Ring-opening supramolecular polymerization controlled by orthogonal non-covalent interactions

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SUPPORTING INFORMATION

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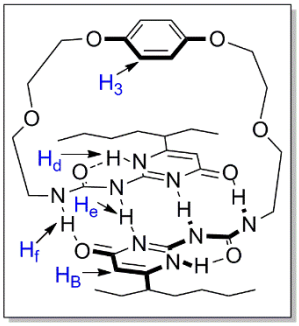
1. Materials and methods

All reactions were carried out under normal pressure unless noted. The commercially available reagents and solvents were either employed as purchased or dried according to procedures described in the literature. All yields were given as isolated yields. **N1**[S1], **N2**[S2], **N3**[S2], **N4**[S3], **N5**[S4], **L1**[S5] and **M3**[S6] were prepared according to literature procedure. NMR spectra were recorded on a Bruker AVANCE III 300 MHz or a Bruker AVANCE III 400MHz spectrometer with internal standard tetramethylsilane (TMS) and solvent signals as internal references, where $CDCl_3$ were dried using neutral aluminum oxide. NOESY experiments were performed on a Bruker AVANCE III 400 MHz spectrometer. DOSY experiments were performed on a Bruker AVANCE III 600 MHz spectrometer. Low-resolution electrospray ionization mass spectra (LR-ESI-MS) were obtained on LCMS2020. High-resolution electrospray ionization mass spectra (HR-ESI-MS) were recorded on an Agilent Technologies 6540 UHD Accurate-Mass. Viscosity measurements were carried out with Ubbelohde micro viscometers (Shanghai Liangjing Glass Instrument Factory, 0.40 mm inner diameter) at 298 K in chloroform and toluene.

2. ^{1}H-^{1}H NOESY of M2 and M3



Scheme S1. Structure of **M2** in its cyclic form

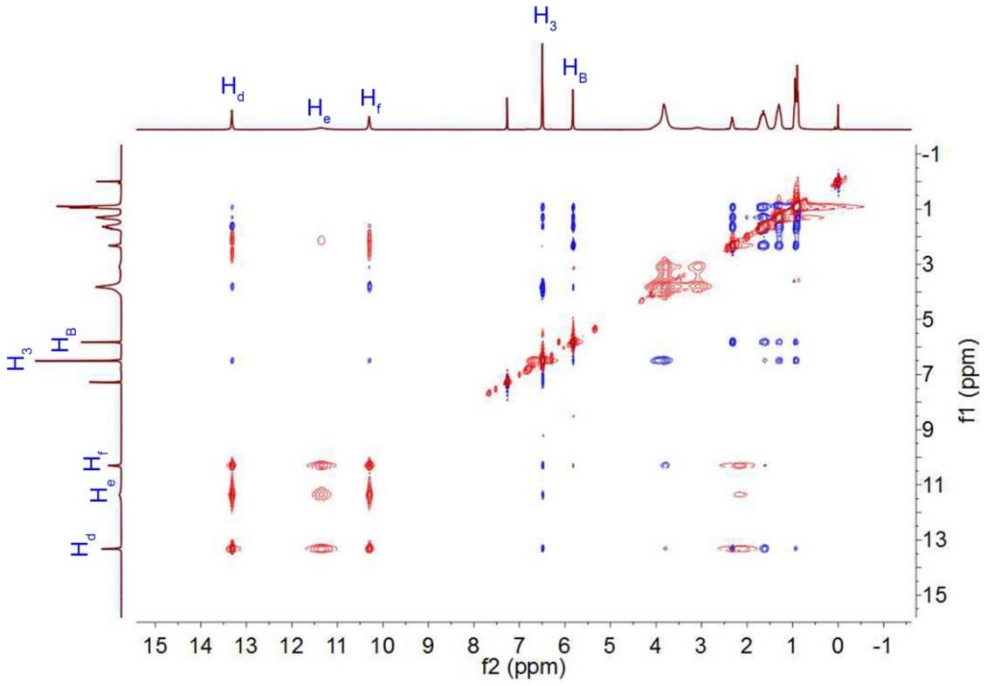
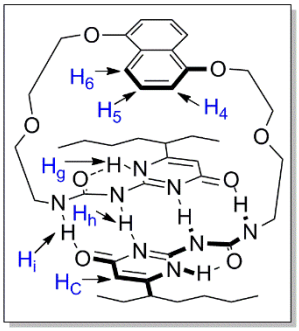


Figure S1. NOESY (400 MHz, $CDCl_3$, 298 K, 64 mM) of **M2**.



Scheme S2. Structure of **M3** in its cyclic form

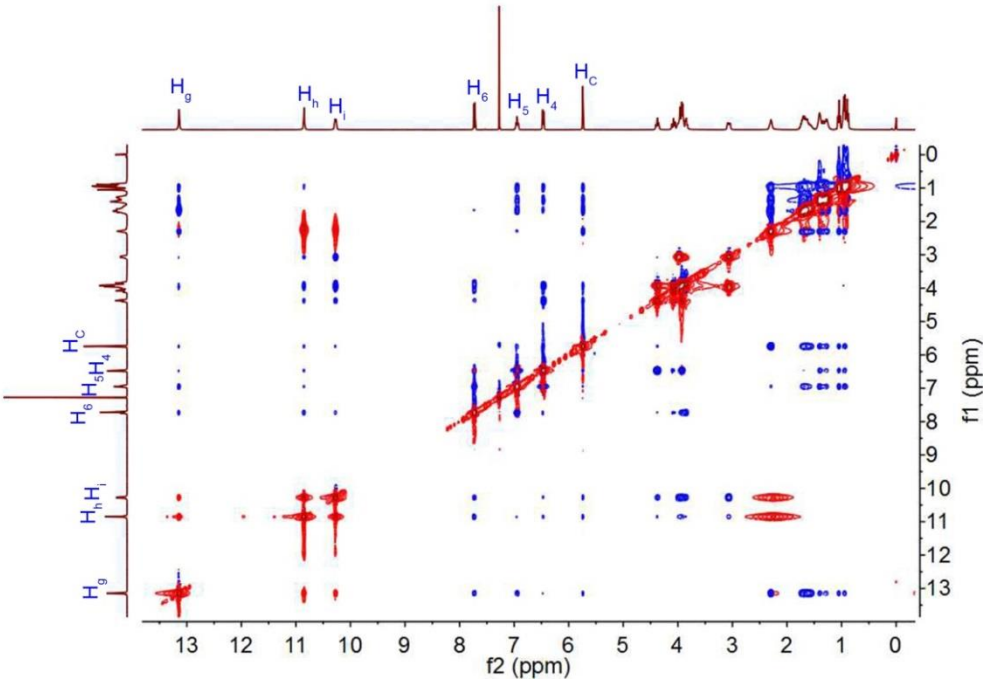


Figure S2. NOESY (400 MHz, $CDCl_3$, 298 K, 64 mM) of **M3**.

3. DOSY of **M1** and **M3**

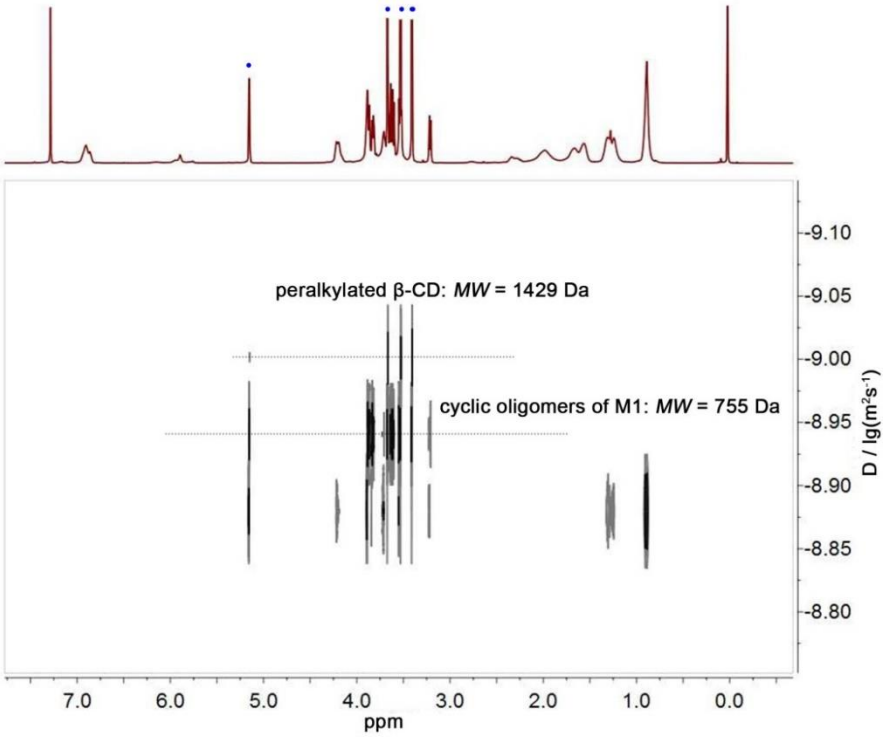


Figure S3. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of **M1** in 4 mM with the addition of peralkylated *β*-CD as internal standard.

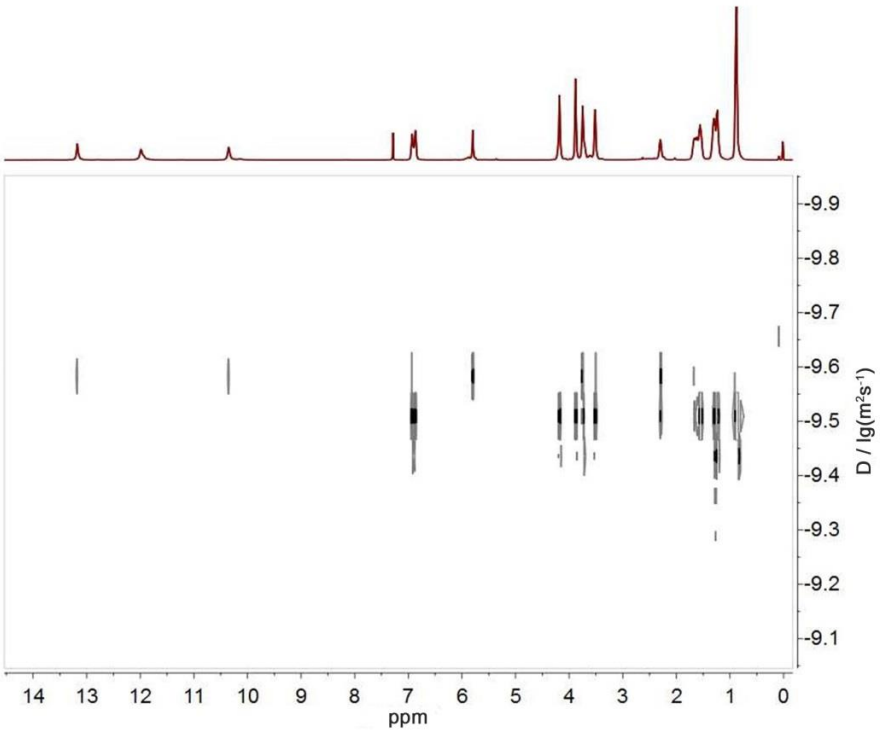


Figure S4. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of **M1** in 64 mM.

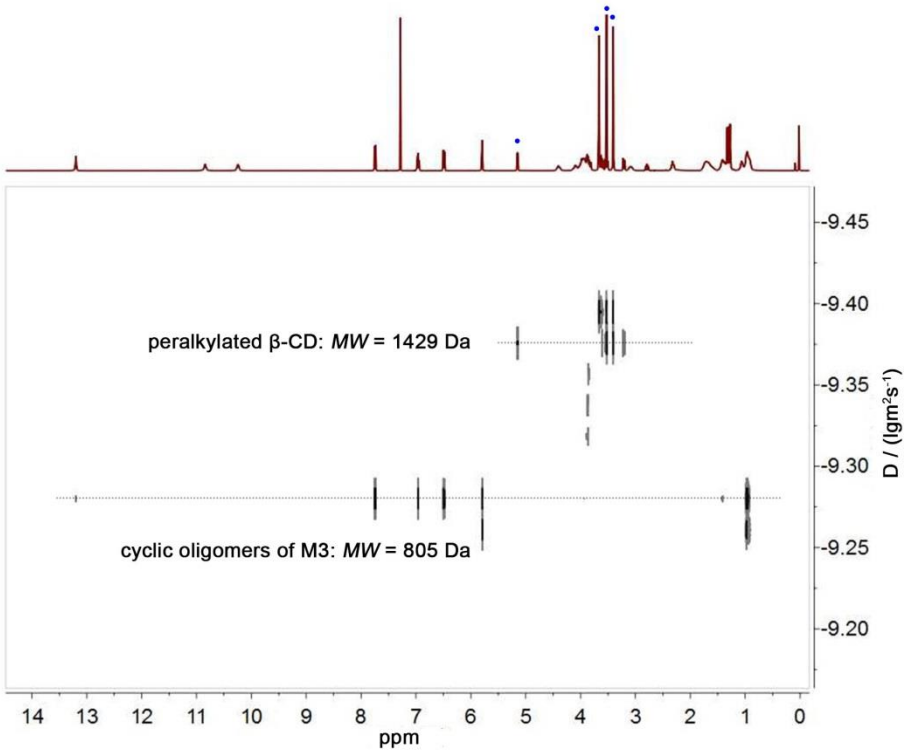


Figure S5. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of **M3** in 16 mM with the addition of peralkylated *β*-CD as internal standard.

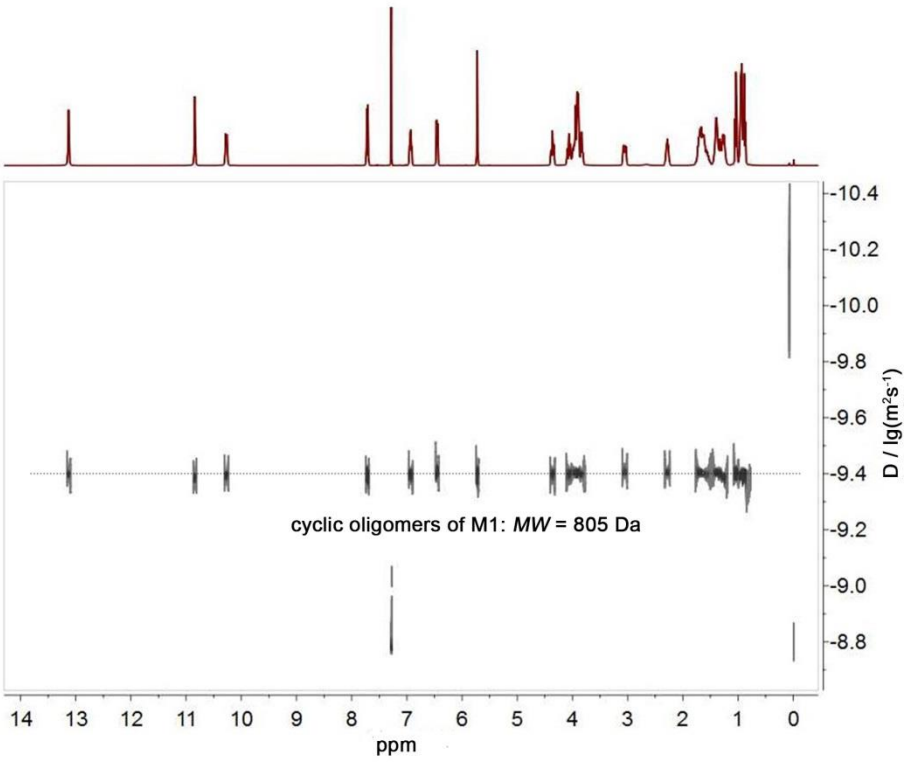


Figure S6. DOSY spectra (600 MHz, $CDCl_3$, 298 K) of **M3** in 200 mM.

4. Viscosity measurements of M1 and M2

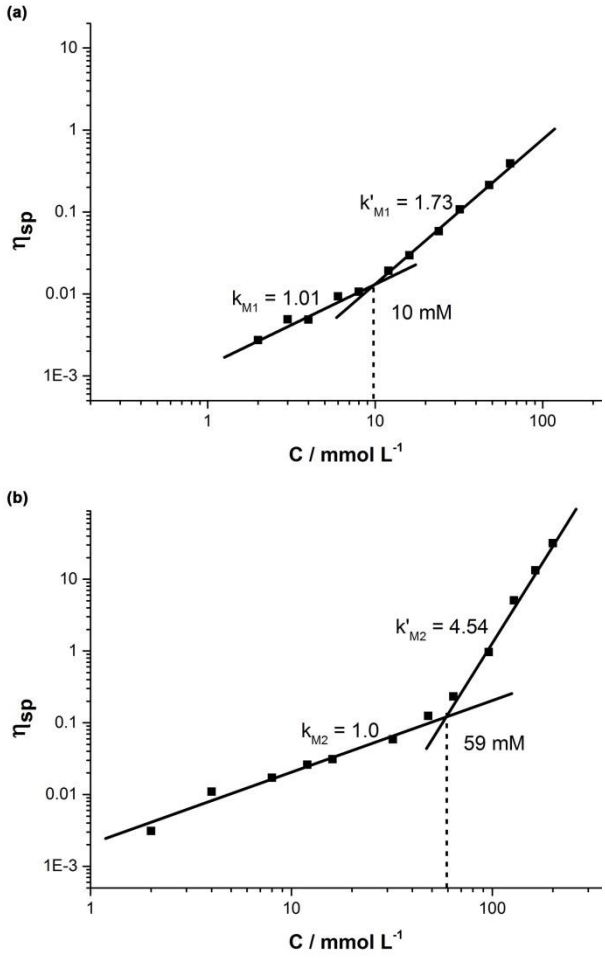
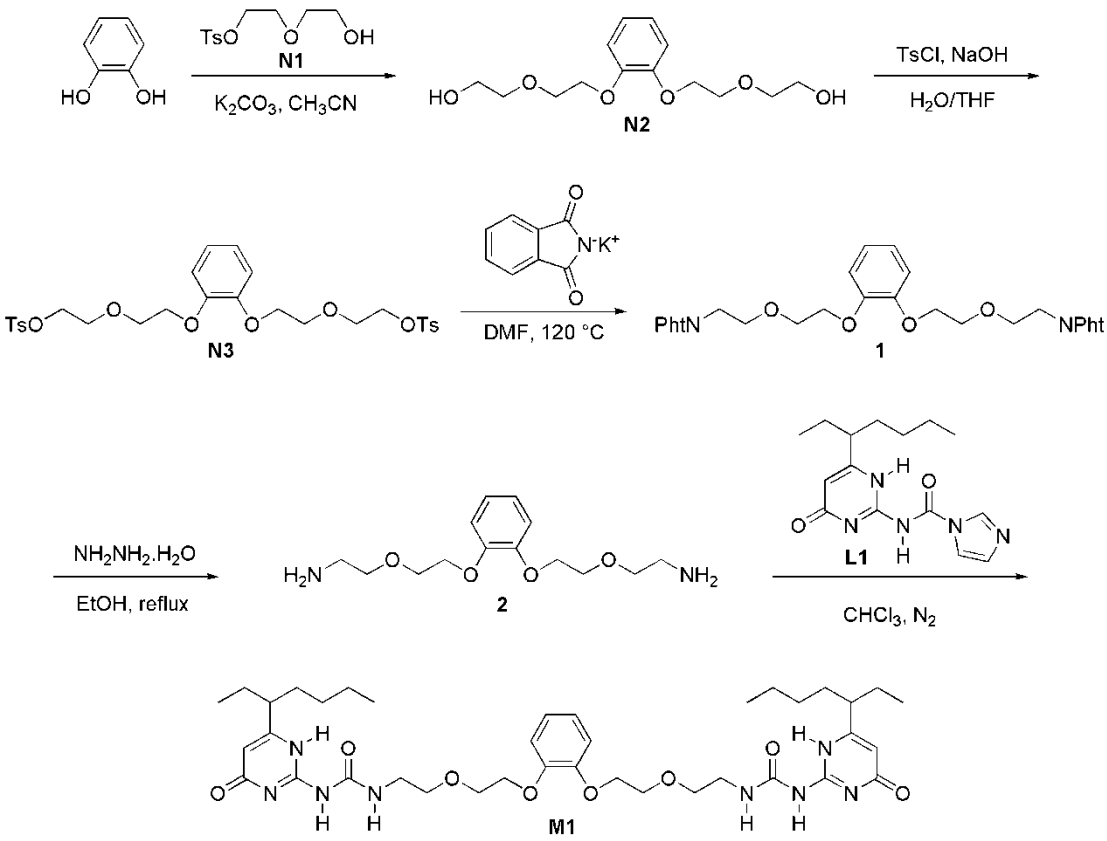


Figure S7. Specific viscosity of toluene solutions of **M1** (a), **M2** (b) versus the concentration (298 K). Values on the curves indicate the slope.

5. Synthetic procedures and characterization of M1



Scheme S3. Synthesis of the **M1**

5.1 Synthesis of Compound **1**

To a solution of compound **N3** (3.67 g, 6.17 mmol) in DMF (60 mL) was added potassium phthalimide (3.43 g, 18.51 mmol) at room temperature under N_2 atmosphere. The reaction mixture was heated at 120 ℃ for 12 h and then poured into water (100 mL). The resulting mixture was extracted with CH_2Cl_2 (100 mL × 3) and the combined extracts were washed with H_2O (100 mL × 6), brine (50 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was chromatographed over silica gel (eluent: dichloromethane/ethyl acetate = 15:1, v/v) to afford compound **1** as a white solid (2.70 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 5.5 Hz, *J* = 3.0 Hz, 4H, NPht-*H*), 7.71 (dd, *J* = 5.5 Hz, *J* = 3.0 Hz, 4H, NPht-*H*), 6.83 (s, 4H, Ar-*H*), 4.08 (m, 4H, C*H*$_2$), 3.92 (m, 4H, C*H*$_2$), 3.84 (m, 8H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.4, 149.0, 134.0, 132.2, 123.3, 121.7, 115.1, 69.4, 69.0, 68.3, 37.5 ppm. ESI-MS: m/z calcd for $[M + Na]^+$ = 567.17, found = 567.05 (100%); HR-ESI-MS ($C_{30}H_{28}N_2O_8$): m/z calcd for $[M + Na]^+$ = 567.1738, found = 567.1734.

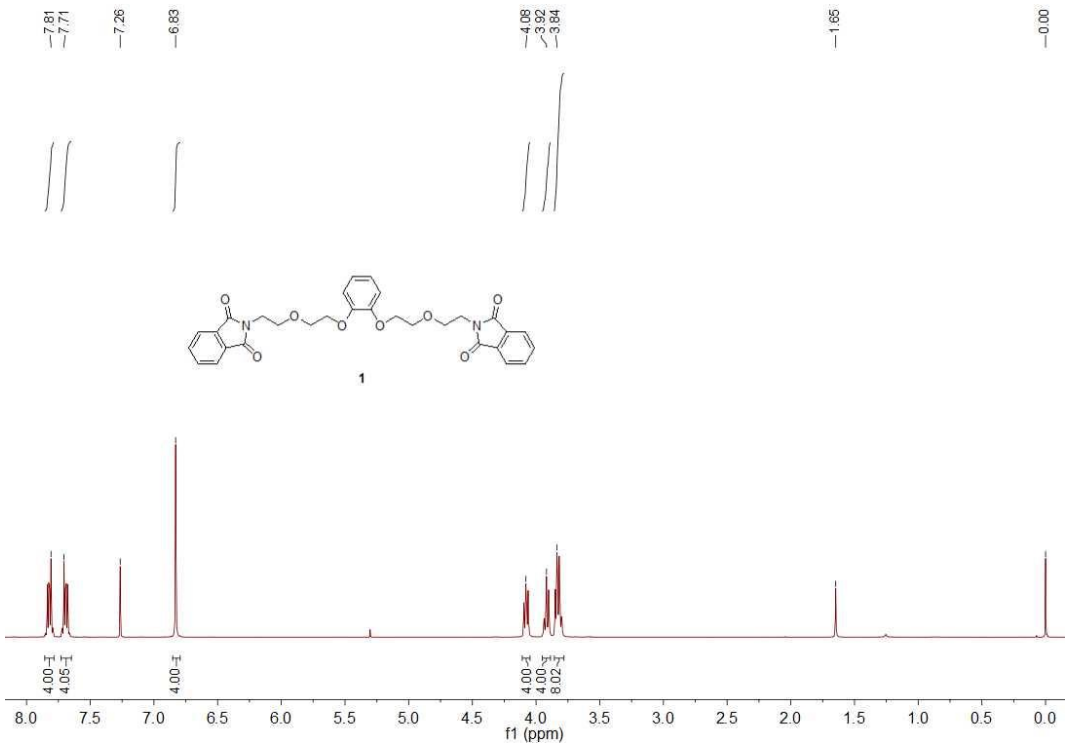


Figure S8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **1**

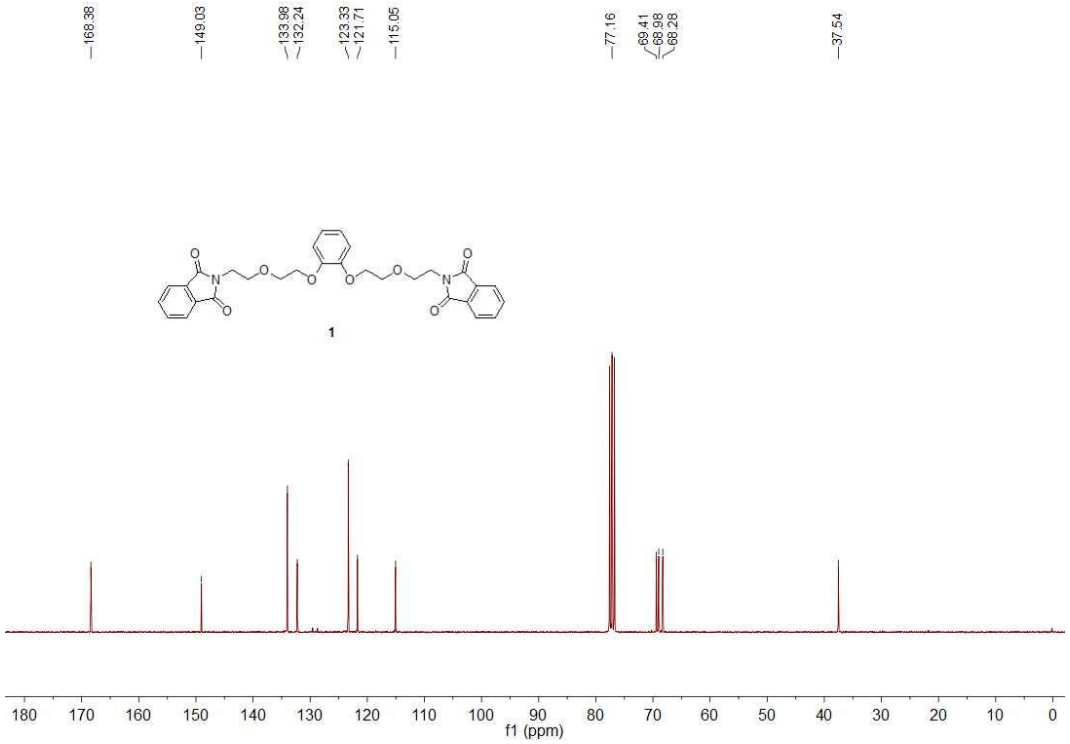


Figure S9. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for **1**

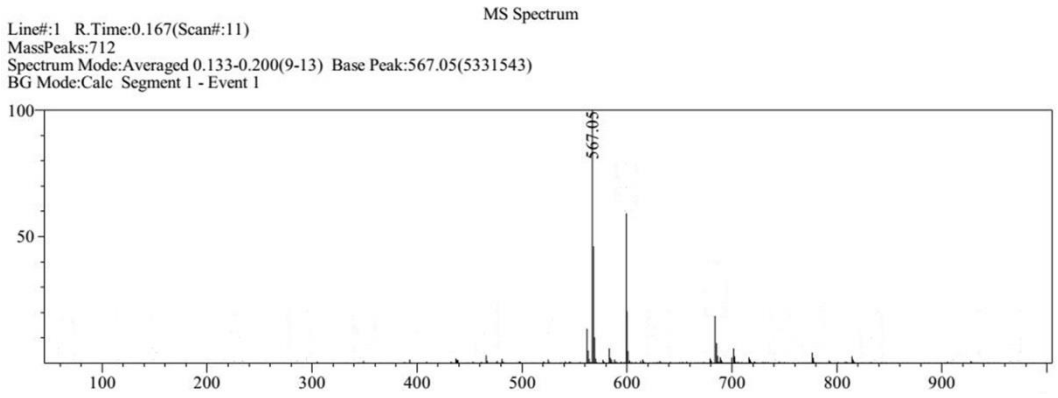


Figure S10. Electrospray ionization mass spectrum of **1**

5.2 Synthesis of Compound **2**

To a solution of **1** (0.90 g, 1.65 mmol) in EtOH (50 mL) was added hydrazine monohydrate (0.50 g, 9.90 mmol) and the mixture was then refluxed for 24 hours under N_2 atmosphere. The solvent was removed under vacuum. The residue was dissolved in water (60 mL) and the resulting mixture was extracted with CH_2Cl_2 (100 mL × 3) and the combined extracts were washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give **2** as light yellow oil (0.41 g, 87%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.92 (s, 4H, Ar-*H*), 4.16 (m, 4H, C*H*$_2$), 3.86 (m, 4H, C*H*$_2$), 3.63 (d, *J* = 5.2 Hz, 4H, C*H*$_2$), 2.92 (t, *J* = 5.1 Hz, 4H, C*H*$_2$), 2.44 (s, 4H, N*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.3, 121.2, 113.9, 72.3, 69.0, 68.1, 41.1 ppm. ESI-MS: m/z calcd for $[M + H]^+$ = 285.18, found = 285.10 (100%); $[M + Na]^+$ = 307.16, found = 307.05 (8%); HR-ESI-MS ($C_{14}H_{24}N_2O_4$): m/z calcd for $[M + H]^+$ = 285.1809, found = 285.1811.

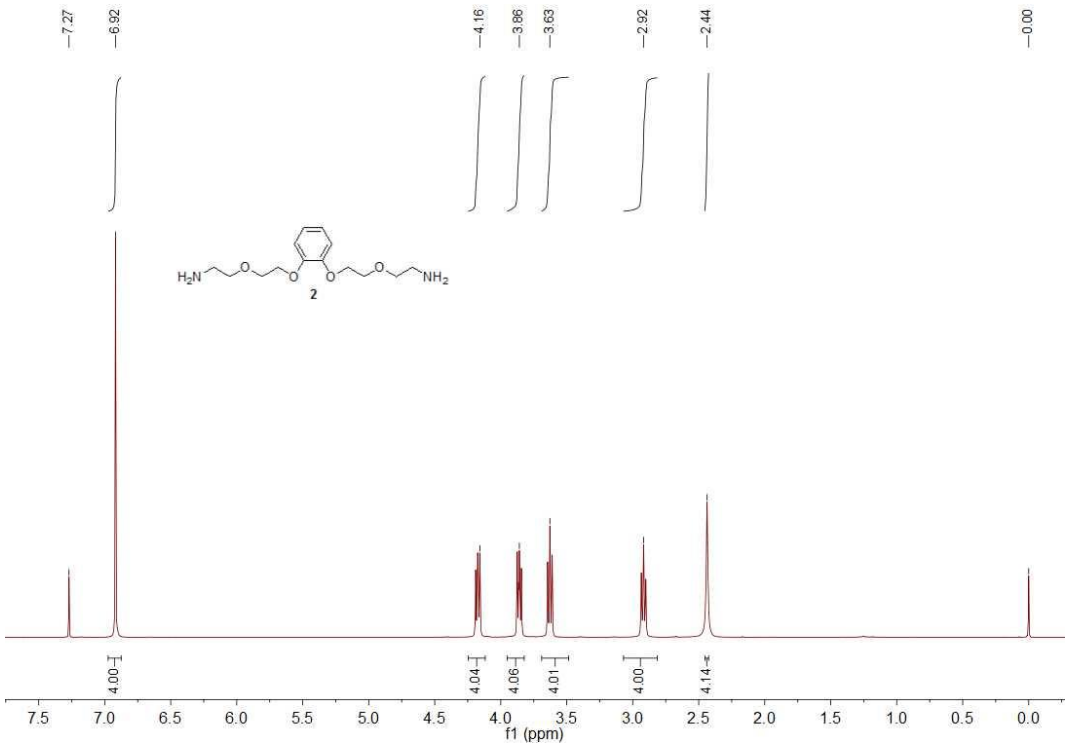


Figure S11. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **2**

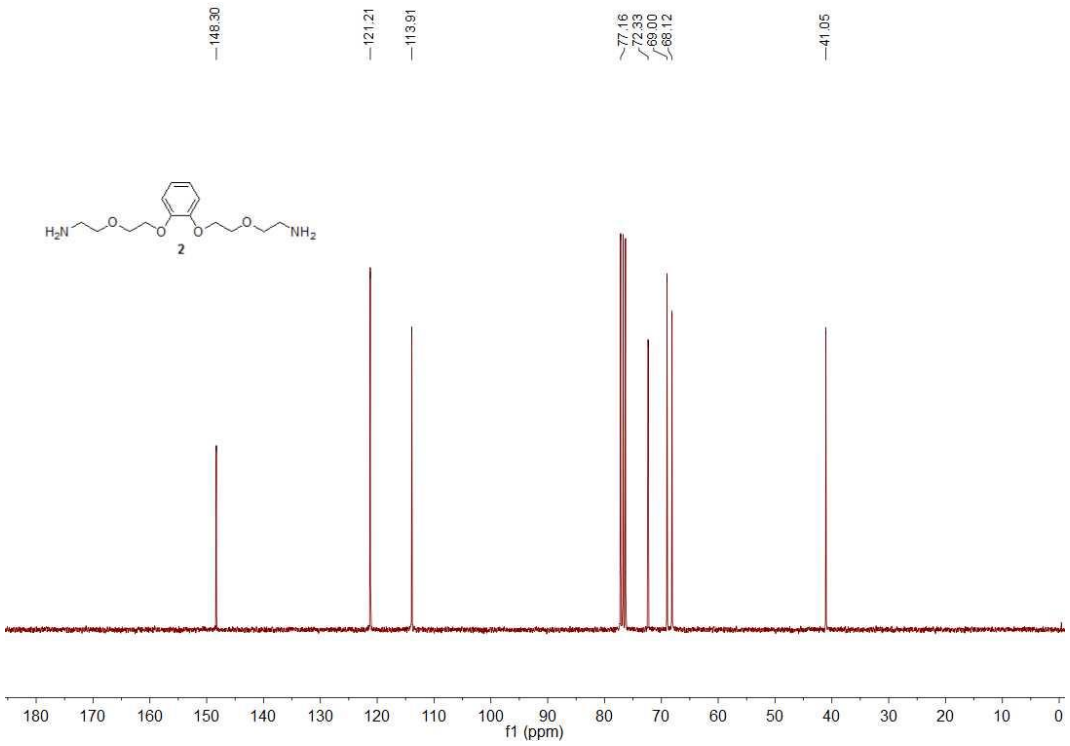


Figure S12. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for **2**

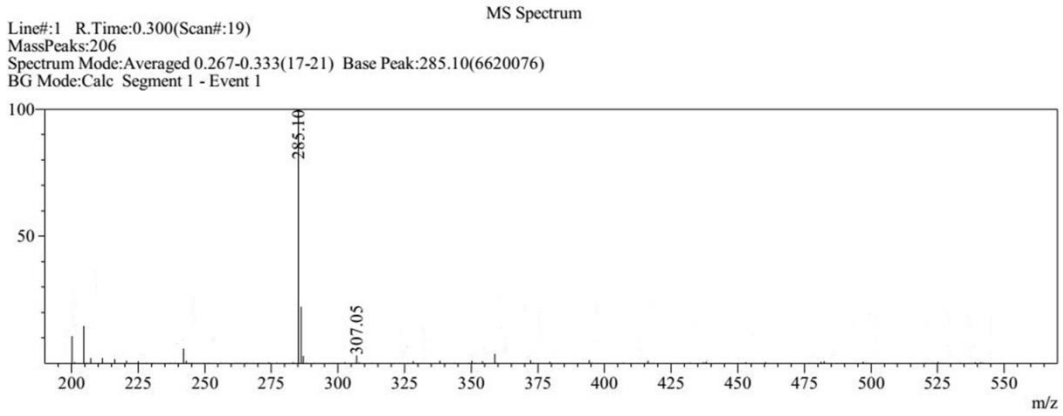


Figure S13. Electrospray ionization mass spectrum of **2**

5.3 Synthesis of Compound **M1**

Imidazolide **L1** (0.94 g, 3.09 mmol) and **2** (0.40 g, 1.41 mmol) were dissolved in 30 mL of dry $CHCl_3$ and this solution was stirred for 12 hours under nitrogen at room temperature. To the reaction mixture 20 mL of $CHCl_3$ was added and the organic layer was washed with 1 M HCl (50 mL), saturated $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography over silica gel (eluent: $CHCl_3$/MeOH = 100:1, v/v) to afford compound **M1** as a colorless viscous solid (0.90 g, 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.16 (br s, 2H, N*H*), 11.98 (br s, 2H, N*H*), 10.34 (br s, 2H, N*H*), 6.86 (d, *J* = 18.6 Hz, 4H, Ar-*H*), 6.14-5.35 (m, 2H, alkylidene-*H*), 4.17 (m, 4H, OCH_2), 4.06-3.78 (m, 4H, OCH_2), 3.80-3.22 (m, 8H, OCH_2), 2.29 (m, 2H, C*H*(CH_2)$_2$), 1.81-1.35 (m, 8H, CH_2), 1.35-1.12 (m, 8H, CH_2), 1.03-0.68 (m, 12H, CH_3) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 170.7, 161.1, 154.4, 151.6, 148.4, 121.3, 114.4, 105.1, 69.4, 68.9, 68.3, 47.9, 39.2, 32.9, 29.1, 26.5, 22.2, 13.9, 11.8 ppm. ESI-MS: m/z calcd for $[M + H]^+$ = 755.45, found = 755.35 (81%); $[M + Na]^+$ = 777.43, found = 777.30 (100%); HR-ESI-MS ($C_{38}H_{58}N_8O_8$): m/z calcd for $[M + H]^+$ = 755.4450, found = 755.4441.

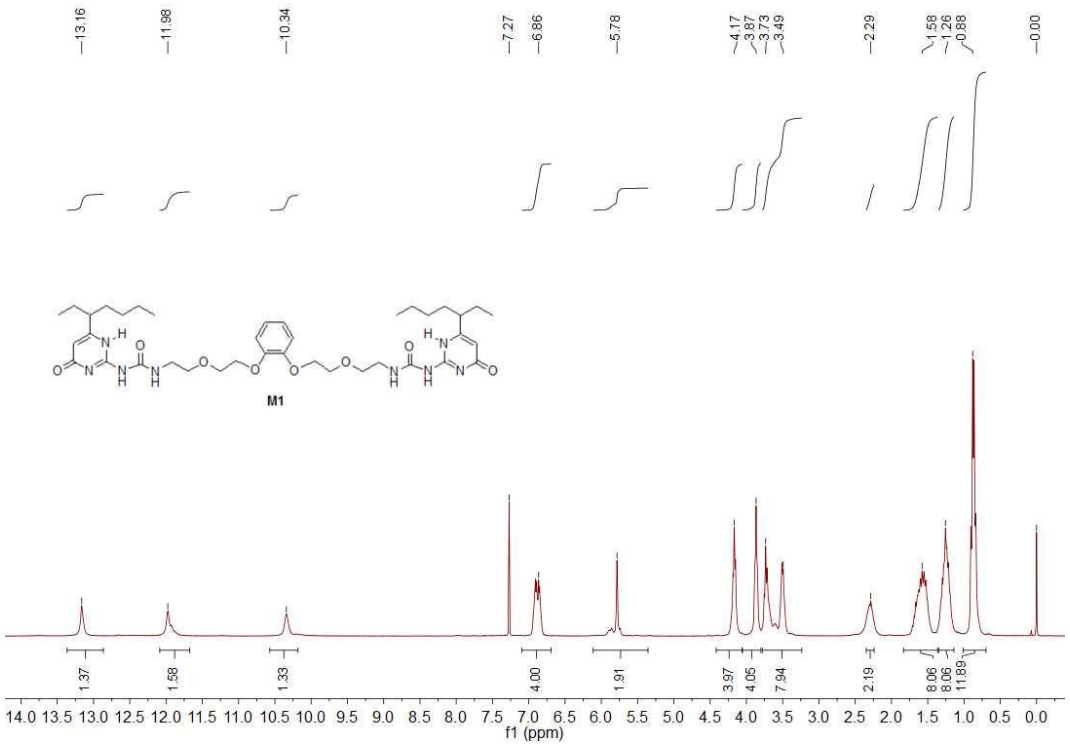


Figure S14. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **M1**

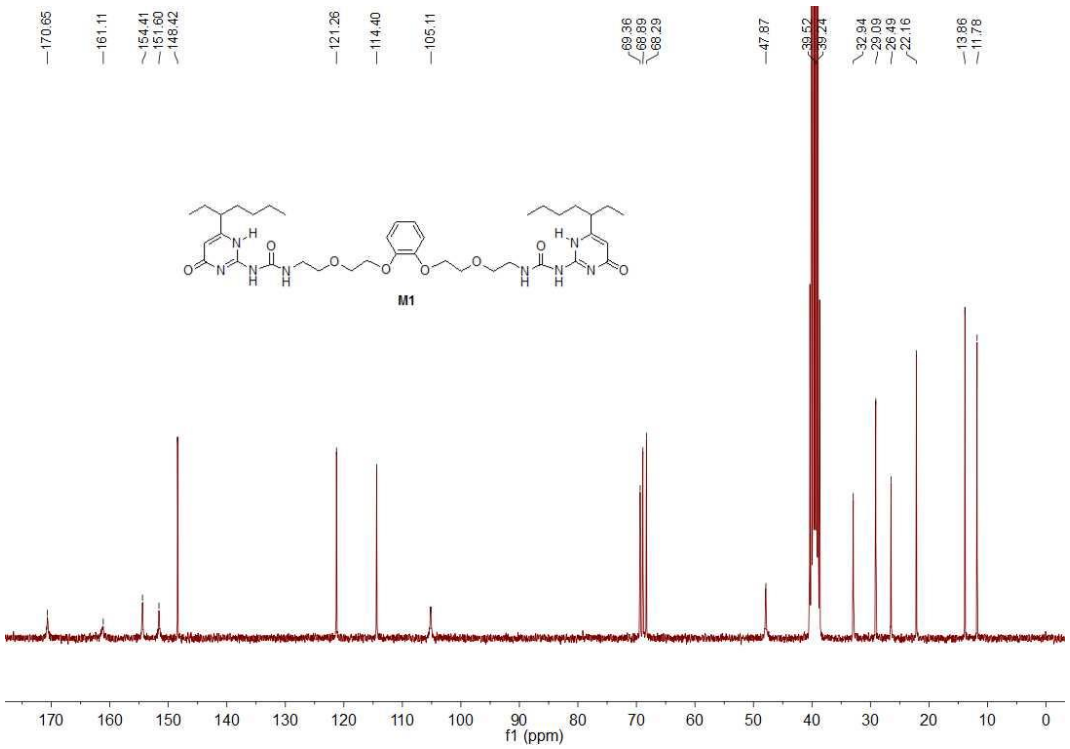


Figure S15. ^{13}C NMR (75 MHz, DMSO-d_6) spectrum for **M1**

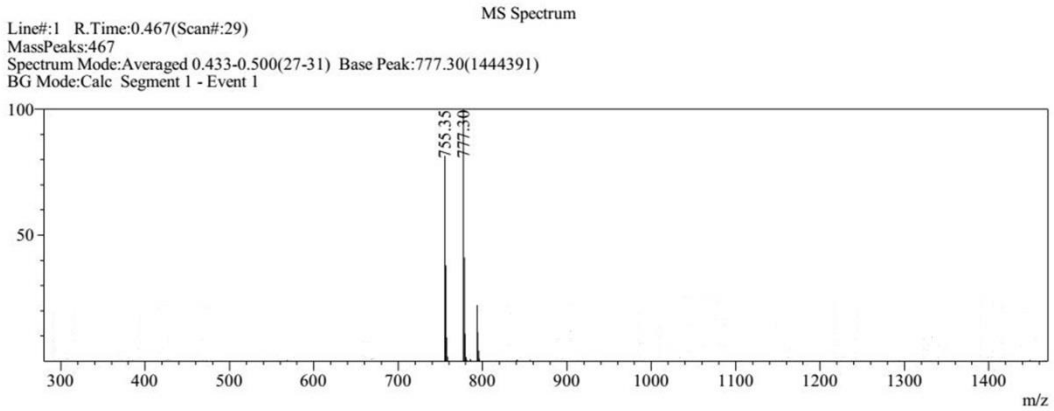
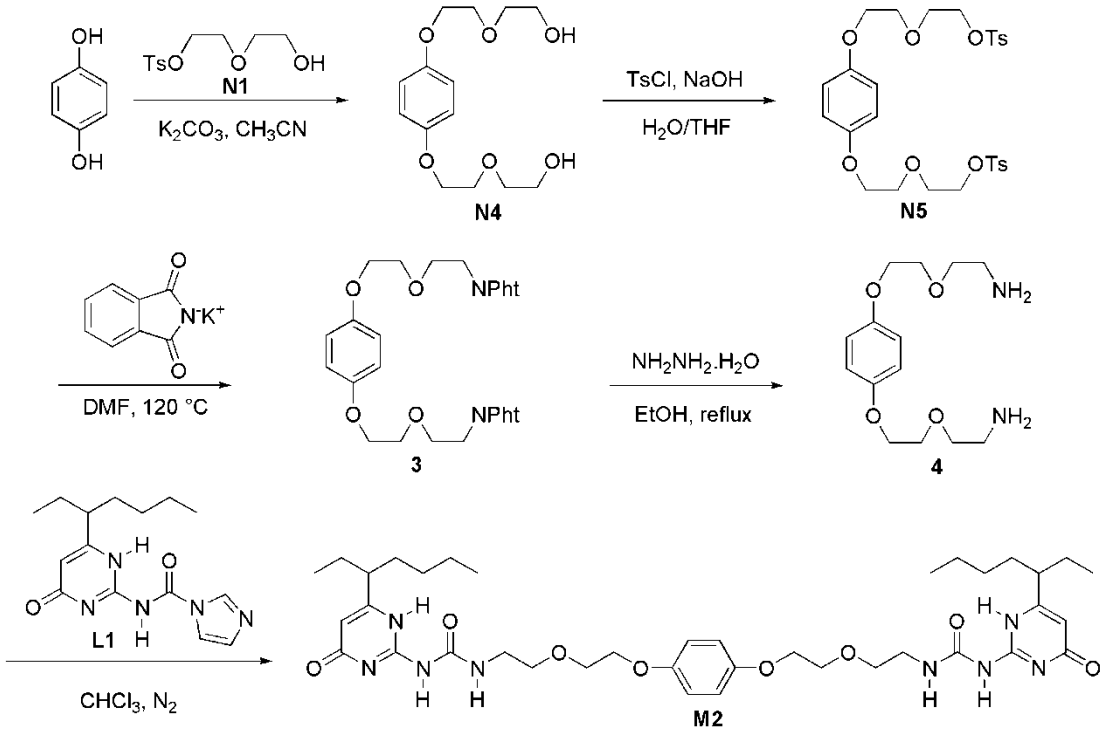


Figure S16. Electrospray ionization mass spectrum of **M1**

6. Synthetic procedures and characterization of M2



Scheme S4. Synthesis of the **M2**

6.1 Synthesis of Compound **3**

To a solution of compound **N5** (4.30 g, 7.23 mmol) in DMF (80 mL) was added potassium phthalimide (4.02 g, 21.69 mmol) at room temperature under N_2 atmosphere. The reaction mixture was heated at 120 °C for 12 h and then poured into water (150 mL). The resulting mixture was extracted with CH_2Cl_2 (100 mL × 3) and the combined extracts were washed with H_2O (100 mL ×

6), brine (50 mL × 3), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was chromatographed over silica gel (eluent: dichloromethane/ethyl acetate = 20:1, v/v) to afford compound **3** as a white solid (2.65 g, 67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 5.5 Hz, *J* = 3.0 Hz, 4H, NPht-*H*), 7.71 (dd, *J* = 5.5 Hz, *J* = 3.1 Hz, 4H, NPht-*H*), 6.70 (s, 4H, Ar-*H*), 3.97 (m, 4H, C*H*$_2$), 3.93 (m, 4H, C*H*$_2$), 3.82 (m, 8H, C*H*$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 153.1, 134.1, 132.2, 123.4, 115.6, 69.4, 68.2, 68.1, 37.4 ppm. ESI-MS: m/z calcd for $[M + H]^+$ = 545.19, found = 545.15 (6%); $[M + Na]^+$ = 567.17, found = 567.10 (100%); HR-ESI-MS ($C_{30}H_{28}N_2O_8$): m/z calcd for $[M + Na]^+$ = 567.1738, found = 567.1719.

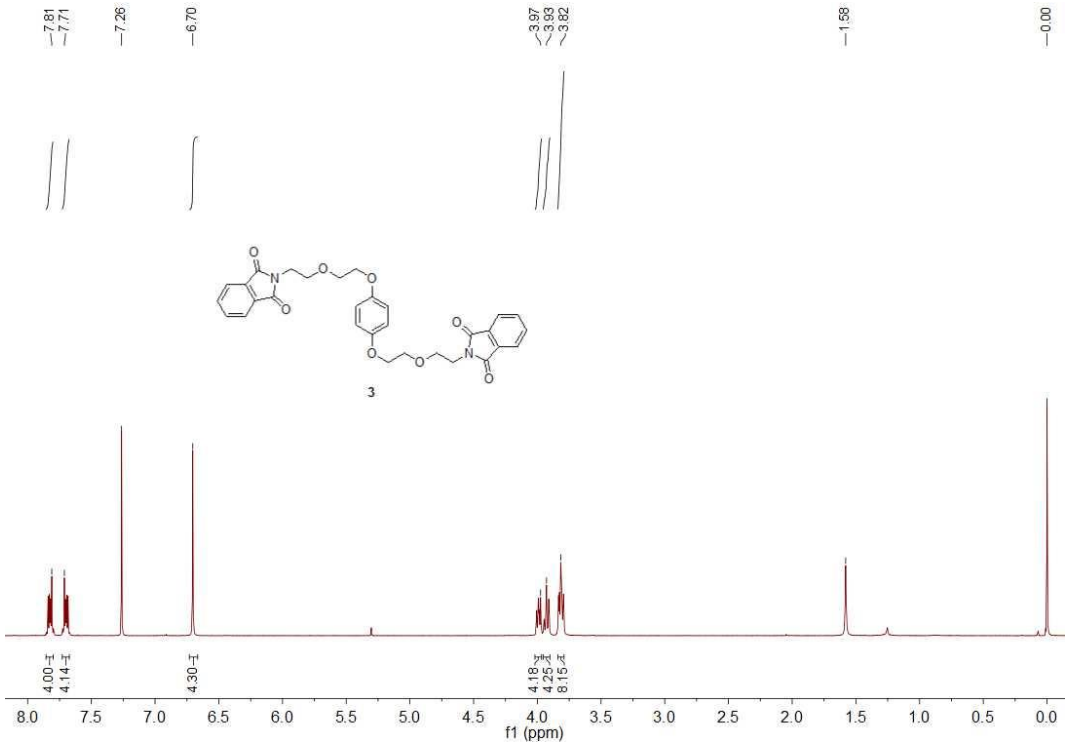


Figure S17. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **3**

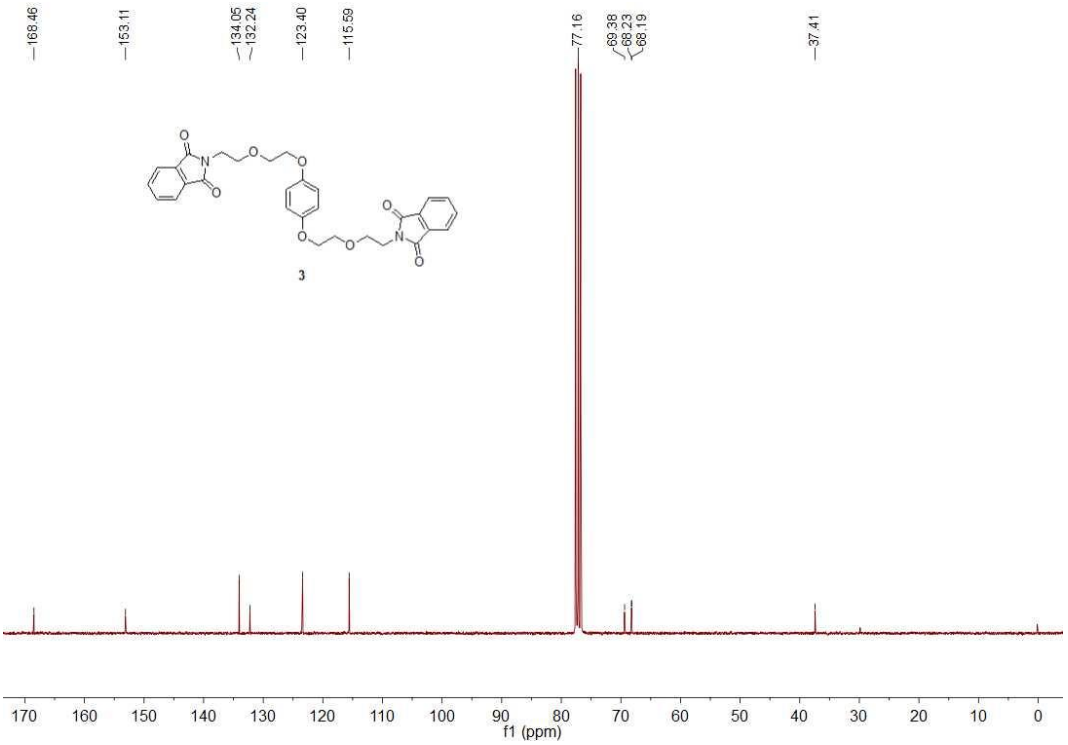


Figure S18. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for **3**

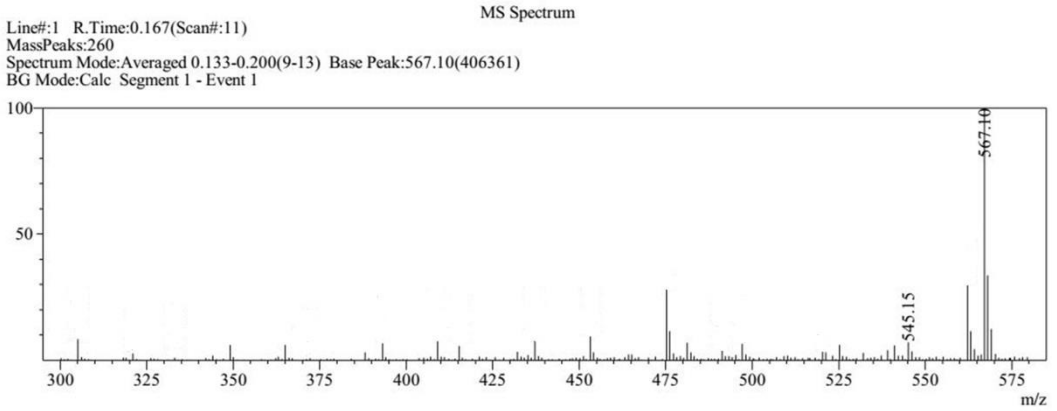


Figure S19. Electrospray ionization mass spectrum of **3**

6.2 Synthesis of Compound **4**

To a solution of **3** (0.73 g, 1.34 mmol) in EtOH (50 mL) was added hydrazine monohydrate (0.40 g, 8.04 mmol) and the mixture was then refluxed for 24 hours under N_2 atmosphere. The solvent was removed under vacuum. The residue was dissolved in water (60 mL) and the resulting mixture was extracted with CH_2Cl_2 (100 mL × 3) and the combined extracts were washed with brine (50 mL × 2), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give **4** as a white solid (0.30 g, 79%). ^1H NMR (300 MHz, $CDCl_3$): δ 6.85 (s, 4H, Ar-*H*), 4.09 (m, 4H,

CH_2), 3.80 (m, 4H, CH_2), 3.57 (d, J = 5.2 Hz, 4H, CH_2), 2.89 (t, J = 5.2 Hz, 4H, CH_2), 1.44 (s, 4H, NH_2) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 152.6, 115.3, 73.2, 68.9, 67.5, 41.4 ppm. ESI-MS: m/z calcd for $[M + H]^+$ = 285.18, found = 285.10 (100%); $[M + Na]^+$ = 307.16, found = 307.10 (81%); HR-ESI-MS ($C_{14}H_{24}N_2O_4$): m/z calcd for $[M + H]^+$ = 285.1809, found = 285.1799.

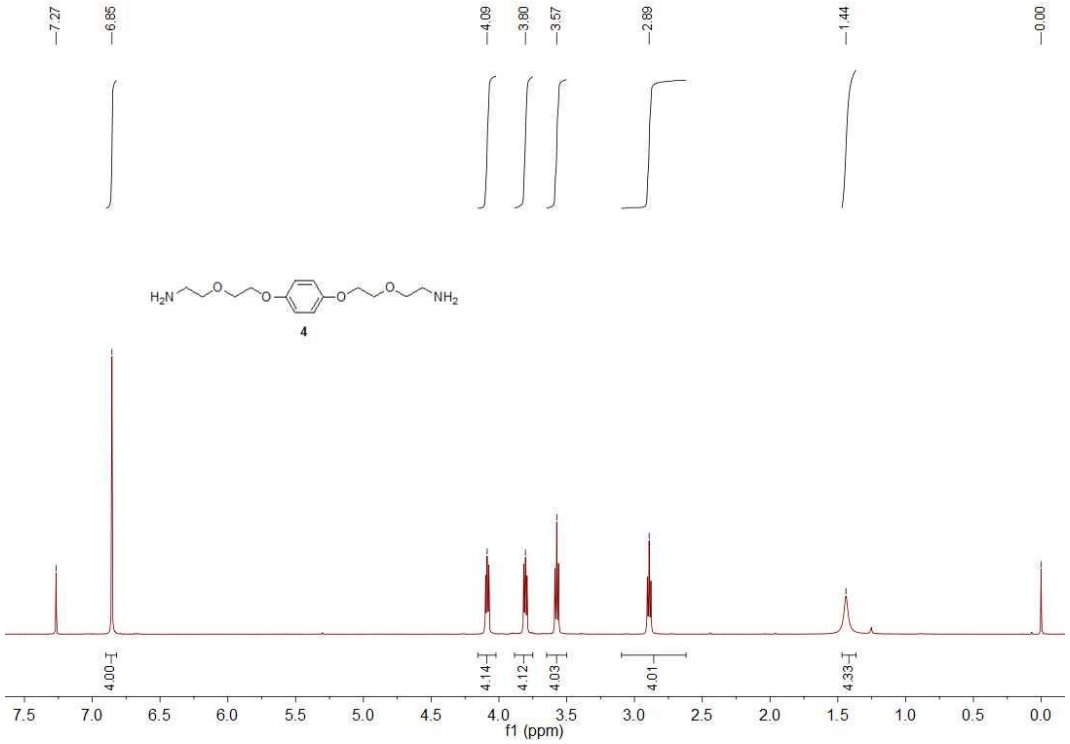


Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **4**

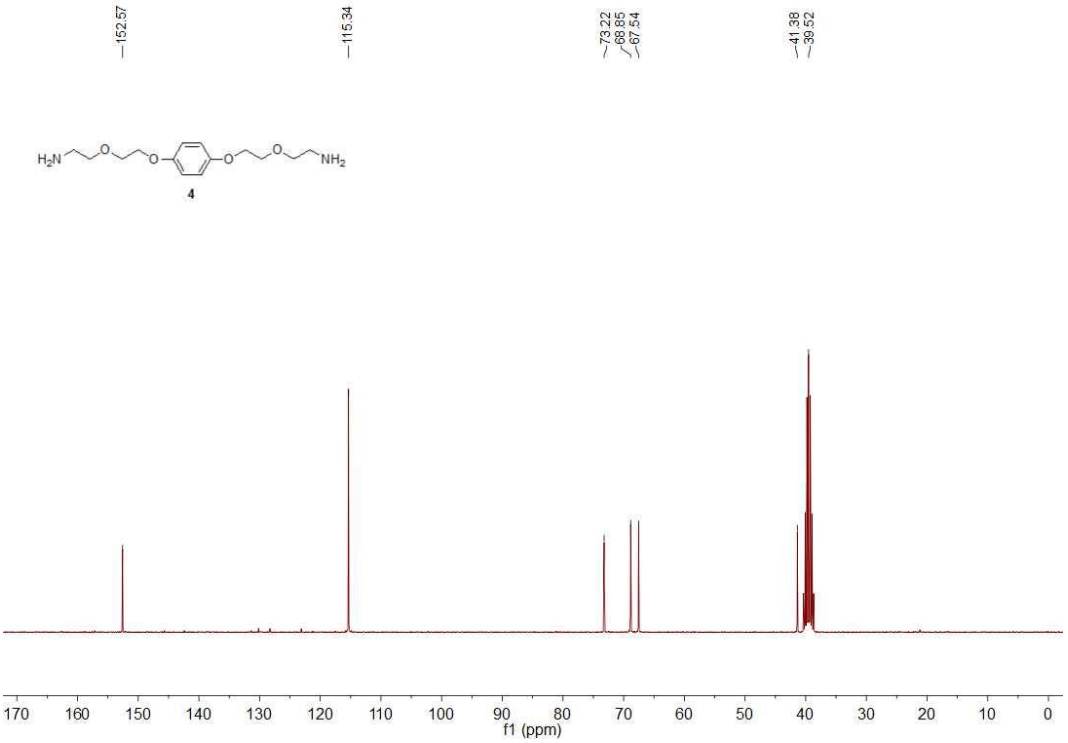


Figure S21. ^{13}C NMR (75 MHz, DMSO-d_6) spectrum for **4**

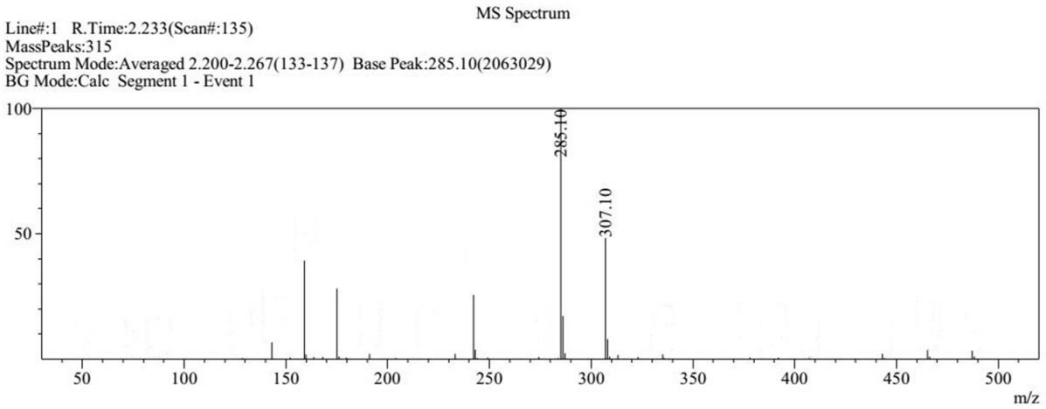


Figure S22. Electrospray ionization mass spectrum of **4**

6.3 Synthesis of Compound **M2**

Imidazolide **L1** (0.70 g, 2.32 mmol) and **4** (0.30 g, 1.06 mmol) were dissolved in 30 mL of dry $CHCl_3$ and this solution was stirred for 12 hours under nitrogen at room temperature. To the reaction mixture 20 mL of $CHCl_3$ was added and the organic layer was washed with 1 M HCl (50 mL), saturated $NaHCO_3$ (50 mL), brine (50 mL), dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was subjected to column chromatography over silica gel (eluent: $CHCl_3$/MeOH = 100:1, v/v) to afford compound **M2** as a colorless transparent solid

(0.74 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.33 (br s, 2H, N*H*), 11.29 (br s, 2H, N*H*), 10.29 (br s, 2H, N*H*), 6.50 (s, 4H, Ar-*H*), 5.84 (s, 2H, alkylidene-*H*), 3.83 (m, 16H, OCH_2), 2.33 (m, 2H, C*H*(CH_2)$_2$), 1.78-1.55 (m, 8H, CH_2), 1.31 (m, 8H, CH_2), 0.90 (m, 12H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 157.2, 155.5, 154.6, 153.2, 114.2, 106.0, 70.5, 69.7, 67.7, 45.5, 40.4, 33.0, 29.5, 26.7, 22.6, 14.1, 11.8 ppm. ESI-MS: m/z calcd for $[M + H]^+$ = 755.45, found = 755.35 (100%); $[M + Na]^+$ = 777.43, found = 777.30 (29%); HR-ESI-MS ($C_{38}H_{58}N_8O_8$): m/z calcd for $[M + H]^+$ = 755.4450, found = 755.4436.

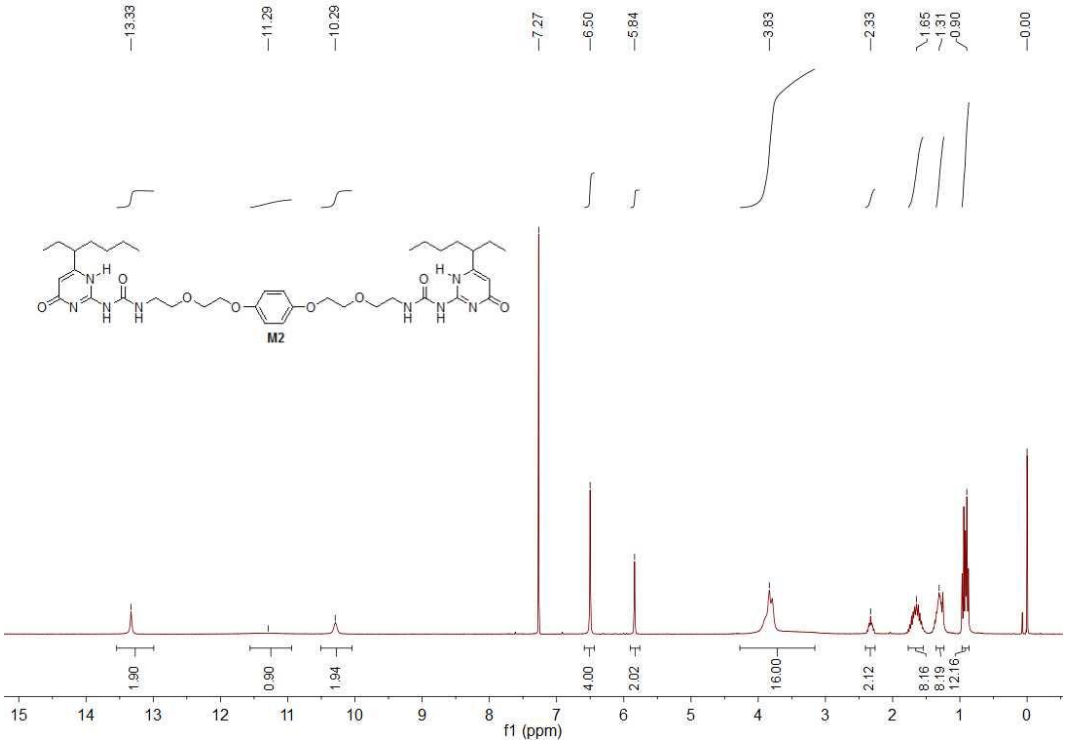


Figure S23. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum for **M2**

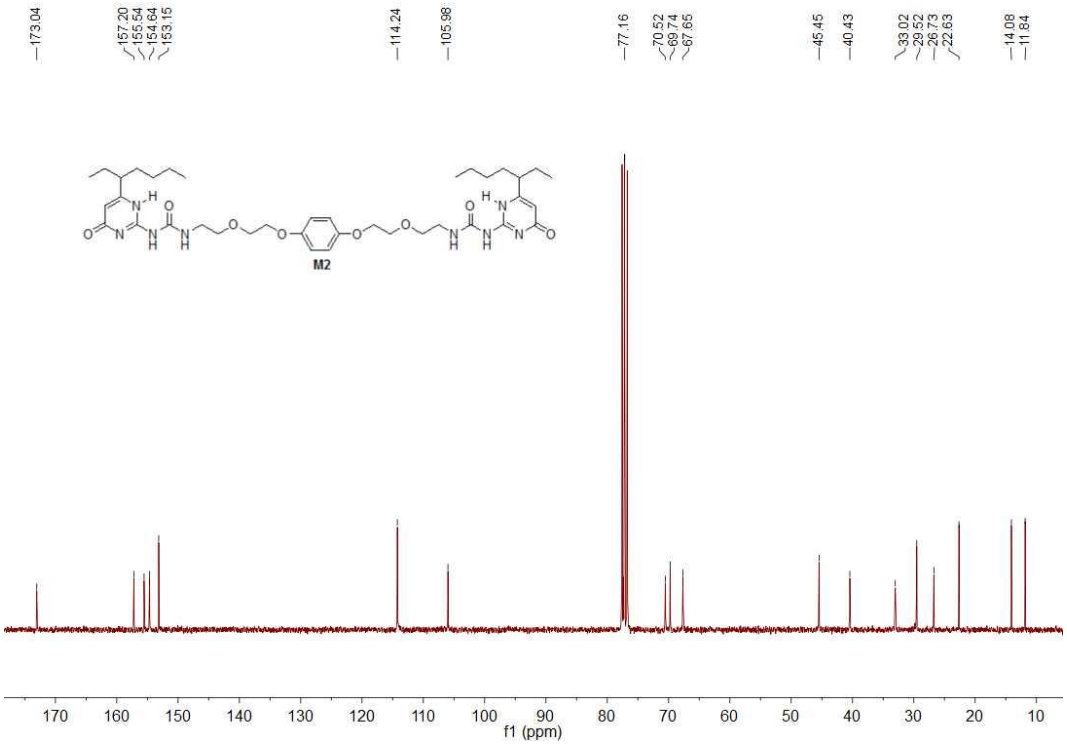


Figure S24. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum for **M2**

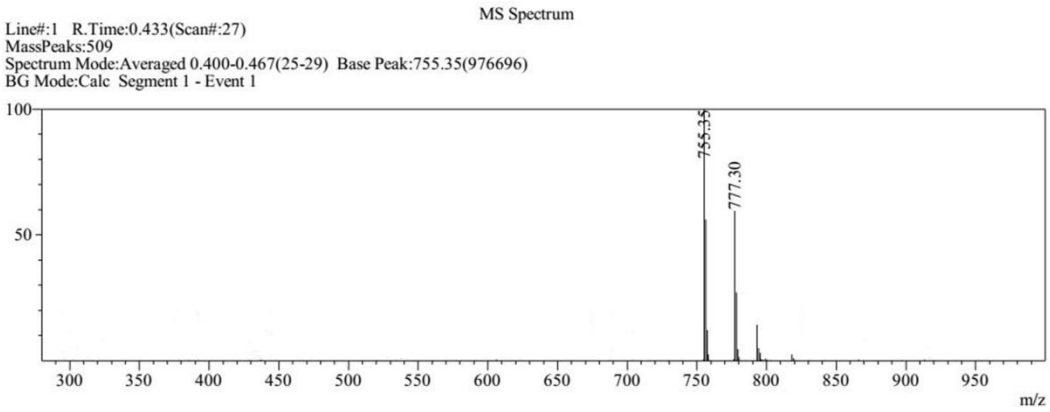


Figure S25. Electrospray ionization mass spectrum of **M2**

7. Reference

S1. Sato, R.; Kozuka, J.; Ueda, M.; Mishima, R.; Kumagai, Y.; Yoshimura, A.; Minoshima, M.; Mizukami, S.; Kikuchi, K., *J. Am. Chem. Soc.*, 2017, **139**, 17397-17404.

S2. Kumar, V.; Sharma, J. N.; Achuthan, P. V.; Hubli, R. C., *RSC Adv.*, 2014, **4**, 805-810.

S3. Young, N. A.; Drew, S. C.; Maniam, S.; Langford, S. J., *Chem. – Asian J.*, 2017, **12**, 1668-1675.

S4. Komarova, E.; Bogomolova, A.; Aldissi, M., *Polym. Int.*, 2015, **64**, 1451-1457.

S5. Keizer, H. M.; Sijbesma, R. P.; Meijer, E. W. *Eur. J. Org. Chem.*, 2004, **2004**, 2553-2555.

S6. Xiao, T.; Feng, X.; Ye, S.; Guan, Y.; Li, S.-L.; Wang, Q.; Ji, Y.; Zhu, D.; Hu, X.; Lin, C.; Pan, Y.; Wang, L., *Macromolecules*, 2012, **45**, 9585-9594.