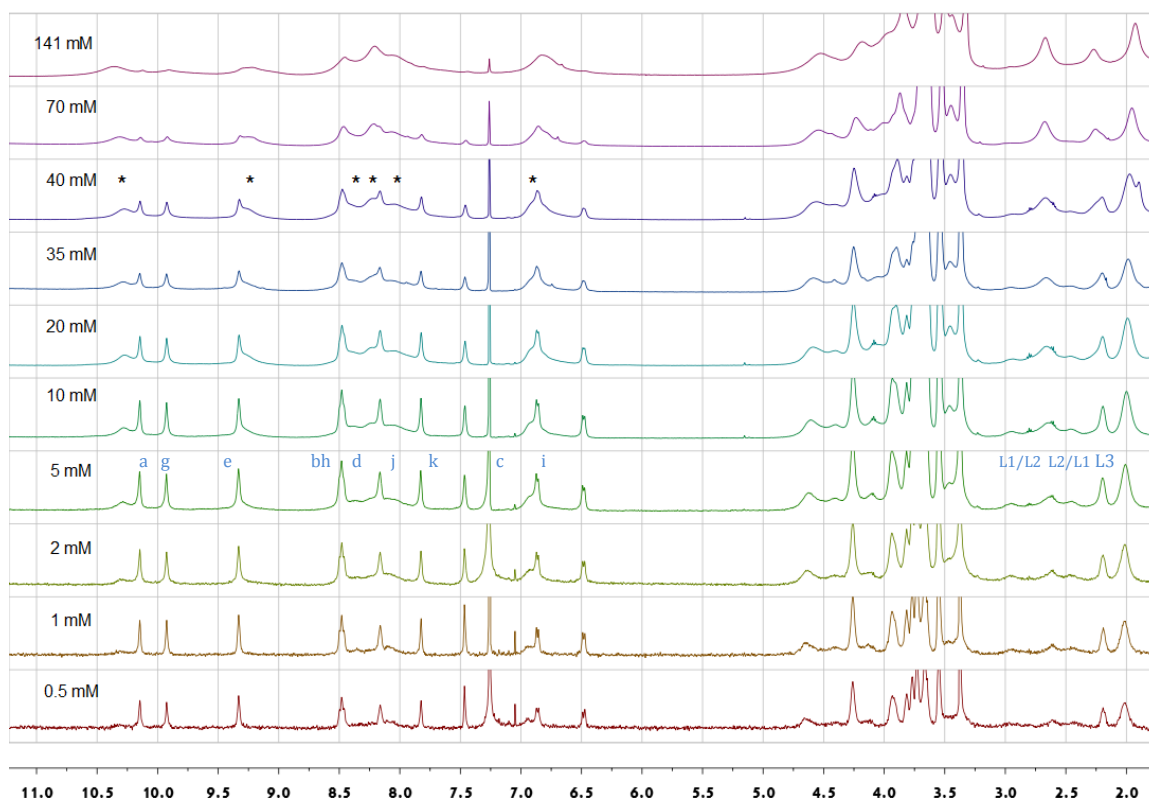
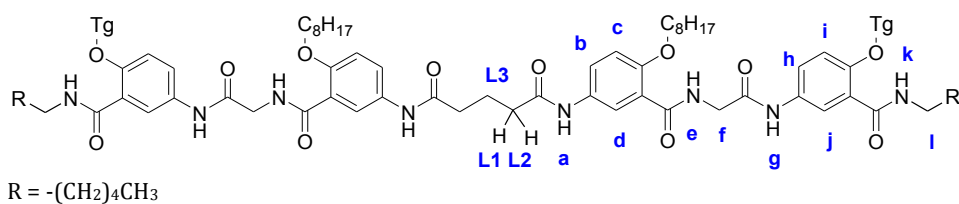
#### 4. <sup>1</sup>H NMR Spectra Recorded at Different Concentrations



**Figure S1.** Concentration-dependent  $^1\text{H}$  NMR experiment of **2** (400 MHz,  $\text{CDCl}_3$ , 298K). All the  $^1\text{H}$  NMR signals remain sharp and well dispersed. The two signals of protons L1 and L2 remain unchanged with increasing concentrations.



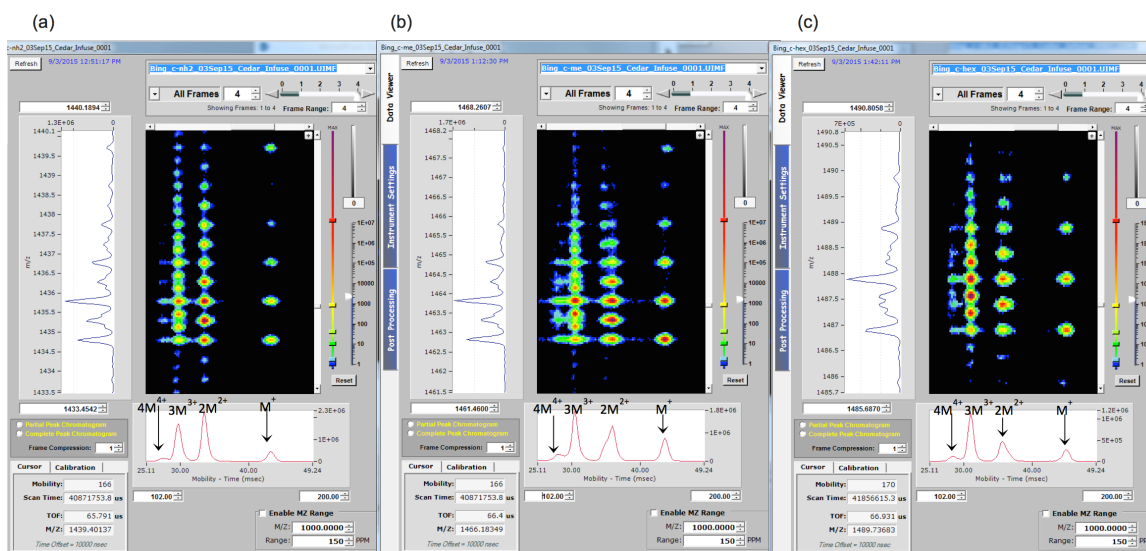
**Figure S2.** Concentration-dependent  $^1\text{H}$  NMR experiment of **3** in  $\text{CDCl}_3$  (400 MHz, 298K). One of the two signals of *L1* and *L2* overlaps with that of the end methyl groups, making it difficult to discern the merged peak (indicated) at  $\sim 2.7$  ppm. Another observation is that the end methyl groups of the folded dimer give one signal, while an extra peak at 3.1 ppm becomes more and more prominent with increasing concentration, indicating the oligomers/polymers formation.



**Figure S3.** Concentration-dependent NMR spectra of compound **4** (500 MHz,  $\text{CDCl}_3$ , 298 K). Backbone signals of aggregates higher than dimer are marked with “\*”. Those aggregates are clearly observed at the concentration as low as 1 mM. The line-broadening of oligomers is probably due to fast exchange among assembled structures. For dimer, protons *L1* and *L2* show two peaks at 2.9 and 2.5 ppm respectively. The signals of *L1* and *L2* merge into a new peak at 2.7 ppm. The intensity of this new peak increases with increasing concentration.

## 5. IMS-MS Instrumental Analysis

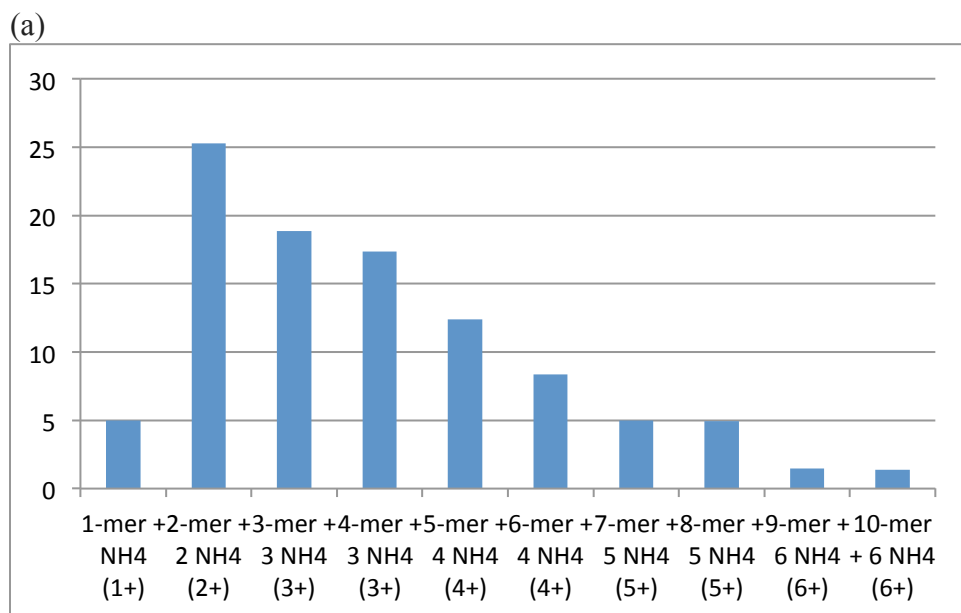
Analysis of the samples of **2**, **3** and **4** was performed using an in-house PNNL built IMS-MS instrument which has previously been described.<sup>3</sup> Briefly, this instrumental platform couples a 1-m IMS separation with an Agilent 6224 TOF MS upgraded to a 1.5 meter flight tube providing resolution of  $\sim 25,000$ . Sample solutions were directly injected into the instrument using a chemically etched fused-silica emitter (20  $\mu\text{m}$  I.D./150  $\mu\text{m}$  O.D., at a potential of 2.6 kV)<sup>4</sup> and transported through a heated capillary inlet (0.43 mm I.D. x 64 mm at 120°C).<sup>5</sup> Once through the heated capillary, the ions were transmitted into the IMS drift cell via ion funnels. Following IMS separation, the ions were refocused using a rear ion funnel and transmitted into the TOF MS, which was set to collect data from 50-14300  $m/z$  for each sample. The signal from the TOF detector was routed to 8-bit Analog-to-Digital converter (ADC) (AP240, Agilent Technologies, Switzerland) and processed using a custom control-software written in C#. <sup>6</sup>

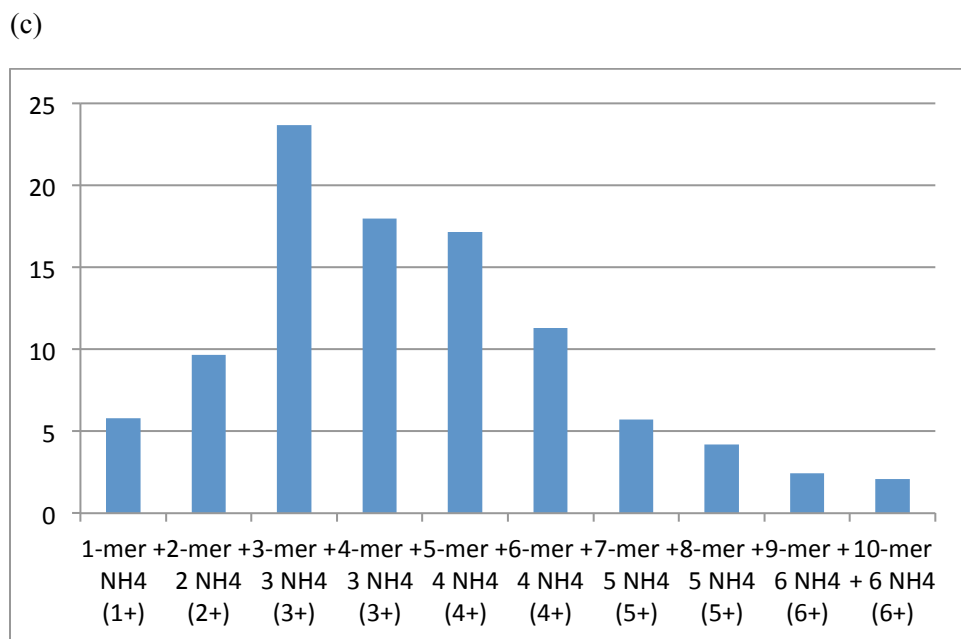
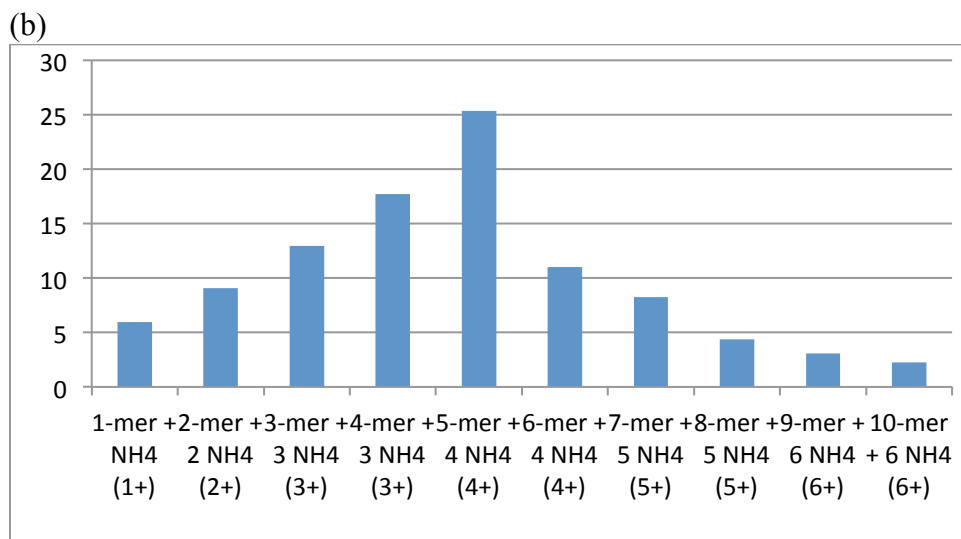


**Figure S4.** Partial IMS-MS spectra of (a) **2**, (b) **3**, and (c) **4** ( $\text{NH}_4^+$  adducts).

**Table S1.** The Ten Most Abundant Complexes with  $\text{NH}_4^+$  Adducts

| Compound 2                    | Pk Area | %     | Compound 3                    | Pk Area  | %     | Compound 4                    | Pk Area | %     |
|-------------------------------|---------|-------|-------------------------------|----------|-------|-------------------------------|---------|-------|
| 1-mer + $\text{NH}_4$ (1+)    | 450244  | 4.97  | 1-mer + $\text{NH}_4$ (1+)    | 826770   | 5.97  | 1-mer + $\text{NH}_4$ (1+)    | 281433  | 5.81  |
| 2-mer + 2 $\text{NH}_4$ (2+)  | 2293357 | 25.29 | 2-mer + 2 $\text{NH}_4$ (2+)  | 1258813  | 9.09  | 2-mer + 2 $\text{NH}_4$ (2+)  | 468164  | 9.66  |
| 3-mer + 3 $\text{NH}_4$ (3+)  | 1709768 | 18.86 | 3-mer + 3 $\text{NH}_4$ (3+)  | 1791863  | 12.94 | 3-mer + 3 $\text{NH}_4$ (3+)  | 1147577 | 23.68 |
| 4-mer + 3 $\text{NH}_4$ (3+)  | 1574243 | 17.36 | 4-mer + 3 $\text{NH}_4$ (3+)  | 2453069  | 17.71 | 4-mer + 3 $\text{NH}_4$ (3+)  | 870718  | 17.96 |
| 5-mer + 4 $\text{NH}_4$ (4+)  | 1125114 | 12.41 | 5-mer + 4 $\text{NH}_4$ (4+)  | 3512411  | 25.36 | 5-mer + 4 $\text{NH}_4$ (4+)  | 831246  | 17.15 |
| 6-mer + 4 $\text{NH}_4$ (4+)  | 758415  | 8.36  | 6-mer + 4 $\text{NH}_4$ (4+)  | 1524561  | 11.01 | 6-mer + 4 $\text{NH}_4$ (4+)  | 548115  | 11.31 |
| 7-mer + 5 $\text{NH}_4$ (5+)  | 451474  | 4.98  | 7-mer + 5 $\text{NH}_4$ (5+)  | 1144799  | 8.27  | 7-mer + 5 $\text{NH}_4$ (5+)  | 276366  | 5.70  |
| 8-mer + 5 $\text{NH}_4$ (5+)  | 446606  | 4.93  | 8-mer + 5 $\text{NH}_4$ (5+)  | 604358   | 4.36  | 8-mer + 5 $\text{NH}_4$ (5+)  | 204080  | 4.21  |
| 9-mer + 6 $\text{NH}_4$ (6+)  | 131772  | 1.45  | 9-mer + 6 $\text{NH}_4$ (6+)  | 422315   | 3.05  | 9-mer + 6 $\text{NH}_4$ (6+)  | 117315  | 2.42  |
| 10-mer + 6 $\text{NH}_4$ (6+) | 125851  | 1.39  | 10-mer + 6 $\text{NH}_4$ (6+) | 311961   | 2.25  | 10-mer + 6 $\text{NH}_4$ (6+) | 101972  | 2.10  |
| Total                         | 9066844 | 100   | Total                         | 13850920 | 100   | Total                         | 4846986 | 100   |

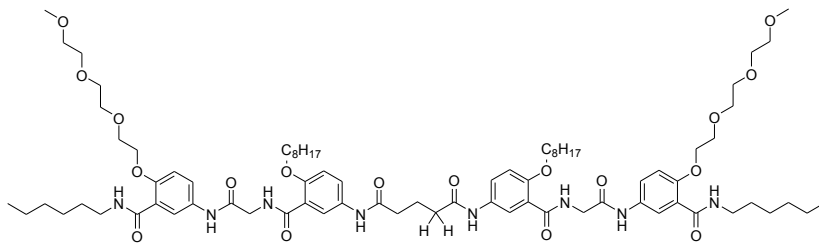




**Figure S5.** The relative abundance of the oligomeric aggregates of (a) **2**, (b) **3** and (c) **4** with ammonium adducts. The numbers on the vertical axes are shown in percentage.

## 6. Diffusion-Ordered Spectroscopy (DOSY)

Diffusion-ordered spectroscopy (DOSY) experiments were performed on a Varian Inova 500 MHz spectrometer under regulated temperature (298 K), with a 5 mm probe. The pulse sequence employed was a bipolar pulse pair simulated echo (BPPSTE). Additional parameters: gradient strength array has 15 increments from 3% to 66% of the maximum gradient strength in a linear ramp, diffusion gradient length is set to 2 ms, and diffusion delay is 100 ms.



4

**Table S2.** DOSY results of **4** in CDCl<sub>3</sub> at 298K

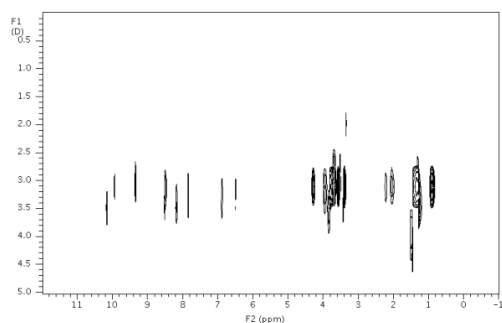
| Concentration of <b>4</b> (hexyl terminals) | $D_4$<br>( $\times 10^{-10}$ m <sup>2</sup> /s) | $D_{TMS}$<br>( $\times 10^{-10}$ m <sup>2</sup> /s) | $D_{TMS}/D_4$ | $D_{CHCl_3}$<br>( $\times 10^{-10}$ m <sup>2</sup> /s) | $D_{CHCl_3}/D_4$ |
|---------------------------------------------|-------------------------------------------------|-----------------------------------------------------|---------------|--------------------------------------------------------|------------------|
| 141 mM                                      | 0.24                                            | N/A <sup>a</sup>                                    | -----         | 10.4                                                   | 43.48            |
| 70 mM                                       | 1.11                                            | 10.3                                                | 9.26          | 15.5                                                   | 13.89            |
| 35 mM                                       | 2.20                                            | 17.3                                                | 8.00          | 19.7                                                   | 9.00             |
| 25 mM                                       | 2.29                                            | 17.1                                                | 7.46          | 20.6                                                   | 9.00             |
| 12 mM                                       | 2.70                                            | 18.5                                                | 6.85          | 20.7                                                   | 7.69             |
| 0.5 mM                                      | 3.28                                            | 19.5                                                | 5.95          | 21.6                                                   | 6.57             |

<sup>a</sup>Value can not be measured accurately.

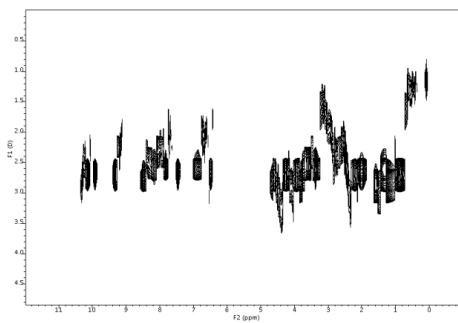
$D_4$ : averaged diffusion coefficient of **4**.

$D_{TMS}$ : diffusion coefficient of TMS.

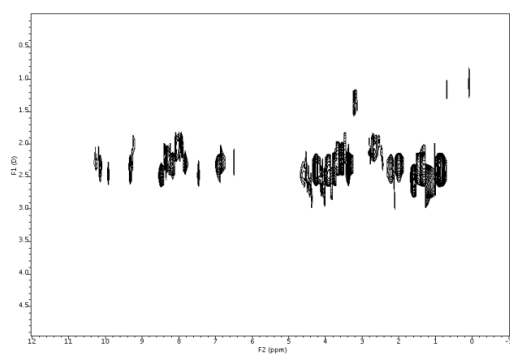
$D_{CHCl_3}$ : diffusion coefficient of CHCl<sub>3</sub>.



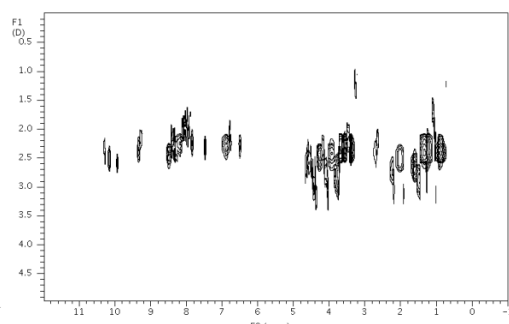
(a)



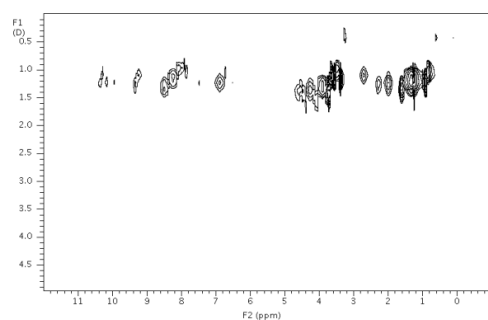
(b)



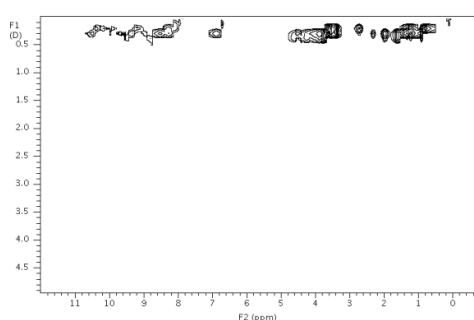
(c)



(d)



(e)

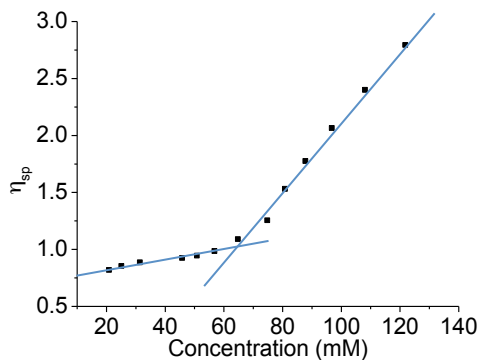


(f)

**Figure S6.** Partial DOSY spectra of **4** in  $\text{CDCl}_3$  (a) 0.5 mM, (b) 12 mM, (c) 25 mM, (d) 35 mM, (e) 70 mM, and (f) 141 mM.

## 7. Viscosity Measurements

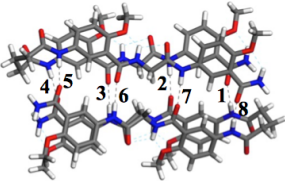
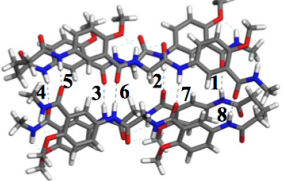
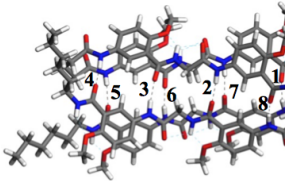
Viscosity measurements were carried out at ambient temperature (298K) on a Brookfield DV2+Pro Viscometer with a thermostat attached. The sample solutions in  $\text{CHCl}_3$  were filtered through a  $0.45\ \mu\text{m}$  filter to remove dust and debris. The resulting solution was left to stand for 1 hour before measurements.



**Figure S7.** Specific viscosity of **3** versus concentration in  $\text{CHCl}_3$ . The results suggest that there are two-stage aggregations. Combined with NMR data, dimeric assembly dominates at low concentrations, while larger aggregates are favored at high concentrations. The slopes are  $0.0063 \pm 0.0004\ \text{cP/mM}$  at low concentrations and  $0.0506 \pm 0.0020\ \text{cP/mM}$  at high concentrations, respectively.

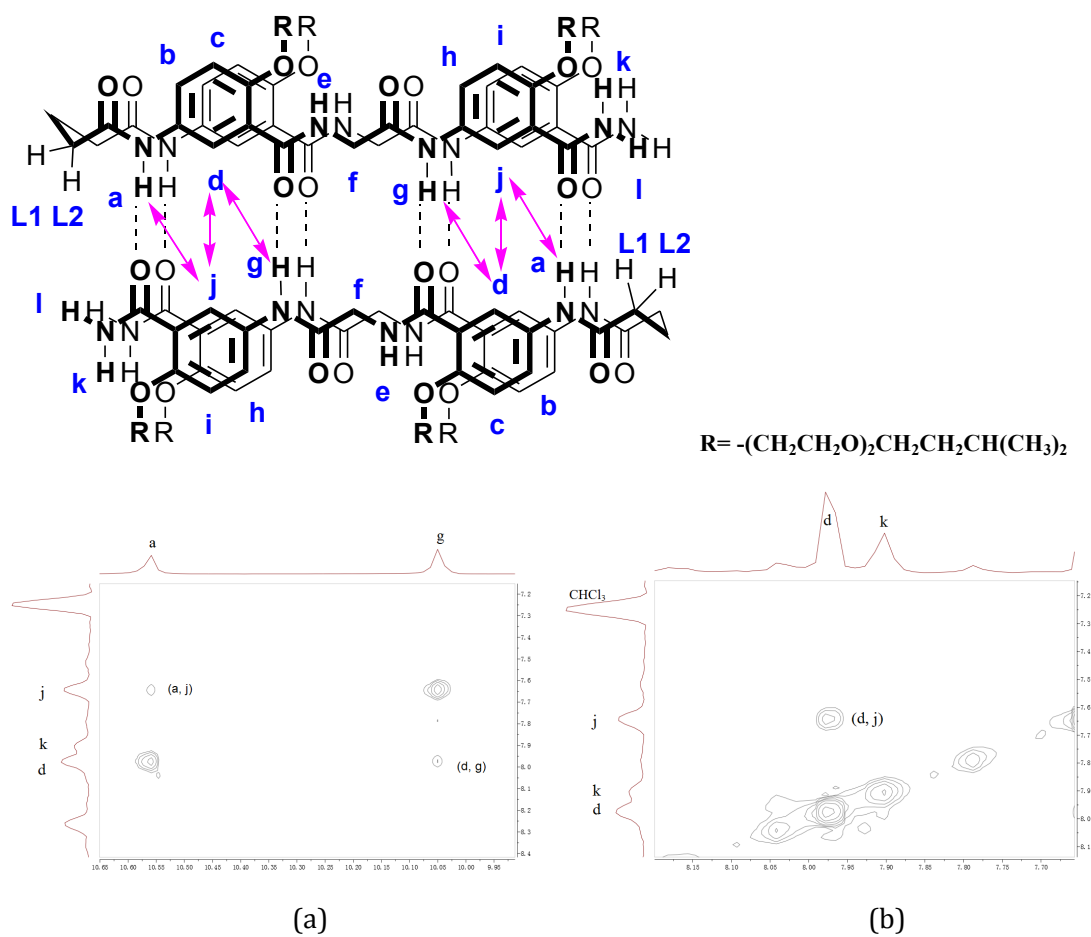
## 8. Computational Study

B3LYP/6-31G(d) optimizations were performed on the dimers of compounds 2, 3, and 4 (with all R1 and R2 groups being replaced by methyl groups) in Gaussian 09 software package. The three dimers with eight intermolecular hydrogen bonds are obtained after optimizations both shown in Figures S9 and S10.

|     | (a)                                                                               |           | (b)                                                                               |           | (c)                                                                                |           |
|-----|-----------------------------------------------------------------------------------|-----------|-----------------------------------------------------------------------------------|-----------|------------------------------------------------------------------------------------|-----------|
|     |  |           |  |           |  |           |
|     | Length (Å)                                                                        | Angle (°) | Length (Å)                                                                        | Angle (°) | Length (Å)                                                                         | Angle (°) |
| HB1 | 1.986                                                                             | 171.7     | 2.025                                                                             | 161.9     | 2.071                                                                              | 169.3     |
| HB2 | 1.900                                                                             | 174.1     | 1.912                                                                             | 169.4     | 1.913                                                                              | 160.2     |
| HB3 | 1.902                                                                             | 173.6     | 1.914                                                                             | 160.8     | 1.904                                                                              | 173.0     |
| HB4 | 1.985                                                                             | 171.4     | 2.103                                                                             | 161.3     | 1.996                                                                              | 166.0     |
| HB5 | 1.961                                                                             | 175.0     | 1.963                                                                             | 172.3     | 2.003                                                                              | 169.6     |
| HB6 | 1.908                                                                             | 175.7     | 1.924                                                                             | 167.7     | 1.872                                                                              | 171.7     |
| HB7 | 1.909                                                                             | 175.8     | 1.886                                                                             | 175.7     | 1.965                                                                              | 167.6     |
| HB8 | 1.961                                                                             | 174.6     | 1.978                                                                             | 173.1     | 2.002                                                                              | 163.1     |

**Figure S8.** Optimized structures of the dimers of compounds (a) 2, (b) 3, and (c) 4. The bond lengths and bond angles of the eight intermolecular hydrogen bonds (HB) of each dimers are listed.

## 9. 2D-NOESY Spectra



**Figure S9.** Partial NOESY spectra of **2** in CDCl<sub>3</sub> (500MHz, 298K, 3 mM).

## 10. Reference

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2. X. W. Yang, S. Martinovic, R. D. Smith and B. Gong, *J. Am. Chem. Soc.* 2003, **125**, 9932.
3. E. S. Baker, B. H. Clowers, F. Li, K. Tang, A. V. Tolmachev and D. C. Prior, *J. Am. Soc. Mass Spectrom.* 2007, **18**, 1176-87.
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5. T. Kim, A. V. Tolmachev, R. Harkewicz, D. C. Prior, G. Anderson and H. R. Udseth, *Anal. Chem.* 2000, **72**, 2247.
6. Y. M. Ibrahim, E. S. Baker, W. F. 3rd Danielson, R. V. Norheim, D. C. Prior, G. A. Anderson M. E. Belov and R. D. Smith, *Int. J. Mass Spectrom.* 2015, **377**, 655.