

## Supporting Information

# Engineering Digital Polymer Based on Thiol-Maleimide Michael Coupling Toward Effective Writing and Reading

Baolei Liu<sup>a</sup>, Qiunan Shi<sup>a</sup>, Lihua Hu<sup>b</sup>, Zhihao Huang<sup>a</sup>, Xiulin Zhu<sup>a,c</sup>, Zhengbiao Zhang<sup>\*a</sup>

<sup>a</sup>State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials; Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application; College of Chemistry, Chemical Engineering and Materials Science, Soochow University  
Suzhou, 215123, China.

<sup>b</sup>Analysis and Testing Center, Soochow University, Suzhou 215123, China.

<sup>c</sup>Global Institute of Software Technology, No 5. Qingshan Road, Suzhou National HiTech District, Suzhou 215163, China.

### Correspondence:

E-mail: [zhangzhengbiao@suda.edu.cn](mailto:zhangzhengbiao@suda.edu.cn)

## **Table of contents**

<b>SECTION A. Experimental Section</b> .....	3
1. Materials.....	3
2. Analysis Techniques.....	3
3. Synthetic Protocols.....	5
3.1 Monomer 0 and monomer 1.....	5
3.2 Discrete oligomers from monomer 1.....	6
3.3 Sequence-defined oligomers.....	12
3.4 Oxidation of thioether groups.....	14
<b>SECTION B. Supplementary Figures</b> .....	16
<b>SECTION C. MALDI Analysis of Digital Oligomers</b> .....	28
<b>SECTION D. Validating Experiment: Ester Group Facilitating Ionization of Oligomer in MALDI process</b> .....	40
<b>SECTION E. Reference</b> .....	41

## SECTION A. Experimental Section

### 1. Materials

Unless otherwise noted, commercially available reagents were purchased from Sigma-Aldrich, Acros Organic, Alfa Aesar, TCI, Energy chemical, Adams and Sinopharm Chem. Dry tetrahydrofuran (THF), dichloromethane (DCM), toluene and N,N-dimethylformamide (DMF) were collected fresh from an Innovative Technology PS-MD-5 solvent purification system. All other dry solvents used were dried over 4 Å molecular sieves and stored under argon.

### 2. Analysis Techniques

**SEC.** The number-average molecular weight ( $M_n$ ) and polydispersity ( $D = M_w/M_n$ ) of the polymers were determined using a size exclusion column TOSOH HLC-8320 equipped with refractive index and UV detectors using two TSKgel Super Multipore HZ-N (4.6 × 150 mm, 3 μm beads size) columns arranged in series. THF was used as the eluent at a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software, and molecular weights were calculated with polystyrene (PS) standards.

**NMR.** All  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) using tetramethylsilane (TMS) as the internal standard at room temperature. The  $^1\text{H}$  NMR spectra were referenced to 7.26 ppm in  $\text{CDCl}_3$  or 2.54 ppm in  $\text{DMSO-d}_6$ , and  $^{13}\text{C}$  NMR spectra were referenced to 77.00 ppm in  $\text{CDCl}_3$ .

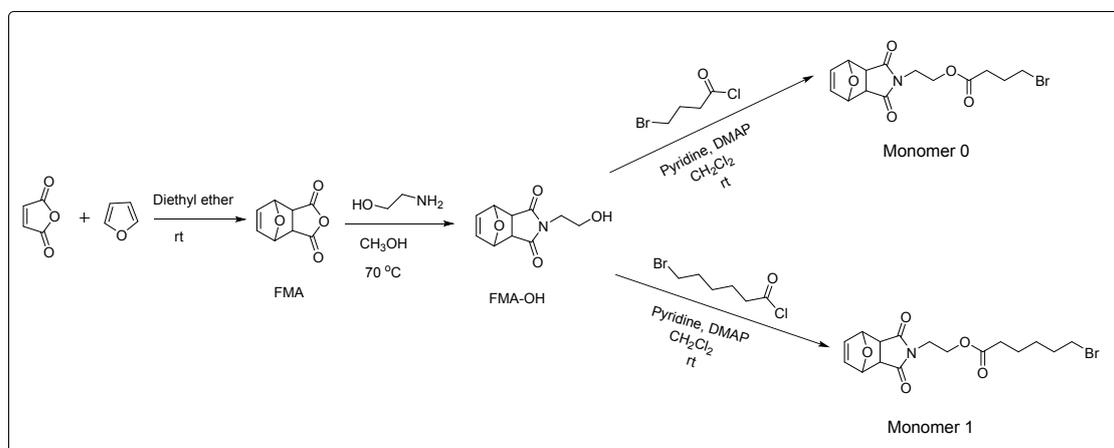
**Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF).** MALDI-TOF mass spectroscopy (MS) were acquired on an UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) equipped with a an Nd:YAG smart beam-II laser with 355-nm wavelength, 200 Hz firing rate and 500 shots per measurement. The instrument was calibrated prior to each measurement with external PMMA (Sigma-Aldrich, analytical standard, for GPC 2,000 and 4,000) at the molecular weight under consideration. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity.

**Tandem MALDI-TOF MS/MS analysis.** An UltrafleXtreme MALDI-TOF mass spectrometer (Bruker Daltonics, Germany) was employed for the tandem MS/MS measurements by using the LIFT mode. The system is equipped with a Nd:YAG smart beam-II laser with 355-nm wavelength and 1k Hz firing rate. After the first TOF unit, ions generated by the MALDI process were accelerated at 7.50 kV through a grid at 6.85 kV into a precursor ion selector (PCIS). In this region, the ions pass through a timed-ion-selector device that is able to select one parent with associated fragments from a mixture for subsequent fragmentation in the LIFT cell. After the parent ion at a given  $m/z$  was selected by the timed-ion-selector, it passed through a retarding lens where the ions were decelerated and then passed into the LIFT cell. Fragmentation was performed in the simple metastable decomposition mode, and the fragments were further accelerated by 19 kV in the LIFT cell, passed through a post lift metastable suppressor (PLMS), into the reflector, and finally to the detector. MS and MS/MS data were further processed using FlexAnalysis 1.3 software package. Trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix and was prepared in CHCl<sub>3</sub> at a concentration of 20 mg/mL. The cationizing agent sodium trifluoroacetate was prepared in ethanol at a concentration of 10 mg/mL. The matrix and cationizing salt solutions were mixed in a ratio of 10/1 (v/v). All samples were dissolved in CHCl<sub>3</sub> at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the target plate was inserted into the MALDI-TOF mass spectrometer.

**Thermogravimetric analyses (TGA).** TGA were performed on a thermogravimetric analyzer (Discovery TGA, USA) at a heating rate of 10 °C /min from room 30 to 600 °C under the nitrogen atmosphere.

### 3. Synthetic Protocols

#### 3.1 Monomer 0 and monomer 1



**Scheme S1.** Synthesis of the monomer.

**FMA:** A solution of maleic anhydride (4.47 g, 45.59 mmol) and furan (6.6 mL, 91.18 mmol) in 100 mL diethyl ether was stirred at room temperature for 48 h. The mixture was filtered and the filter cake was washed with cold diethyl ether (3×50 mL), dried in reduced pressure at 25 °C overnight to afford FMA as white solid in a yield of 70% (5.30 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.58 (s, 2H), 5.43 (d, *J* = 21.2 Hz, 2H), 3.14 (d, *J* = 21.3 Hz, 2H).

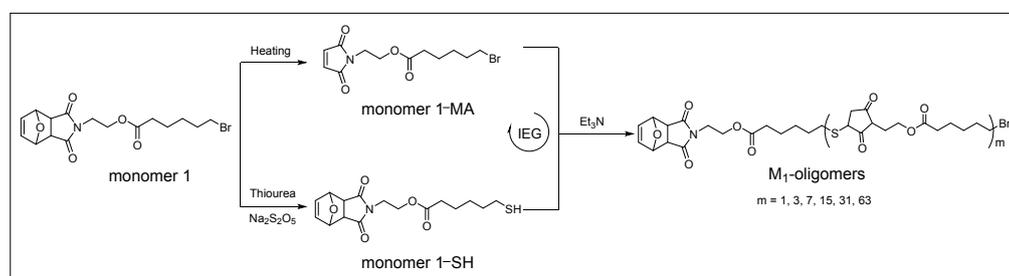
**FMA-OH:** 5.30 g of FMA (31.90 mmol) was dissolved in 150 mL anhydrous methanol in a round bottom flask. Ethanolamine (2.9 mL, 47.89 mmol) was added dropwise at 0 °C by addition funnel. Subsequently, the solution was slowly heated to 70 °C and refluxed under this temperature for 24 h. The mixture was cooled to room temperature and allowed to stand in a freezer overnight. The precipitate was filtered and the filter cake was washed with cold methanol (3×40 mL), dried in vacuum at 25 °C overnight to afford FMA-OH as white crystalline solid (3.74 g, yield 56%). <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>, ppm): δ 6.55 (s, 2H), 5.12 (s, 2H), 4.78 (t, *J* = 4.9 Hz, 1H), 3.48 – 3.37 (m, 4H), 2.92 (s, 2H).

**Monomer 0:** Under argon atmosphere, FMA-OH (1.80 g, 8.60 mmol) and 4-dimethylaminopyridine (0.11 g, 0.86 mmol) were dissolved in dry dichloromethane (50 mL) in a three-necked flask. 4-bromobutyryl chloride (1.59 g, 8.60 mmol) was added dropwise at 0 °C in an ice bath. The mixture was stirred at room temperature

and monitored by TLC. After completion, the mixture was extracted with saturated  $\text{NaHCO}_3$  (20 mL), water ( $3 \times 20$  mL). The organic layer was combined, concentrated in vacuum and dried with anhydrous  $\text{Na}_2\text{SO}_4$ . The crude product was purified by column chromatography on silica gel eluting with PE/EA (1/1) to give monomer 0 (2.46 g, 80%) as a pale yellow oil.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.52 (s, 2H), 5.29 (d,  $J = 9.3$  Hz, 2H), 4.25 (dd,  $J = 6.8, 3.8$  Hz, 2H), 3.83 – 3.68 (m, 2H), 3.52 – 3.39 (m, 2H), 2.88 (s, 2H), 2.46 (t,  $J = 7.2$  Hz, 2H), 2.24 – 2.05 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  176.03, 172.27, 136.56, 80.94, 60.77, 47.48, 37.85, 32.51, 27.54.

**Monomer 1:** The procedure is similar to **Monomer 0** mentioned above. Monomer 1 as a pale yellow oil (2.81 g, yield 83%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.52 (s, 2H), 5.30 (d,  $J = 24.3$  Hz, 2H), 4.23 (t,  $J = 5.4$ , 2H), 3.73 (dd,  $J = 19.7$  Hz, 14.4, 2H), 3.41 (t,  $J = 6.8$ , 2H), 2.87 (s, 2H), 2.28 (t,  $J = 7.4$ , 2H), 1.98 – 1.78 (m, 2H), 1.70 – 1.36 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  176.00, 173.14, 136.55, 80.92, 60.55, 47.47, 37.92, 34.65 – 31.44, 27.57, 23.74.

### 3.2 Discrete oligomers from monomer 1

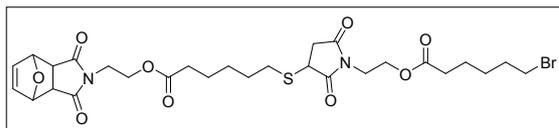


**Scheme S2.** Synthetic route of discrete oligomers from monomer 1 by IEG strategy.

**monomer 1-MA:** A solution of monomer 1 (5.46 g, 14.14 mmol) in 150 mL toluene was refluxed at  $110^\circ\text{C}$  under argon flow for about 6 h.<sup>1</sup> TLC showed that the reaction was complete. Toluene was evaporated under reduced pressure. The crude product was directly used in next thiol-Michael coupling without purification.

**monomer 1-SH:** A solution of thiourea (2.10 g, 28.28 mmol) in  $\text{C}_2\text{H}_5\text{OH}$  (50 ml) was stirred at  $65^\circ\text{C}$  for 30 min. Subsequently, monomer 1 (5.46 g, 14.14 mmol) in 30 mL  $\text{C}_2\text{H}_5\text{OH}$  was added. The reaction was monitored by TLC. After completion, the solvent was evaporated under reduced pressure and the residue was re-dissolved in

DCM (124 mL). Sodium pyrosulfite (5.37 g, 28.28 mmol) in H<sub>2</sub>O (62 mL) was added. The mixture was refluxed at 50 °C under argon atmosphere overnight.<sup>2</sup> The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with DCM (3×30 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.



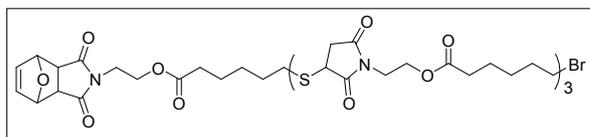
**M1-dimer:** monomer 1-SH and monomer 1-MA were dissolved in dry CHCl<sub>3</sub> (300 mL) in a three-necked flask.

Triethylamine (5.9 mL, 42.42 mmol) was added dropwise at 25 °C under argon atmosphere and the mixture was stirred for about 10 h. TLC showed the mixture was complete. The reaction mixture was quenched with 100 mL water, extracted with 300 mL saturated NaHCO<sub>3</sub>(aq.). The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. After column chromatography on silica gel (EA/PE = 2/1), M1-dimer (6.79 g) was obtained as a pale yellow oil in 73% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.52 (s, 2H), 5.26 (s, 2H), 4.34 – 4.12 (m, 4H), 3.86 – 3.65 (m, 5H), 3.41 (t, *J* = 6.7 Hz, 2H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 1H), 3.00 – 2.66 (m, 4H), 2.53 (dd, *J* = 18.7, 3.6 Hz, 1H), 2.28 (dd, *J* = 13.0, 7.1 Hz, 4H), 1.98 – 1.78 (m, 2H), 1.65 (qt, *J* = 9.3, 4.7 Hz, 6H), 1.52 – 1.28 (m, 4H).

**M1-dimer-MA:** A solution of M1-dimer (3.39 g, 5.16 mmol) in toluene (100 mL) was refluxed at 110 °C under argon flow and monitored by TLC. After completion, the solvent was evaporated in vacuum. The crude product was directly used in next thiol-Michael coupling without purification.

**M1-dimer-SH:** 784.32 mg of thiourea was dissolved in dry C<sub>2</sub>H<sub>5</sub>OH (60 mL) in round bottom flask. The mixture was heated at 65 °C for 30 min and 3.39 g of M1-dimer in THF (20 mL) was added. TLC showed the reaction was complete. The mixture was concentrated in vacuum and the residue was re-dissolved DCM (46 mL). The Sodium pyrosulfite (1.96 g, 10.32 mmol) and 18-Crown-6 (137.3 mg, 0.52 mmol) in 23 mL water was added. The mixture was refluxed at 50 °C under argon atmosphere overnight. The reaction was cooled to room temperature and the organic

layer was separated. The aqueous layer was further extracted with DCM (3×30 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.



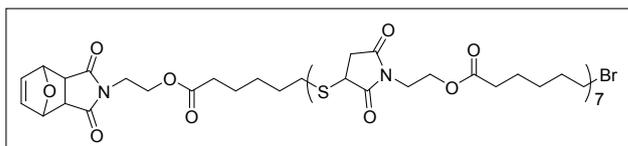
**M1-tetramer:** Under argon atmosphere, M1-dimer-MA and M1-dimer-SH were dissolved in

anhydrous CHCl<sub>3</sub> (150 mL) in a three-necked flask attached to a slow-addition apparatus. Triethylamine (2.2 mL, 15.48 mmol) was added dropwise at 25 °C and the mixture was stirred overnight. The reaction mixture was quenched with 80 mL water, extracted with 200 mL saturated aqueous NaHCO<sub>3</sub>. The combined organic phases was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. After column chromatography on silica gel (EA/PE = 4/1), M1-tetramer (4.77 g) was obtained as a pale yellow oil in 77% yield. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.52 (s, 2H), 5.26 (s, 2H), 4.36 – 4.12 (m, 8H), 3.90 – 3.66 (m, 11H), 3.41 (t, *J* = 6.8 Hz, 2H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 3H), 2.98 – 2.67 (m, 8H), 2.53 (dd, *J* = 18.7, 3.7 Hz, 3H), 2.28 (ddd, *J* = 7.4, 6.6, 2.9 Hz, 8H), 1.98 – 1.79 (m, 2H), 1.71 – 1.32 (m, 22H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.39, 176.00, 174.56, 173.17, 136.55, 80.91, 60.54, 47.44, 39.02, 38.02, 37.86 – 37.59, 36.06, 33.64, 32.33, 31.47, 28.61, 28.09, 27.54, 24.10, 23.74. MALDI-TOF for M1-tetramer, Calcd: *m/z* = 1153.3 [M + Na-Furan]<sup>+</sup>; Found: 1153.4 [M + Na-Furan]<sup>+</sup>.

**M1-tetramer-MA:** A solution of M1-tetramer (2.35 g, 1.96 mmol) in toluene (100 mL) was refluxed at 110 °C under argon flow and monitored by <sup>1</sup>H NMR. After completion, the solvent was evaporated in vacuum. The crude product was directly used in next thiol-Michael coupling without purification.

**M1-tetramer-SH:** 297.9 mg of thiourea was dissolved in dry C<sub>2</sub>H<sub>5</sub>OH (40 mL) in round bottom flask. The mixture was heated at 65 °C for 30 min and 2.35 g of M1-tetramer in THF (10 mL) was added. The mixture was refluxed at 65 °C for 24 h. The solvent was evaporated in vacuum and the residue was re-dissolved in DCM (17 mL), treated with 18-Crown-6 (105.6 mg, 0.4 mmol) and sodium pyrosulfite (744.8 mg,

3.92 mmol) in water (9 mL). The mixture was refluxed at 50 °C under argon atmosphere for 12 h. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with DCM (3×30 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.



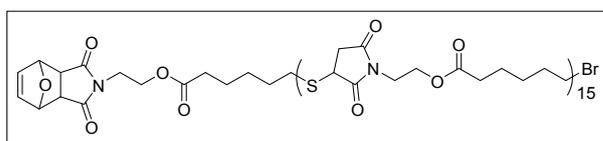
**M1-octamer:** Under argon atmosphere, M1-tetramer-SH and M1-tetramer-MA were dissolved

in anhydrous CHCl<sub>3</sub> (90 mL) in a three-necked flask. Triethylamine (817.3 μL, 5.88 mmol) was added via a 1 mL syringe over 3 min and the mixture was stirred 25 °C overnight. TLC showed that the reaction was complete. The reaction mixture was quenched with 45 mL water, extracted with 90 mL saturated aqueous NaHCO<sub>3</sub>. The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with DCM/MeOH (40/1) to give M1-octamer (2.73 g, 61%) as a pale yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.53 (s, 2H), 5.26 (s, 2H), 4.34 – 4.13 (m, 16H), 3.89 – 3.66 (m, 23H), 3.41 (t, *J* = 6.8 Hz, 2H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 7H), 2.98 – 2.65 (m, 16H), 2.53 (dd, *J* = 18.7, 3.7 Hz, 7H), 2.38 – 2.18 (m, 16H), 1.94 – 1.77 (m, 2H), 1.77 – 1.54 (m, 30H), 1.52 – 1.32 (m, 16H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.40, 176.00, 174.57, 173.19, 136.56, 80.92, 60.5, 47.46, 39.03, 38.04, 36.07, 33.64, 32.35, 31.5, 28.62, 28.11, 27.56, 24.12, 23.75. MALDI-TOF for M1-octamer, Calcd: *m/z* = 2237.7 [M + Na-Furan]<sup>+</sup>; Found: 2238.0 [M + Na-Furan]<sup>+</sup>.

**M1-octamer-MA:** A solution of M1-octamer (1.35 g, 0.60 mmol) in toluene (50 mL) was refluxed at 110 °C under argon flow and monitored by <sup>1</sup>H NMR. After completion, the solvent was evaporated in vacuum. The crude product was directly used in next thiol-Michael coupling without purification.

**M1-octamer-SH:** 91.2 mg of thiourea (1.20 mmol) was dissolved in dry C<sub>2</sub>H<sub>5</sub>OH (20 mL) in round bottom flask. The mixture was heated at 65 °C for 30 min and 1.35 g of M1-octamer in THF (15 mL) was added. The mixture was refluxed at 65 °C for 24 h.

The solvent was evaporated in vacuum and the residue was re-dissolved in DCM (8 mL), treated with 18-Crown-6 (14.8 mg, 0.06 mmol) and sodium pyrosulfite (342.0 mg, 1.80 mmol) in water (4 mL). The mixture was refluxed at 50 °C under argon atmosphere for 18 h. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with DCM (3×10 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.

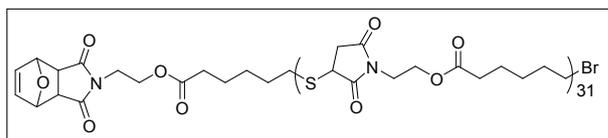


**M1-hexamer:** Under argon atmosphere, M1-octamer-SH and M1-octamer-MA were dissolved in

anhydrous CHCl<sub>3</sub> (60 mL) in a three-necked flask. Triethylamine (250.2 μL, 1.80 mmol) was added via a 1 mL syringe over 3 min and the mixture was stirred 25 °C overnight. TLC showed that the reaction was complete. The reaction mixture was quenched with 30 mL water, extracted with 30 mL saturated aqueous NaHCO<sub>3</sub>. The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with DCM/MeOH (30/1) to give M1-hexamer (1.55 g, yield 58%) as a pale yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.52 (s, 2H), 5.26 (s, 2H), 4.34 – 4.13 (m, 32H), 3.88 – 3.65 (m, 47H), 3.41 (t, *J* = 6.8 Hz, 2H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 15H), 2.98 – 2.65 (m, 34H), 2.53 (dd, *J* = 18.7, 3.7 Hz, 15H), 2.28 (t, *J* = 7.4 Hz, 32H), 1.94 – 1.79 (m, 2H), 1.74 – 1.52 (m, 62H), 1.54 – 1.28 (m, 32H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.39, 174.56, 173.23, 136.55, 80.92, 60.59, 47.46, 39.03, 38.18, 37.91, 36.07, 33.64, 31.51, 28.63, 28.12, 27.57, 24.12, 23.76. MALDI-TOF for M1-hexamer, Calcd: *m/z* = 4406.4 [M + Na-Furan]<sup>+</sup>; Found: 4406.8 [M + Na-Furan]<sup>+</sup>.

**M1-hexamer-MA:** A solution of M1-hexamer (0.75 g, 0.17 mmol) in toluene (20 mL) was refluxed at 110 °C under argon flow and monitored by <sup>1</sup>H NMR. After completion, the solvent was evaporated in vacuum. The crude product was directly used in next thiol-Michael coupling without purification.

**M1-hexamer-SH:** 64.6 mg of thiourea (0.85 mmol) was dissolved in dry C<sub>2</sub>H<sub>5</sub>OH (15 mL) in round bottom flask. The mixture was heated at 65 °C for 30 min and 0.75 g of M1-hexamer in THF (15 mL) was added. The mixture was refluxed at 65 °C for 48 h. The solvent was evaporated in vacuum and the residue was re-dissolved in DCM (4 mL), treated with 18-Crown-6 (22.5 mg, 0.09 mmol) and sodium pyrosulfite (161.5 mg, 0.85 mmol) in water (2 mL). The mixture was refluxed at 50 °C under argon atmosphere for 24 h. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with DCM (3×10 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.

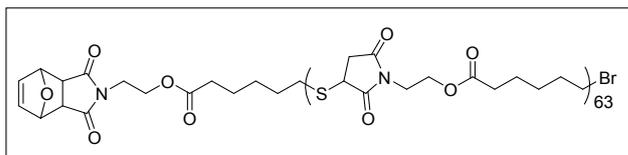


**M1-32mer:** Under argon atmosphere, M1-hexamer-SH and M1-hexamer-MA were dissolved in anhydrous CHCl<sub>3</sub> (45 mL) in a three-necked flask. Triethylamine (118.1 μL, 0.85 mmol) was added via a 1 mL syringe over 2 min and the mixture was stirred 25 °C for 24 h. The reaction mixture was quenched with 20 mL water, extracted with 20 mL saturated aqueous NaHCO<sub>3</sub>. The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with DCM/MeOH (20/1) to give M1-32mer (0.79 g, yield 53%) as a yellow sticky oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.52 (s, 2H), 5.26 (s, 2H), 4.31 – 4.16 (m, 64H), 3.84 – 3.66 (m, 95H), 3.41 (t, *J* = 6.8 Hz, 2H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 31H), 2.82 (ddt, *J* = 46.0, 12.6, 7.6 Hz, 64H), 2.53 (dd, *J* = 18.7, 3.7 Hz, 31H), 2.28 (t, *J* = 7.4 Hz, 64H), 1.94 – 1.78 (m, 2H), 1.73 – 1.52 (m, 126H), 1.52 – 1.31 (m, 64H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.41, 174.57, 173.24, 77.86 – 76.69, 76.63, 60.60, 39.04, 38.19, 36.08, 33.71, 31.51, 28.64, 28.12, 24.13. MALDI-TOF for M1-32mer, Calcd: *m/z* = 8752.5 [M + Na-Furan]<sup>+</sup>; Found: 8753.4 [M + Na-Furan]<sup>+</sup>.

**M1-32mer-MA:** A solution of M1-hexamer (0.39 g, 0.04 mmol) in toluene (10 mL) was refluxed at 110 °C under argon flow and monitored by <sup>1</sup>H NMR. After

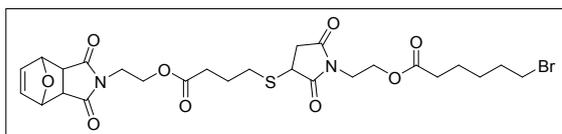
completion, the solvent was evaporated in vacuum. The crude product was directly used in next thiol-Michael coupling without purification.

**M1-32mer-SH:** 33.4 mg of thiourea (0.44 mmol) was dissolved in dry C<sub>2</sub>H<sub>5</sub>OH (10 mL) in round bottom flask. The mixture was heated at 65 °C for 30 min and 0.39 g of M1-hexamer in THF (10 mL) was added. The mixture was refluxed at 65 °C for 48 h. The solvent was evaporated in vacuum and the residue was re-dissolved in DCM (3.0 mL), treated with 18-Crown-6 (2.1 mg, 0.008 mmol) and sodium pyrosulfite (83.6 mg, 0.44 mmol) in water (1.0 mL). The mixture was refluxed at 50 °C under argon atmosphere for 24 h. The reaction was cooled to room temperature and the organic layer was separated. The aqueous layer was further extracted with DCM (3×10 mL). The combined organic phase was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure to afford crude product which was directly used in next thiol-Michael coupling without purification.



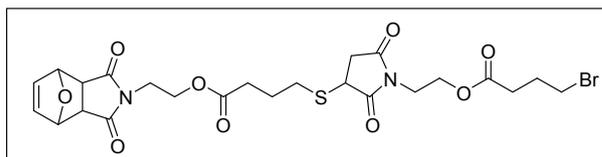
**M1-64mer:** Under argon atmosphere, M1-32mer-SH and M1-32mer-MA were dissolved in anhydrous CHCl<sub>3</sub> (30 mL) in a three-necked flask. Triethylamine (61.2 μL, 0.44 mmol) was added via a 1 mL syringe over 2 min and the mixture was stirred 25 °C for 48 h. The reaction mixture was quenched with 15 mL water, extracted with 20 mL saturated aqueous NaHCO<sub>3</sub>. The combined organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with DCM/MeOH (20/1) to give M1-64mer (0.38 g, yield 49%) as a yellow sticky oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.53 (s, 2H), 5.26 (s, 2H), 4.32 – 4.13 (m, 128H), 3.87 – 3.64 (m, 191H), 3.15 (dd, *J* = 18.7, 9.1 Hz, 63H), 2.82 (dtd, *J* = 19.9, 12.8, 7.4 Hz, 128H), 2.53 (dd, *J* = 18.7, 3.7 Hz, 63H), 2.28 (t, *J* = 7.4 Hz, 128H), 1.76 – 1.52 (m, 254H), 1.53 – 1.30 (m, 128H). MALDI-TOF for M1-64mer, Calcd: *m/z* = 17435.0 [M + Na-Furan]<sup>+</sup>; Found: 17435.1 [M + Na-Furan]<sup>+</sup>.

### 3.3 Sequence-defined oligomers



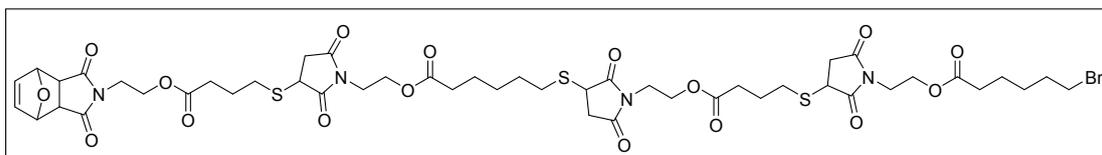
**01-Br:** The procedure is similar to **M1-dimer** mentioned above. 01-Br as a pale yellow oil (1.14 g, yield 75%).  $^1\text{H}$

NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.59 – 6.40 (s, 2H), 5.27 (s, 2H), 4.37 – 4.15 (m, 2H), 3.91 – 3.67 (m, 5H), 3.50 – 3.35 (m, 2H), 3.16 (ddd,  $J = 12.6, 11.1, 5.5$  Hz, 1H), 3.06 – 2.66 (m, 4H), 2.52 (dd,  $J = 9.3, 4.7$  Hz, 1H), 2.46 – 2.35 (m, 2H), 2.30 (dd,  $J = 13.4, 6.1$  Hz, 2H), 2.05 – 1.77 (m, 2H), 1.70 – 1.54 (m, 2H), 1.54 – 1.35 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  176.37, 176.04, 174.52, 173.23, 172.50, 136.57, 80.94, 77.68 – 76.91, 76.63, 60.67, 47.47, 38.68, 38.21, 37.87, 36.00, 33.64, 32.47, 31.02, 27.56, 23.82.



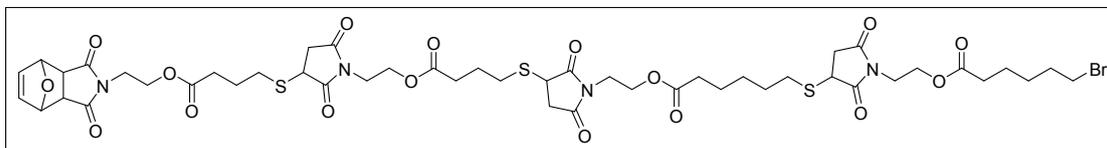
**00-Br:** The procedure is similar to **M1-dimer** mentioned above. 00-Br as a pale yellow oil (2.14 g, yield

71%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.52 (s, 2H), 5.26 (s, 2H), 4.25 (ddd,  $J = 8.2, 5.9, 1.7$  Hz, 4H), 3.90 – 3.68 (m, 5H), 3.46 (t,  $J = 6.5$  Hz, 2H), 3.15 (dd,  $J = 18.7, 9.1$  Hz, 1H), 3.05 – 2.67 (m, 4H), 2.61 – 2.33 (m, 5H), 2.15 (p,  $J = 6.8$  Hz, 2H), 2.04 – 1.85 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  176.42, 176.04, 174.55, 172.44, 136.57, 80.93, 77.69 – 76.88, 76.65, 60.79, 47.46, 38.66, 37.98, 35.97, 32.67, 32.23, 31.02, 27.52, 23.88.

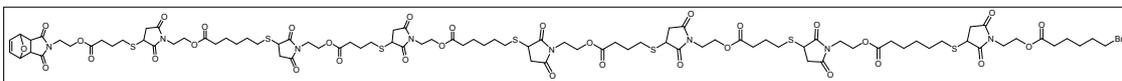


**0101-Br:** The procedure is similar to **M1-tetramer** mentioned above. 0101-Br as a pale yellow oil (0.99 g, yield 76%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  6.53 (s, 2H), 5.26 (d,  $J = 0.8$  Hz, 2H), 4.35 – 4.14 (m, 8H), 3.89 – 3.64 (m, 11H), 3.41 (t,  $J = 6.8$  Hz, 2H), 3.16 (ddd,  $J = 18.7, 9.1, 2.7$  Hz, 3H), 3.06 – 2.64 (m, 8H), 2.62 – 2.21 (m, 11H), 2.07 – 1.77 (m, 8H), 1.65 (tt,  $J = 14.6, 7.3$  Hz, 4H), 1.54 – 1.10 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  176.42, 176.05, 174.57, 173.25, 172.56, 136.58, 80.94, 77.95 – 76.93, 76.63, 70.60, 61.25 – 60.20, 53.46, 47.47, 39.05, 38.73, 38.18,

37.86, 36.04, 33.65, 32.46, 31.52, 31.00, 28.63, 28.11, 27.57, 24.41 – 23.47. MALDI-TOF for 0101-Br, Calcd:  $m/z = 1097.2$  [M + Na-Furan]<sup>+</sup>; Found: 1097.5 [M + Na-Furan]<sup>+</sup>.



**0011-Br:** The procedure is similar to **M1-tetramer** mentioned above. 0011-Br as a pale yellow oil (1.1 g, yield 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.53 (s, 2H), 5.26 (s, 2H), 4.46 – 4.10 (m, 8H), 3.91 – 3.63 (m, 11H), 3.54 – 3.32 (m, 2H), 3.16 (ddd,  $J = 18.7, 9.1, 2.3$  Hz, 3H), 3.07 – 2.65 (m, 8H), 2.64 – 2.46 (m, 3H), 2.46 – 2.35 (m, 4H), 2.35 – 2.20 (m, 4H), 2.10 – 1.74 (m, 8H), 1.75 (d,  $J = 6.2$  Hz, 4H), 1.52 – 1.36 (m, 4H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.42, 176.05, 174.57, 173.25, 172.56, 136.58, 80.94, 77.95 – 76.93, 76.63, 70.60, 61.25 – 60.20, 53.46, 47.47, 39.05, 38.73, 38.18, 37.86, 36.04, 33.65, 32.46, 31.52, 31.00, 28.63, 28.11, 27.57, 24.41 – 23.47. MALDI-TOF for 0011-Br, Calcd:  $m/z = 1097.2$  [M + Na-Furan]<sup>+</sup>; Found: 1097.5 [M + Na-Furan]<sup>+</sup>.



**01010011-Br:** The procedure is similar to **M1-octamer** mentioned above. 01010011-Br as a pale yellow oil (0.64 g, yield 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 6.53 (s, 2H), 5.26 (s, 2H), 4.37 – 4.13 (m, 16H), 3.91 – 3.66 (m, 23H), 3.41 (t,  $J = 6.8$  Hz, 2H), 3.25 – 3.05 (m, 7H), 3.05 – 2.65 (m, 18H), 2.53 (dd,  $J = 18.7, 3.6$  Hz, 7H), 2.46 – 2.35 (m, 8H), 2.30 (ddd,  $J = 9.8, 9.4, 2.8$  Hz, 8H), 2.06 – 1.79 (m, 10H), 1.79 – 1.34 (m, 22H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm): δ 176.43, 176.04, 175.08 – 174.38, 173.25, 172.56, 136.58, 80.94, 77.68 – 76.87, 76.63, 61.07 – 60.30, 47.47, 39.06, 38.73, 38.20, 37.85, 36.04, 33.65, 32.45, 31.53, 30.99, 28.63, 28.12, 27.57, 24.28 – 23.62. MALDI-TOF for 01010011-Br, Calcd:  $m/z = 2125.5$  [M + Na-Furan]<sup>+</sup>; Found: 2126.0 [M + Na-Furan]<sup>+</sup>.

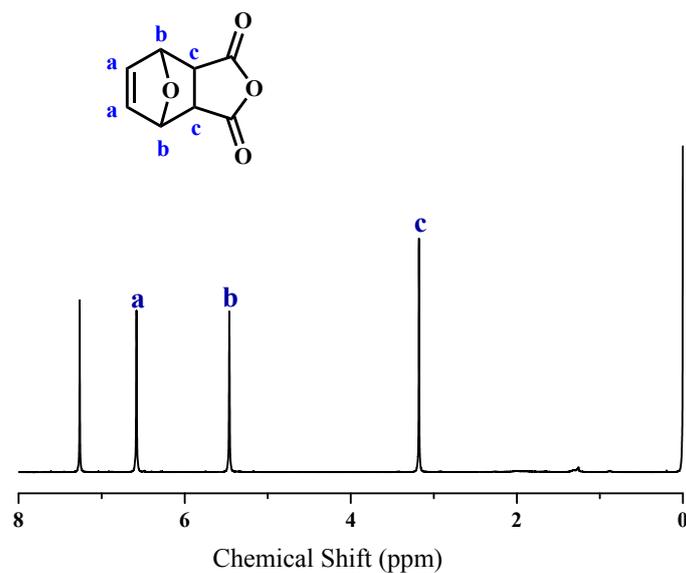
### 3.4 Oxidation of thioether groups

**Sulfoxide:** A 50 mM solution (based on thioether groups) of succinimide thioether-linked oligomer in hexafluoroisopropanol was prepared. The solution was treated with

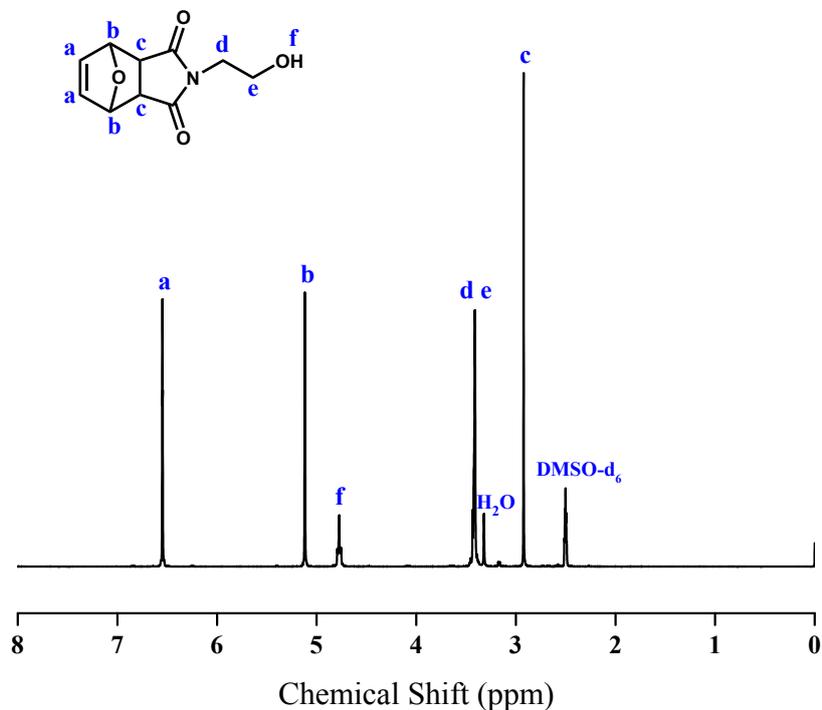
Na<sub>2</sub>EDTA (0.07 eq per thioether group), stirred at room temperature for 1 h. Aqueous 9.8 M H<sub>2</sub>O<sub>2</sub> (2.75 eq per thioether group) was added. The solution was vigorously shaken, allowed to stand at room temperature.<sup>3</sup> TLC showed that the reaction was complete. The reaction was then quenched with aqueous 10% NaHSO<sub>3</sub> and extracted with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel to afford succinimide sulfoxide linked oligomer.

**Sulfone:** A solution of succinimide thioether-linked oligomer in CHCl<sub>3</sub> was treated 3-chloroperbenzoic acid (2 eq per thioether group). The mixture was stirred at 25 °C overnight. The reaction was then quenched with aqueous 10% Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and extracted with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure to afford succinimide sulphone-linked oligomer.

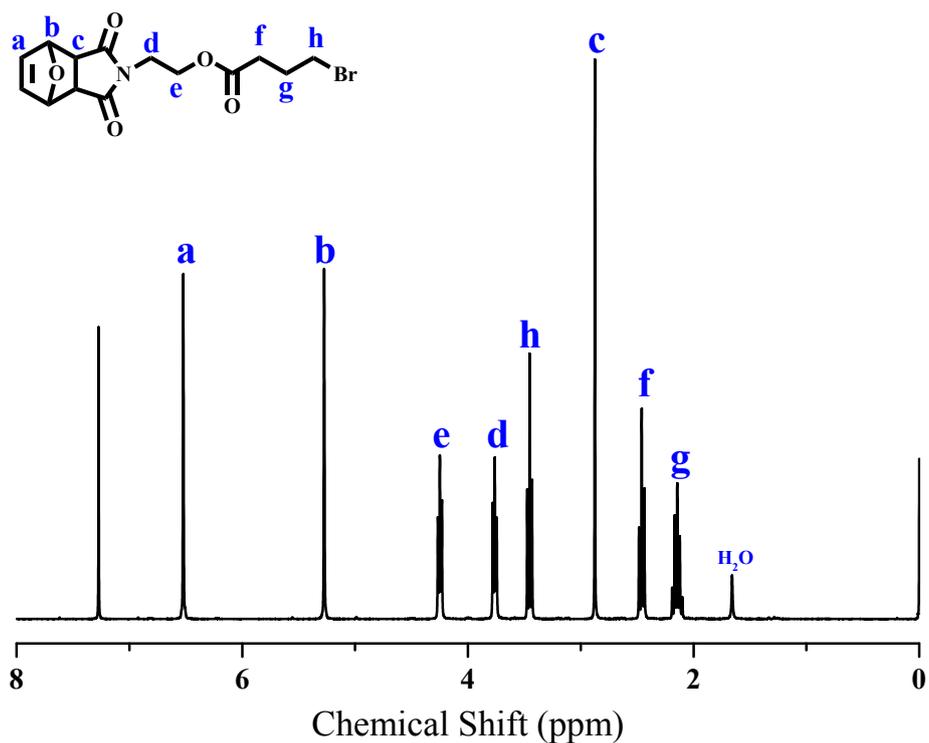
## SECTION B. Supplementary Figures



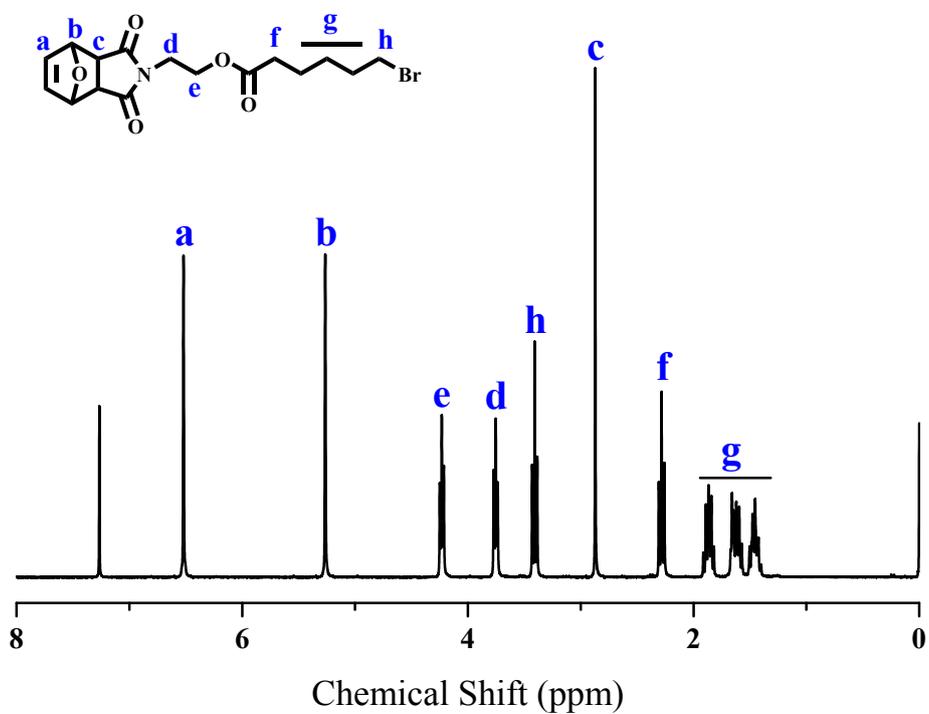
**Figure S1.** <sup>1</sup>H NMR spectrum of compound **FMA** in CDCl<sub>3</sub> (Bruker, 300 MHz, TMS)



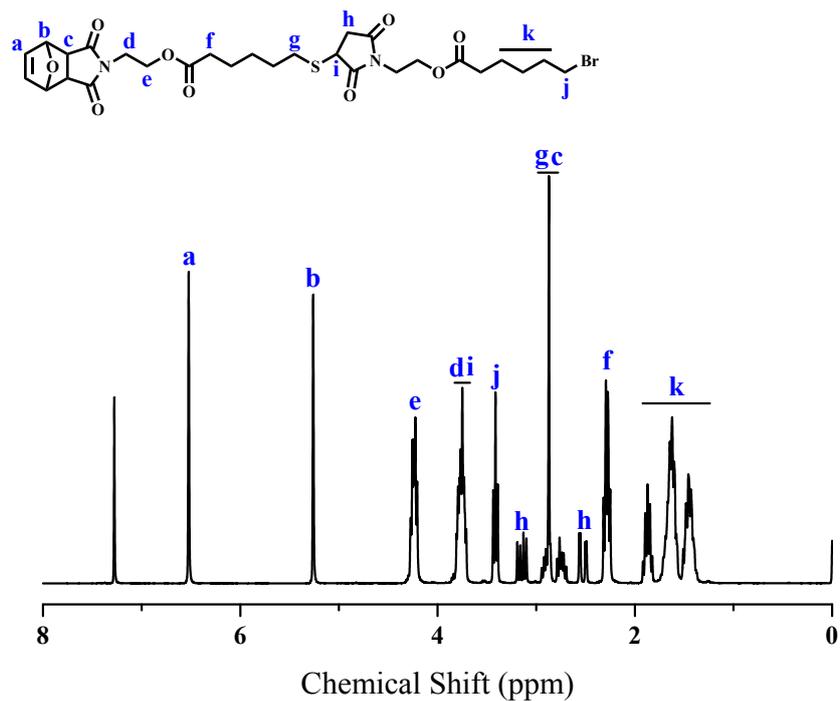
**Figure S2.** <sup>1</sup>H NMR spectrum of compound **FMA-OH** in DMSO-d<sub>6</sub> (Bruker, 300 MHz, TMS)



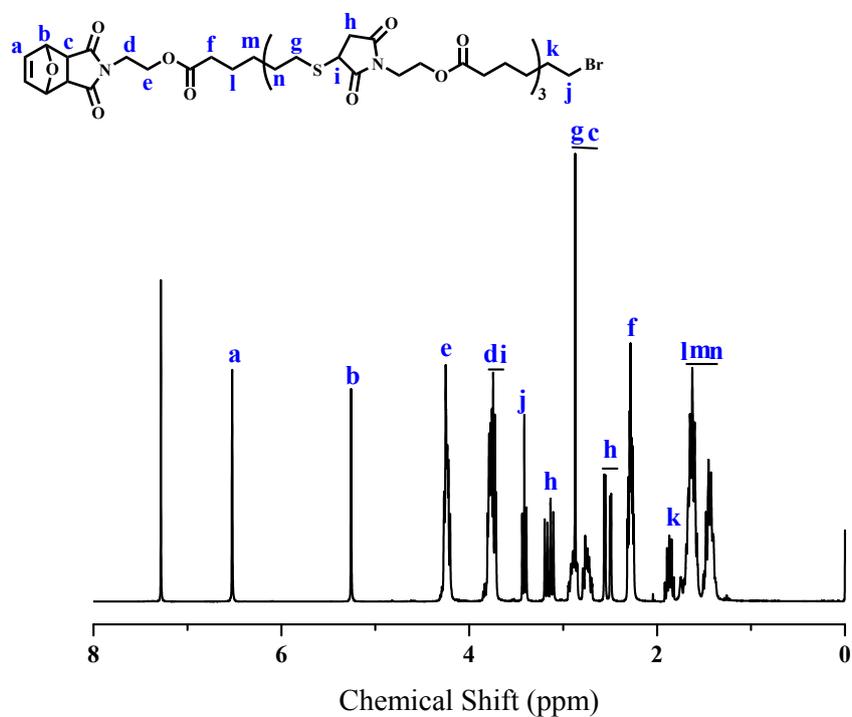
**Figure S3.** <sup>1</sup>H NMR spectrum of compound **monomer 0** in CDCl<sub>3</sub> (Bruker, 300 MHz, TMS)



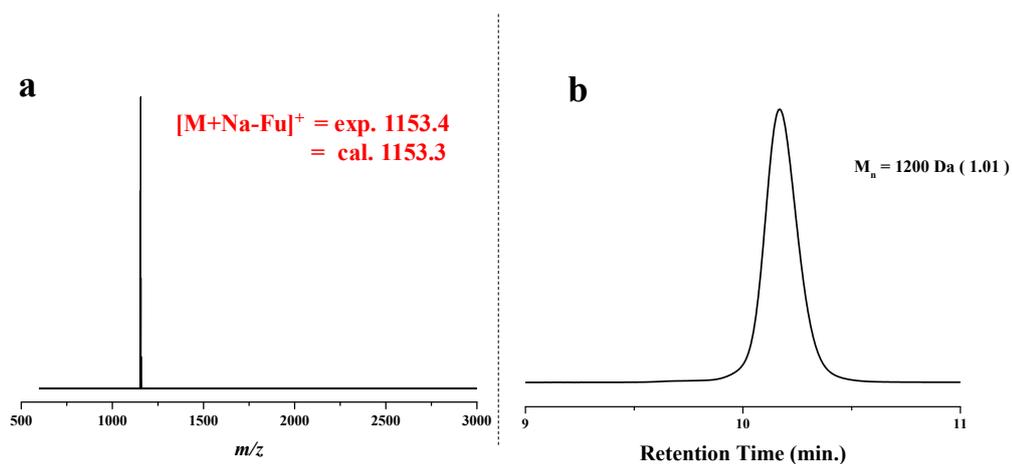
**Figure S4.** <sup>1</sup>H NMR spectrum of compound **monomer 1** in CDCl<sub>3</sub> (Bruker, 300 MHz, TMS)



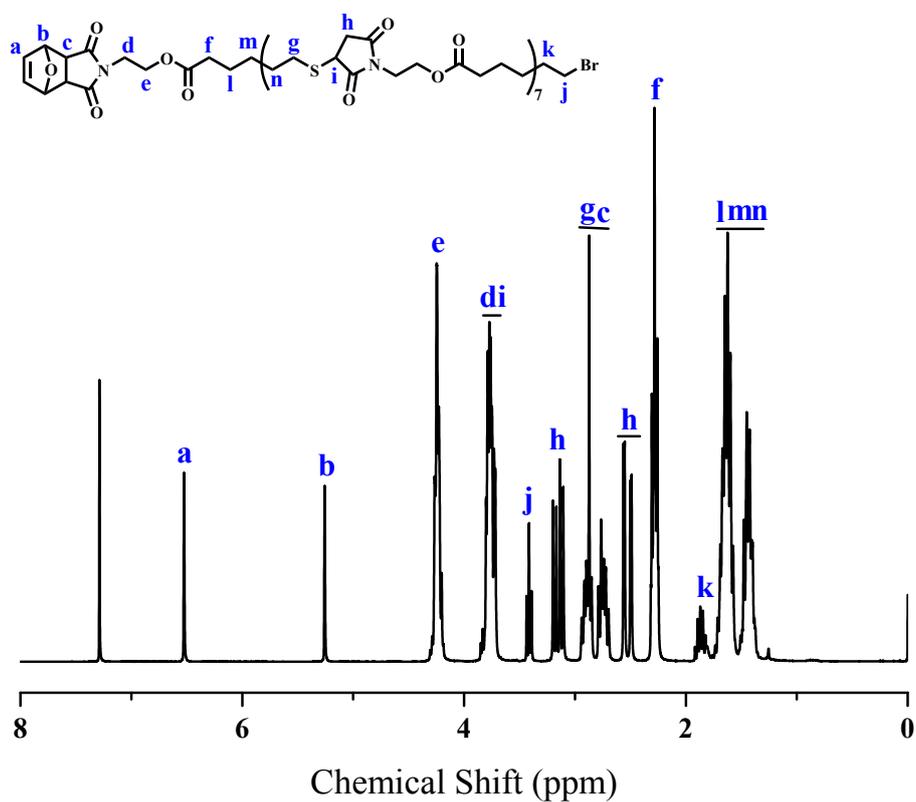
**Figure S5.**  $^1\text{H}$  NMR spectrum of compound **M1-dimer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



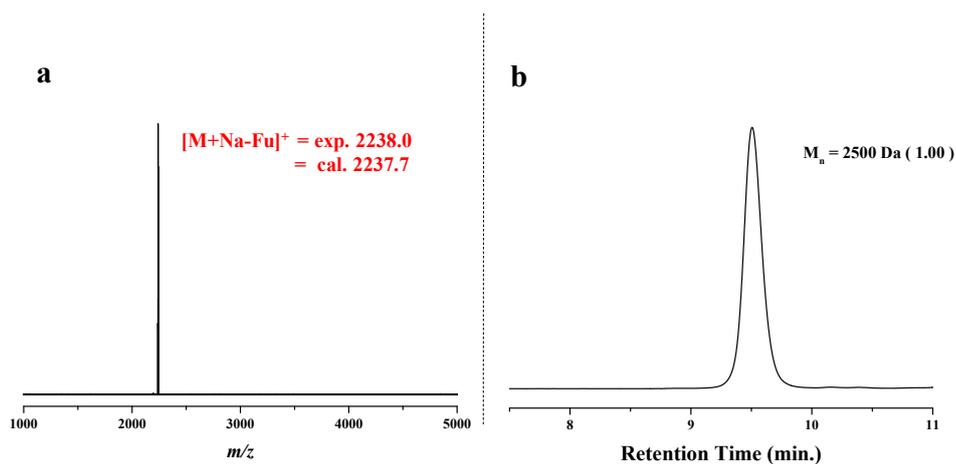
**Figure S6.**  $^1\text{H}$  NMR spectrum of compound **M1-tetramer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



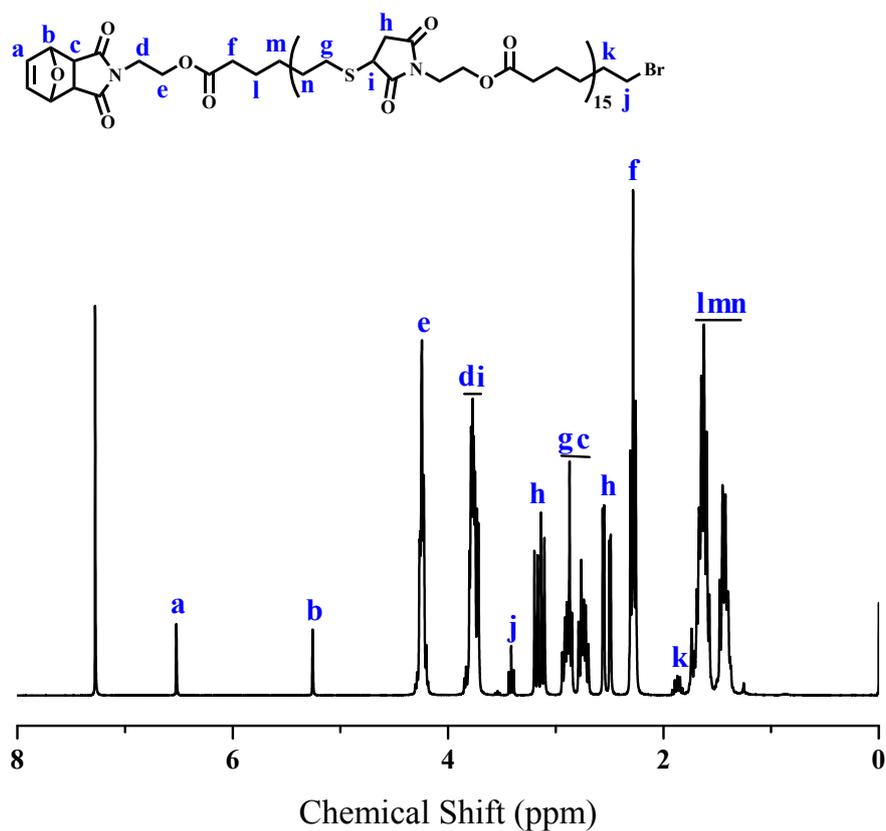
**Figure S7.** (a) MALDI-TOF mass spectrum of **M1-tetramer** by reflectron mode; (b) SEC trace of **M1-tetramer**



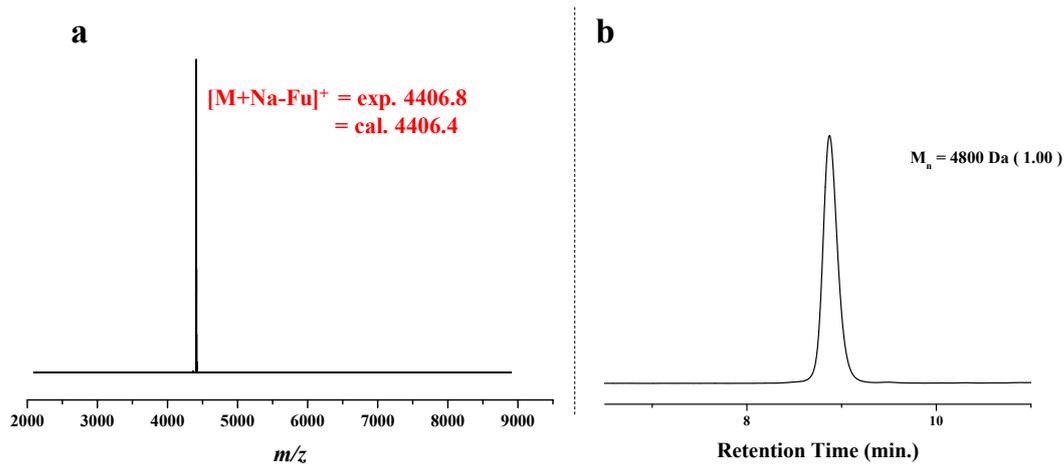
**Figure S8.**  $^1\text{H}$  NMR spectrum of compound **M1-octamer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



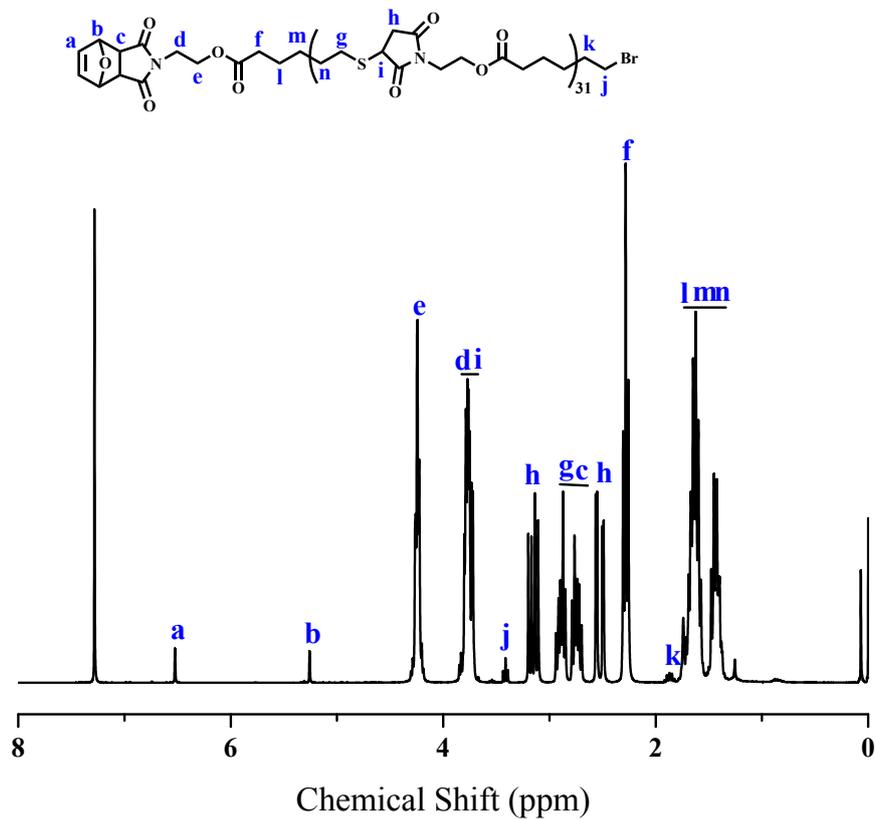
**Figure S9.** (a) MALDI-TOF mass spectrum of **M1-octamer** by reflectron mode; (b) SEC trace of **M1-octamer**



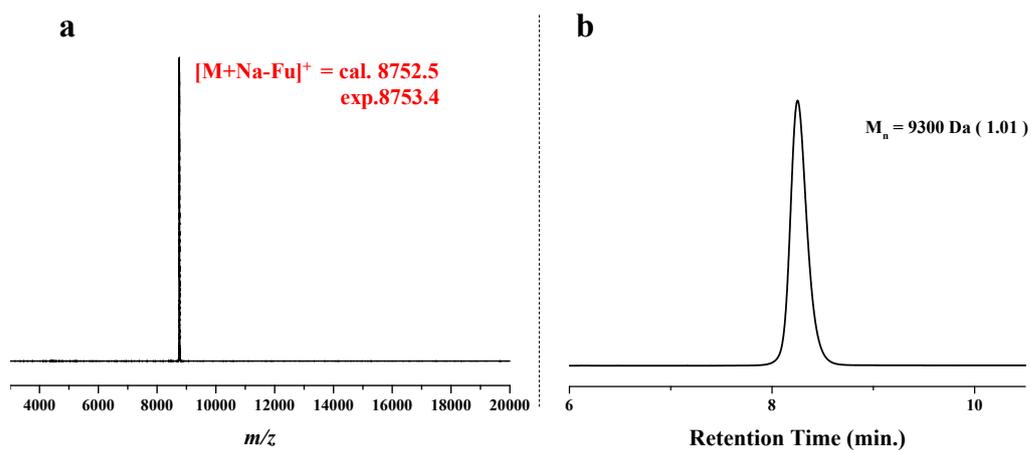
**Figure S10.**  $^1\text{H}$  NMR spectrum of compound **M1-hexamer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



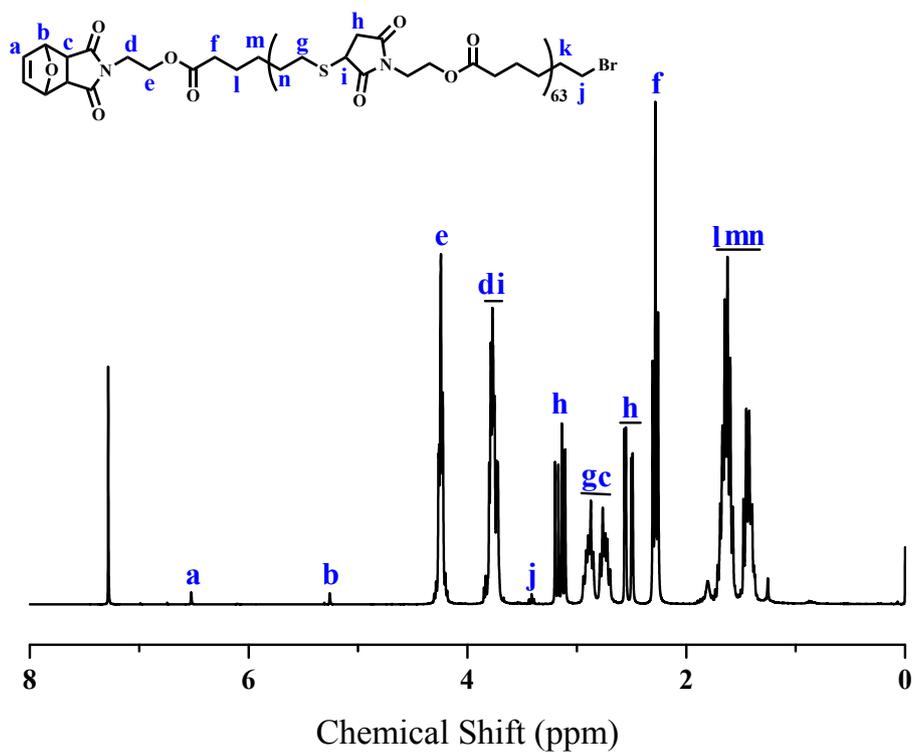
**Figure S11.** (a) MALDI-TOF mass spectrum of **M1-hexamer** by reflectron mode; (b) SEC trace of **M1-hexamer**



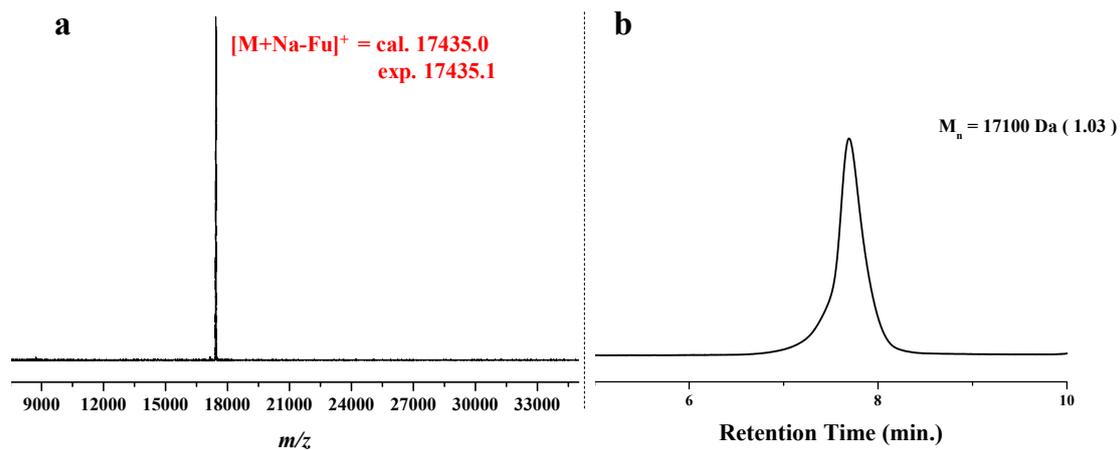
**Figure S12.**  $^1\text{H}$  NMR spectrum of compound **M1-32mer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



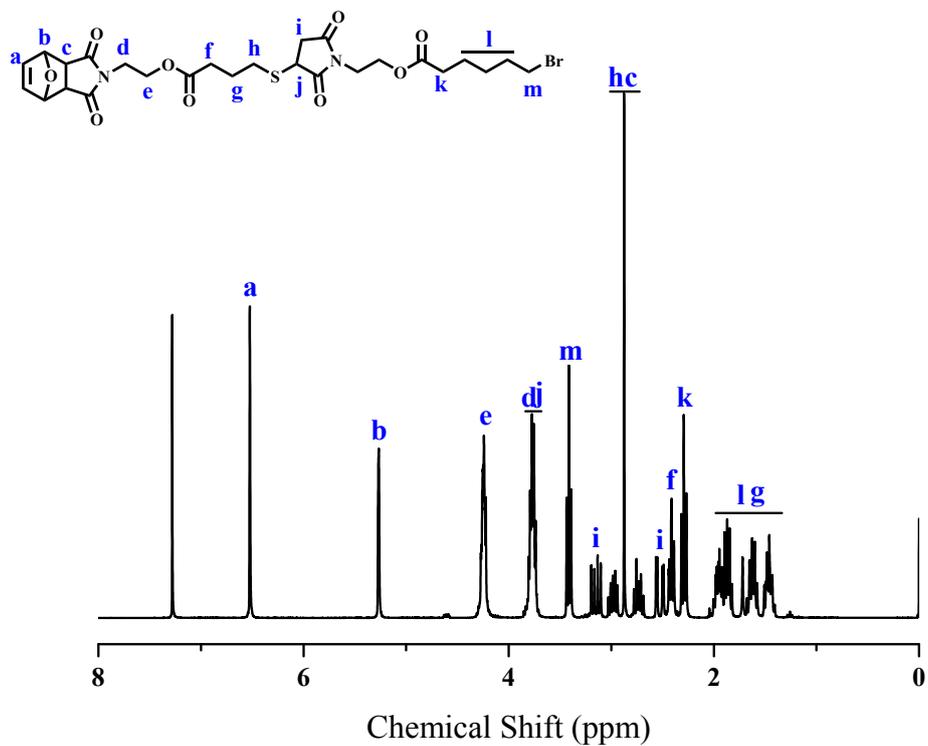
**Figure S13.** (a) MALDI-TOF mass spectrum of **M1-32mer** by linear mode; (b) SEC trace of **M1-32mer**



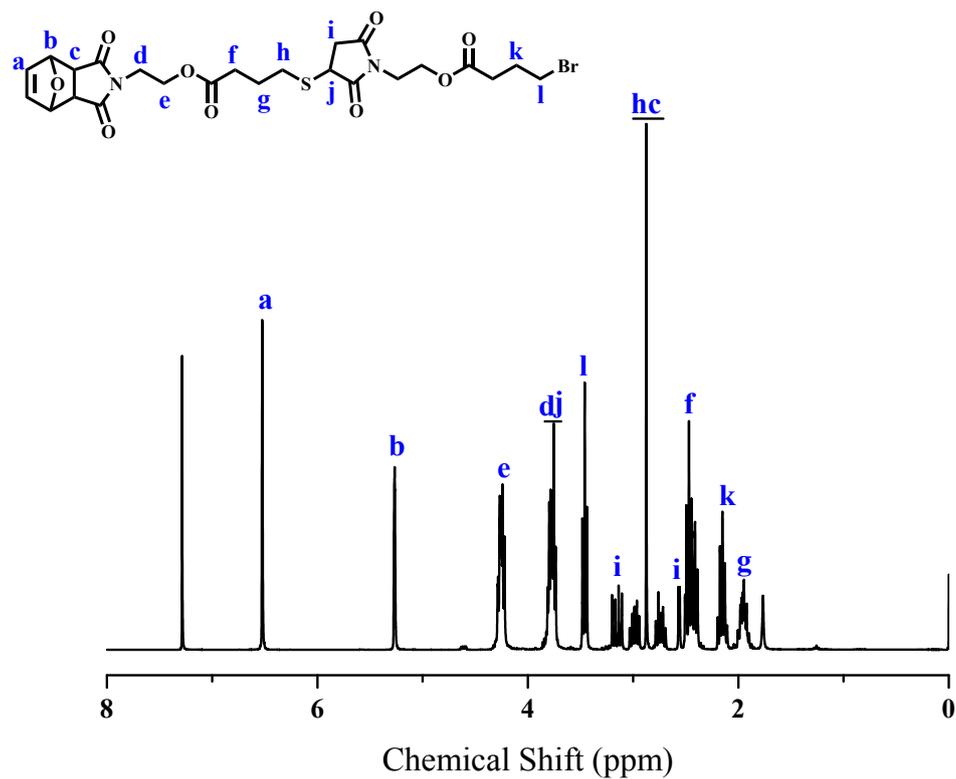
**Figure S14.**  $^1\text{H}$  NMR spectrum of compound **M1-64mer** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



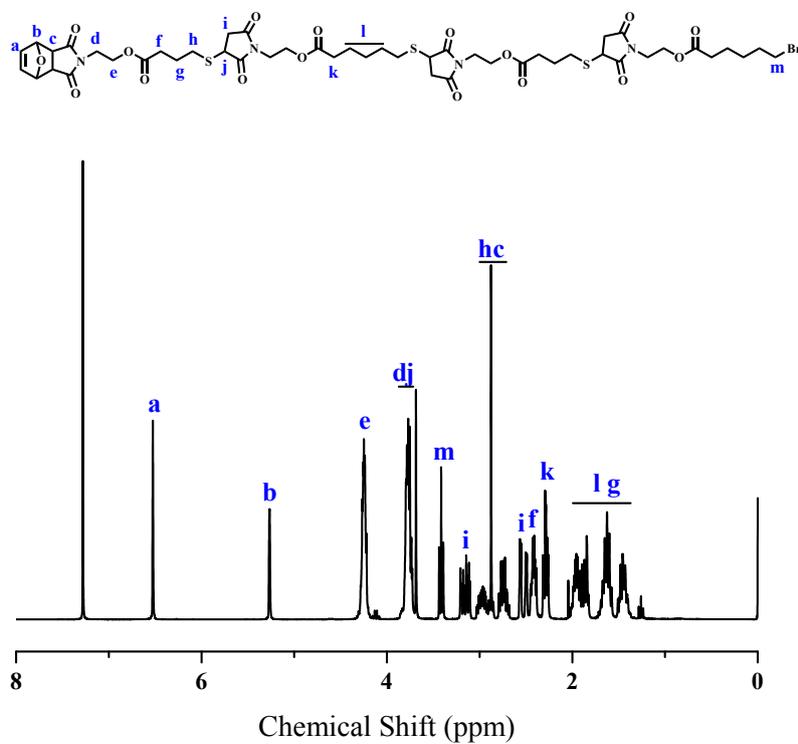
**Figure S15.** (a) MALDI-TOF mass spectrum of **M1-64mer** by linear mode; (b) SEC trace of **M1-64mer**



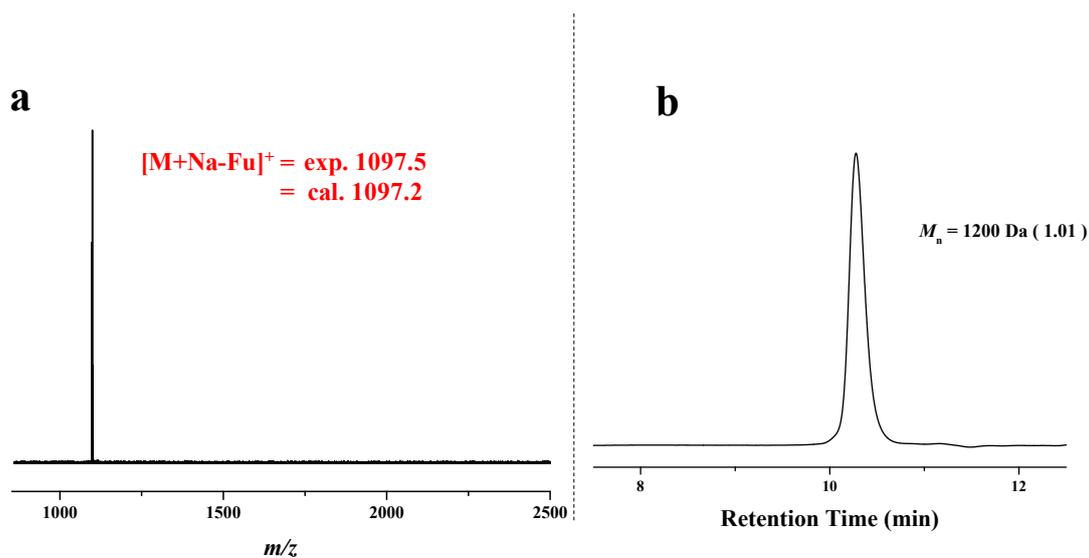
**Figure S16.**  $^1\text{H}$  NMR spectrum of compound **01-Br** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



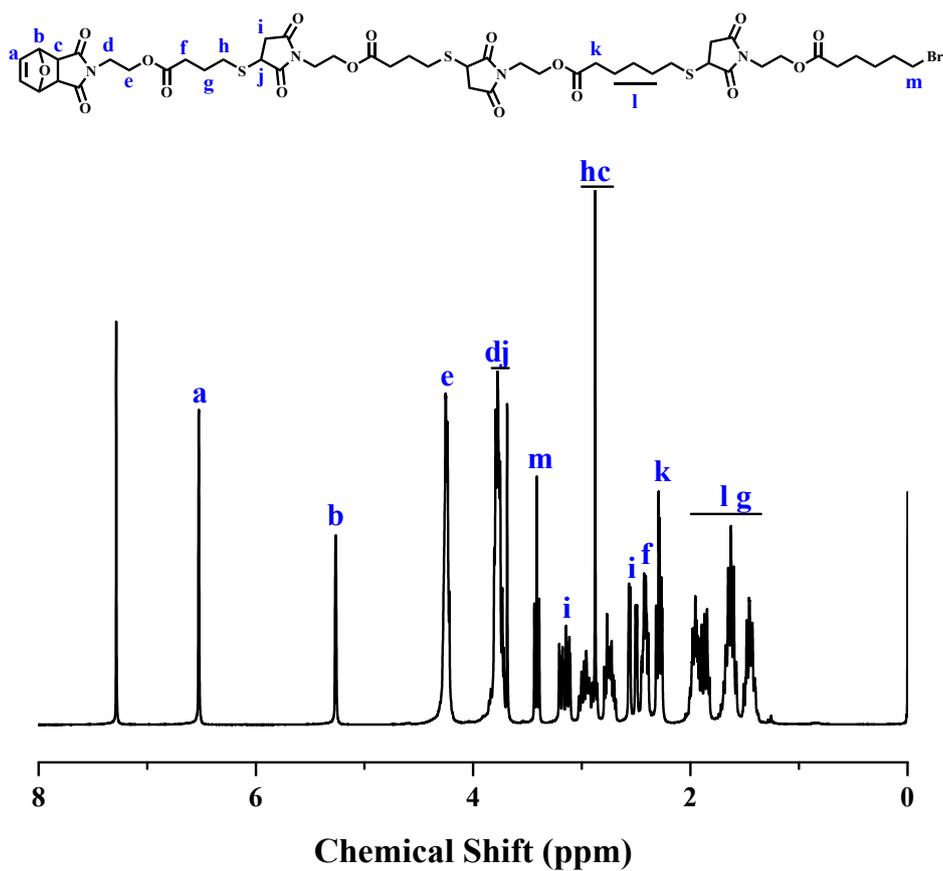
**Figure S17.**  $^1\text{H}$  NMR spectrum of compound **00-Br** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



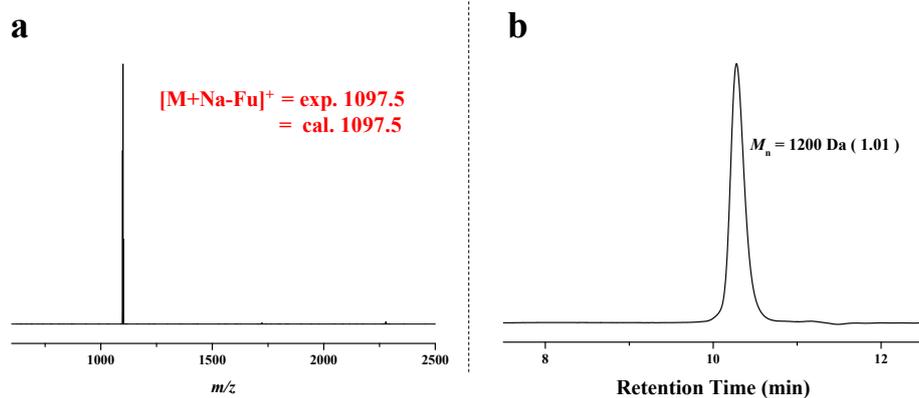
**Figure S18.**  $^1\text{H}$  NMR spectrum of compound **0101-Br** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



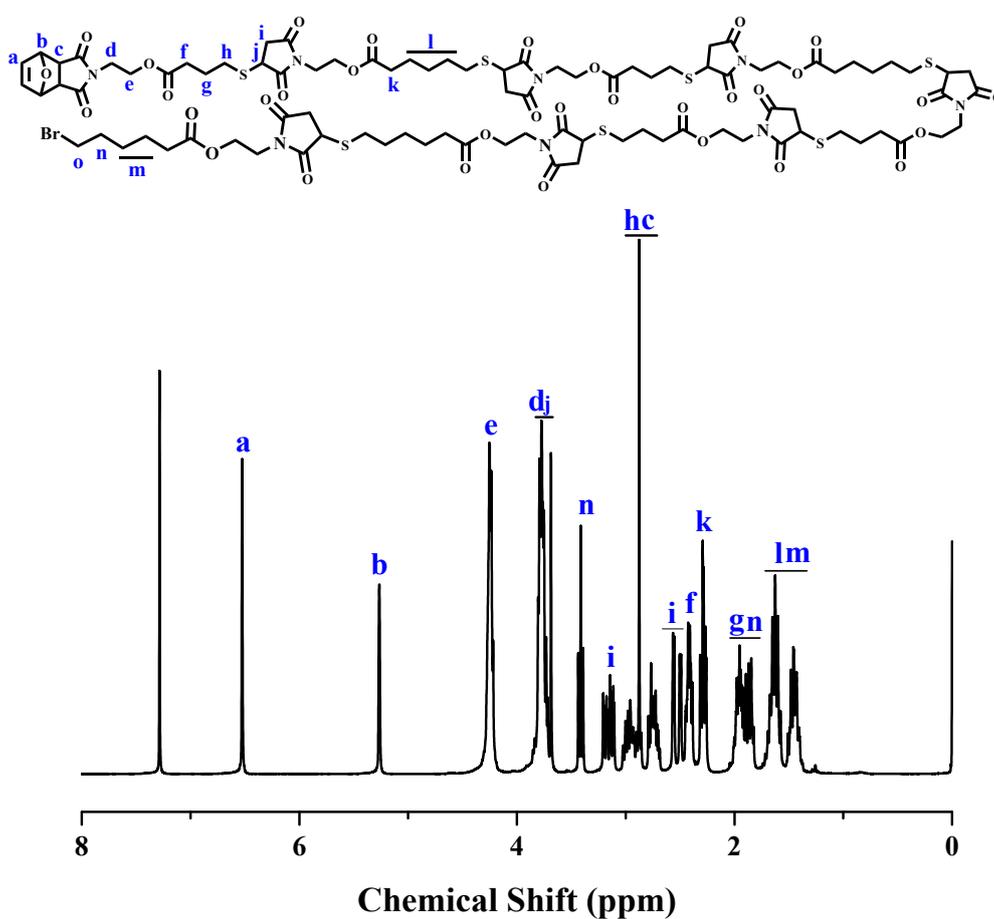
**Figure S19.** (a) MALDI-TOF mass spectrum of **0101-Br** by reflectron mode; (b) SEC trace of **0101-Br**



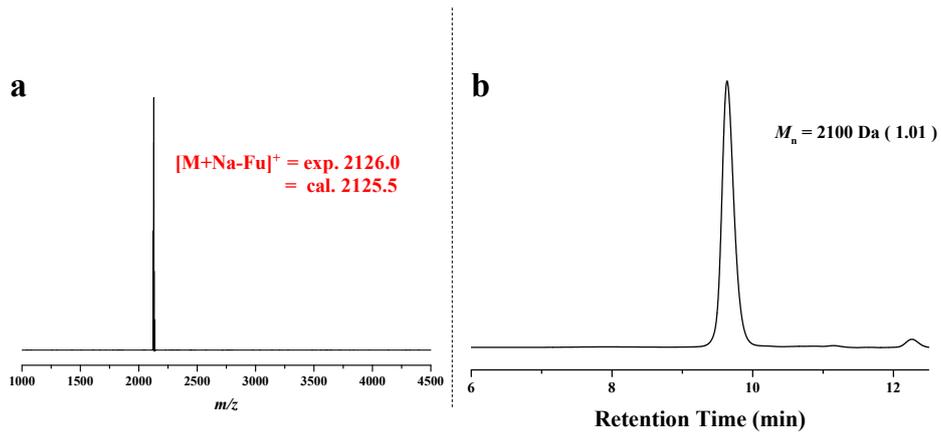
**Figure S20.**  $^1\text{H}$  NMR spectrum of compound **0011-Br** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



**Figure S21.** (a) MALDI-TOF mass spectrum of **0011-Br** by reflectron mode; (b) SEC trace of **0011-Br**

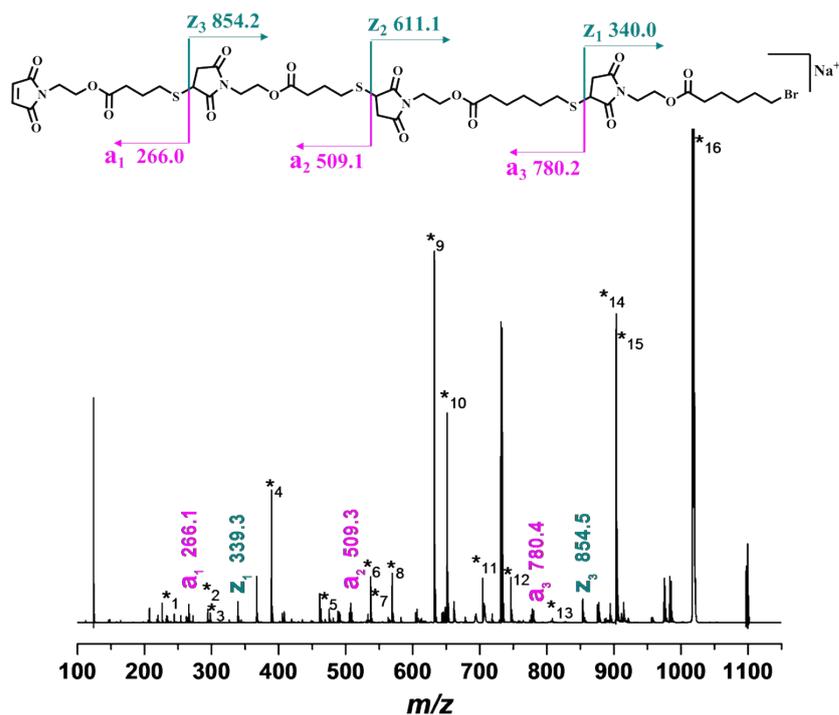


**Figure S22.**  $^1\text{H}$  NMR spectrum of compound **01010011-Br** in  $\text{CDCl}_3$  (Bruker, 300 MHz, TMS)



**Figure S23.** (a) MALDI-TOF mass spectrum of **01010011-Br** by reflectron mode; (b) SEC trace of **01010011-Br**

## SECTION C. MALDI Analysis of Digital Oligomers

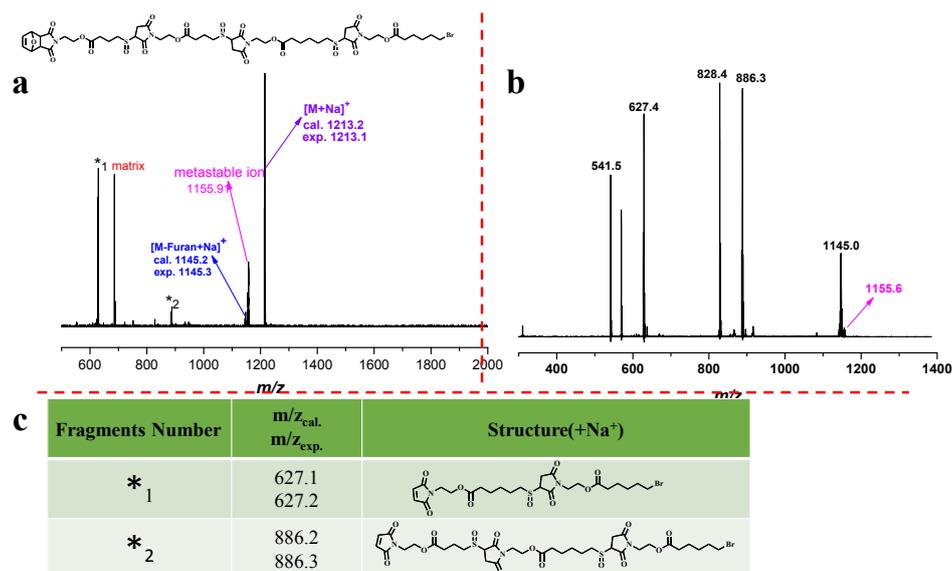


**Figure S24.** MALDI-TOF MS/MS spectrum of 0011-Br.

**Table S1.** Analysis of structures of secondary fragmentations of **0011-Br** in MALDI-TOF MS/MS.

Fragmentation Number	m/z <sub>cal.</sub> m/z <sub>exp.</sub>	Structure(+Na <sup>+</sup> )
* <sub>1</sub>	232.1 232.2	
* <sub>2</sub>	294.1 294.2	
* <sub>3</sub>	298.0 298.1	
* <sub>4</sub>	389.1 389.3	
* <sub>5</sub>	475.1 475.3	
* <sub>6</sub>	531.2 531.4	
* <sub>7</sub>	537.1 537.3	

*8	569.1 569.3	
*9	632.1 632.4	
*10	651.2 651.4	
*11	694.2 694.4	
*12	746.2 746.4	
*13	808.2 808.5	
*14	894.3 894.5	
*15	903.2 903.5	
*16	1017.3 1017.5	



**Figure S25.** (a) MALDI-TOF mass spectrum of **SO-0011-Br**. Intact product ion, fragments and metastable ion were observed. Fragmentation may occur in the ion-source or field-free region.<sup>4</sup> (b) Select ion at  $m/z$  1155.9 as parent ion in lift mode. With LIFTcell and PLMS being off the parent ion and its fragments were detected, indicating that the parent ion at  $m/z$  was metastable. (c) Structure of fragments of **SO-0011-Br** in MALDI-TOF MS.

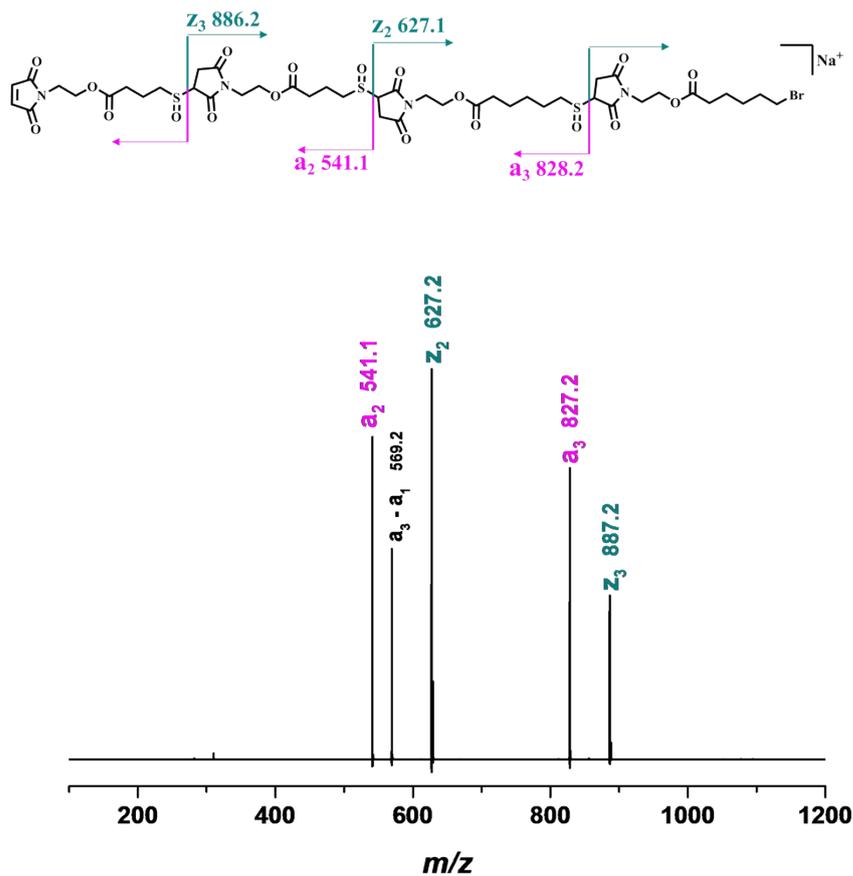


Figure S26. MALDI-TOF MS/MS spectrum of SO-0011-Br.

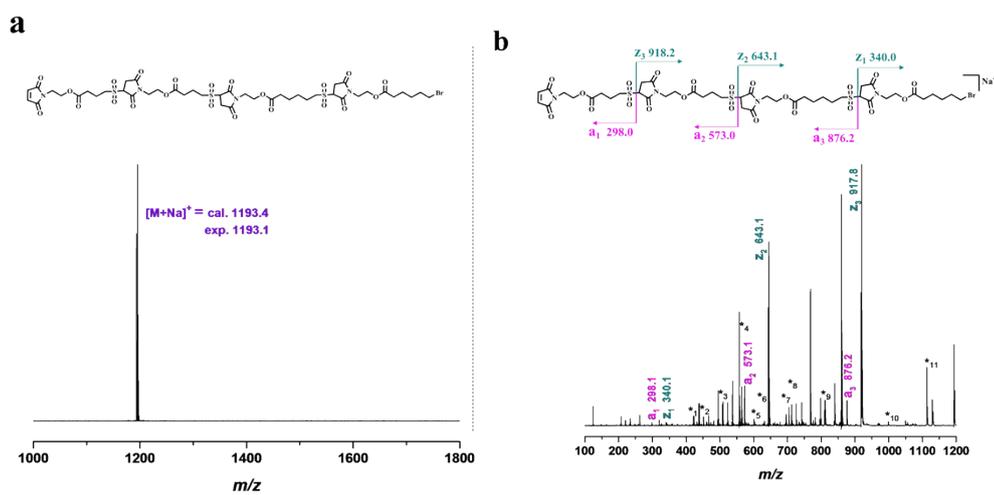
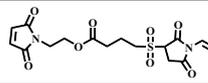
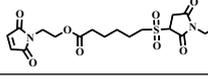
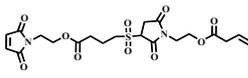
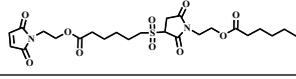
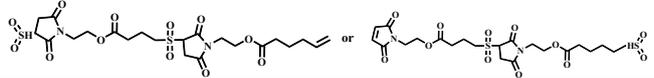
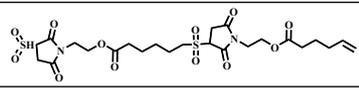
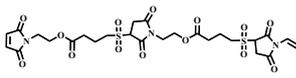
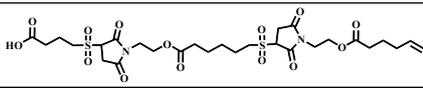
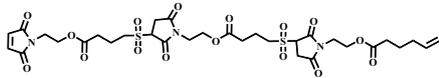
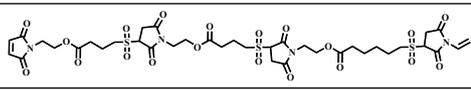
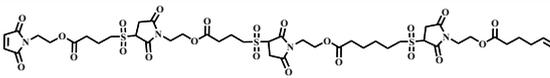


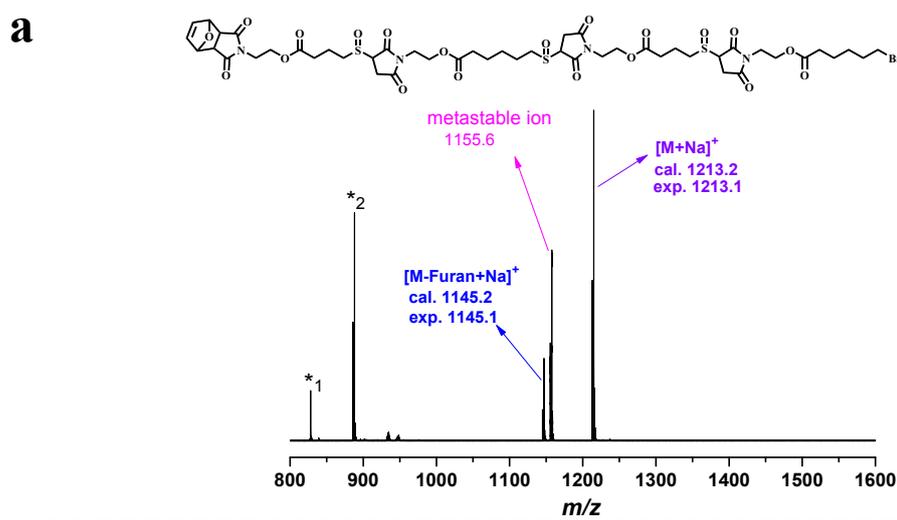
Figure S27. (a) MALDI-TOF MS spectrum of  $SO_2$ -0011-Br. The ion at  $m/z$  1193.1 was selected as parent ion and subjected to LIFT cell. (b) MALDI-TOF MS/MS spectrum of parent ion at  $m/z$  1193.1.

**Table S2.** Analysis of structures of secondary fragmentations of **SO<sub>2</sub>-0011-Br** in MALDI-TOF MS/MS.

Fragmentation Number	m/z <sub>cal.</sub> m/z <sub>exp.</sub>	Structure(+Na <sup>+</sup> )
*1	421.1 421.1	
*2	451.1 451.1	
*3	507.1 507.1	
*4	565.2 565.2	
*5	601.1 601.1	
*6	629.2 629.1	
*7	696.1 696.1	
*8	715.2 715.2	
*9	810.2 810.2	
*10	999.2 999.3	
*11	1113.3 1113.5	



*7	569.1 569.3	
*8	651.2 651.4	
*9	660.2 660.4	
*10	746.2 746.4	
*11	894.3 894.5	
*12	903.2 903.4	
*13	1017.3 1017.5	



**b**

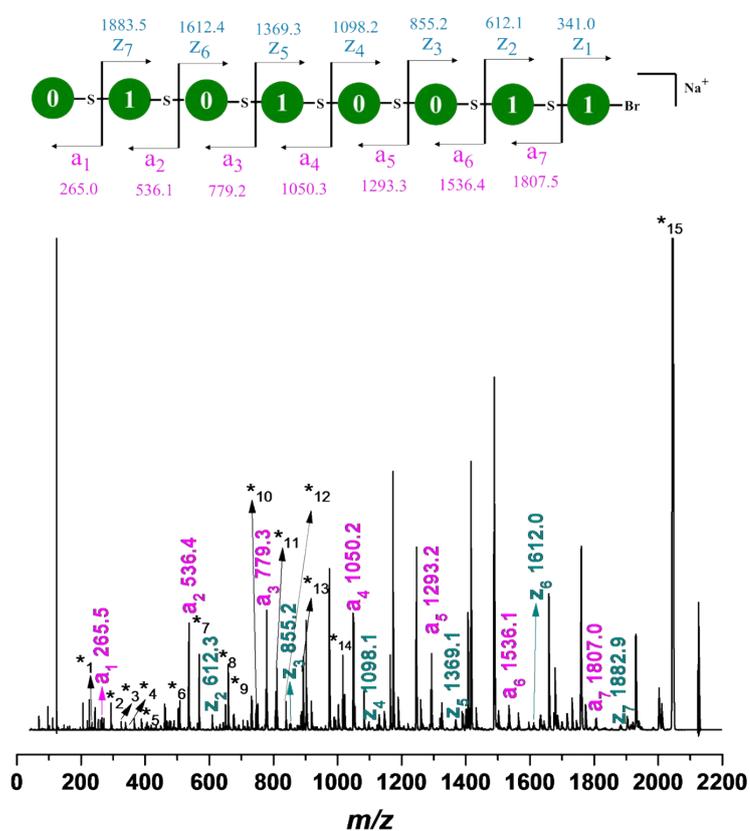
Fragments Number	m/z <sub>cal.</sub> m/z <sub>exp.</sub>	Structure(+Na <sup>+</sup> )
* <sub>1</sub>	828.2 828.5	
* <sub>2</sub>	886.2 886.4	

**Figure S29.** (a) MALDI-TOF mass spectrum of **SO-0101-Br**. (b) Structure analysis of fragments of **SO-0101-Br** in MALDI-TOF MS.



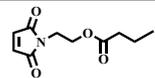
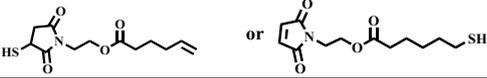
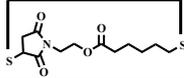
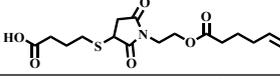
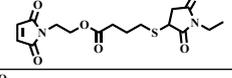
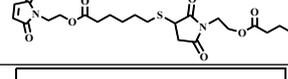
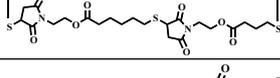
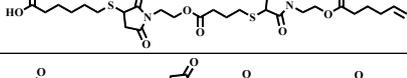
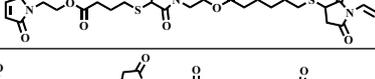
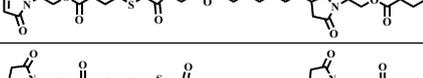
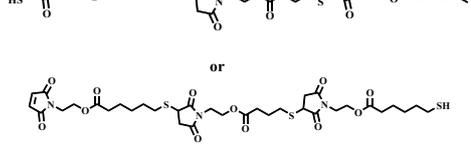
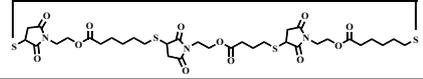
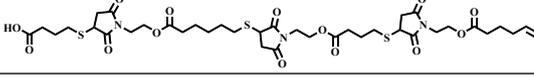
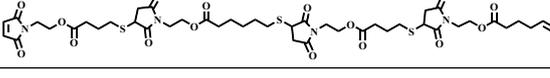
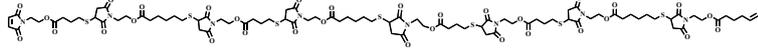
**Table S4.** Analysis of structures of secondary fragmentations of SO<sub>2</sub>-0101-Br in MALDI-TOF MS/MS.

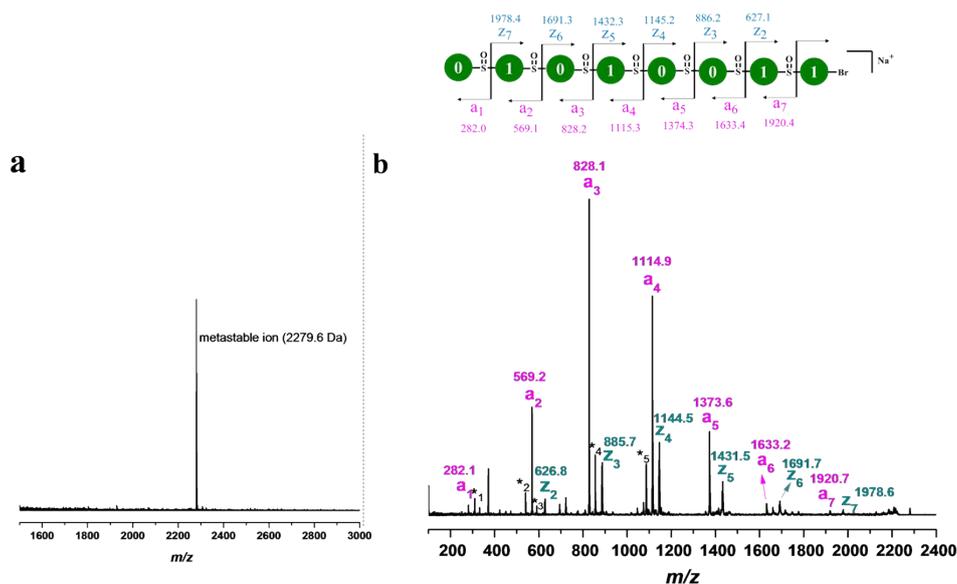
Fragmentation Number	m/z <sub>cal.</sub> m/z <sub>exp.</sub>	Structure(+Na <sup>+</sup> )
*1	326.1 326.1	
*2	421.1 421.1	
*3	537.2 537.2	
*4	724.2 724.2	
*5	810.2 810.2	
*6	999.2 999.4	
*7	1113.3 1113.5	



**Figure S32.** MALDI-TOF MS/MS spectrum of 01010011-Br.

**Table S5.** Analysis of structures of secondary fragmentations of **01010011-Br** in MALDI-TOF MS/MS.

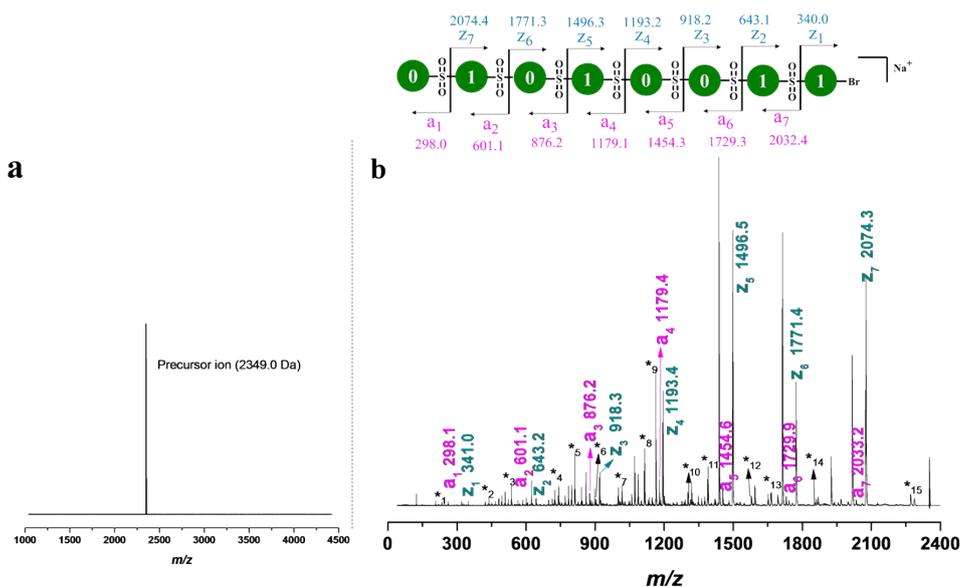
Fragmentation Number	m/z <sub>cal.</sub> m/z <sub>exp.</sub>	Structure(+Na <sup>+</sup> )
*1	234.1 233.6	
*2	294.1 293.5	
*3	326.1 325.5	
*4	380.1 379.5	
*5	391.1 390.4	
*6	505.2 504.4	
*7	569.1 568.3	
*8	651.2 650.4	
*9	660.2 659.3	
*10	748.2 747.3	
*11	808.2 807.3	
*12	840.2 839.3	
*13	894.3 893.3	
*14	1017.3 1016.3	
*15	2045.6 2046.6	



**Figure S33.** (a) MALDI-TOF mass spectrum of **SO-01010011-Br**. The ion at  $m/z$  2279.6 was selected as parent ion and subjected to LIFT cell. (b) MALDI-TOF MS/MS spectrum of parent ion at  $m/z$  2279.6.

**Table S6.** Analysis of structures of secondary fragmentations of **SO-01010011-Br** in MALDI-TOF MS/MS.

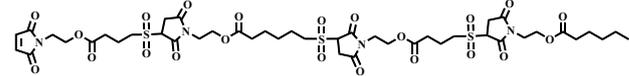
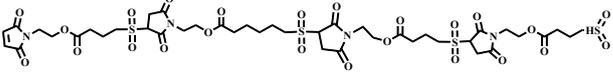
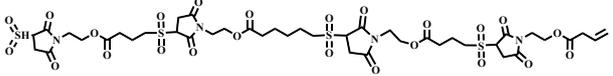
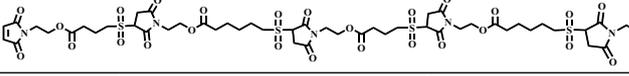
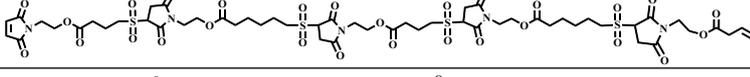
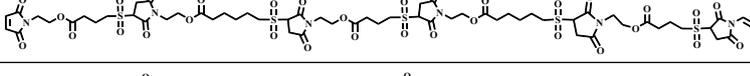
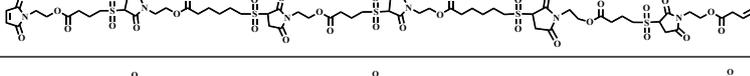
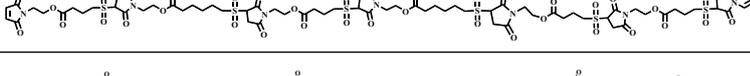
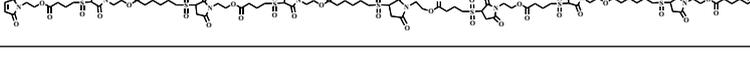
Fragmentation Number	$m/z_{cal.}$ $m/z_{exp.}$	Structure(+Na <sup>+</sup> )
*1	310.1 310.2	
*2	541.1 541.1	
*3	591.1 591.1	
*4	856.2 856.1	
*5	1087.2 1086.9	



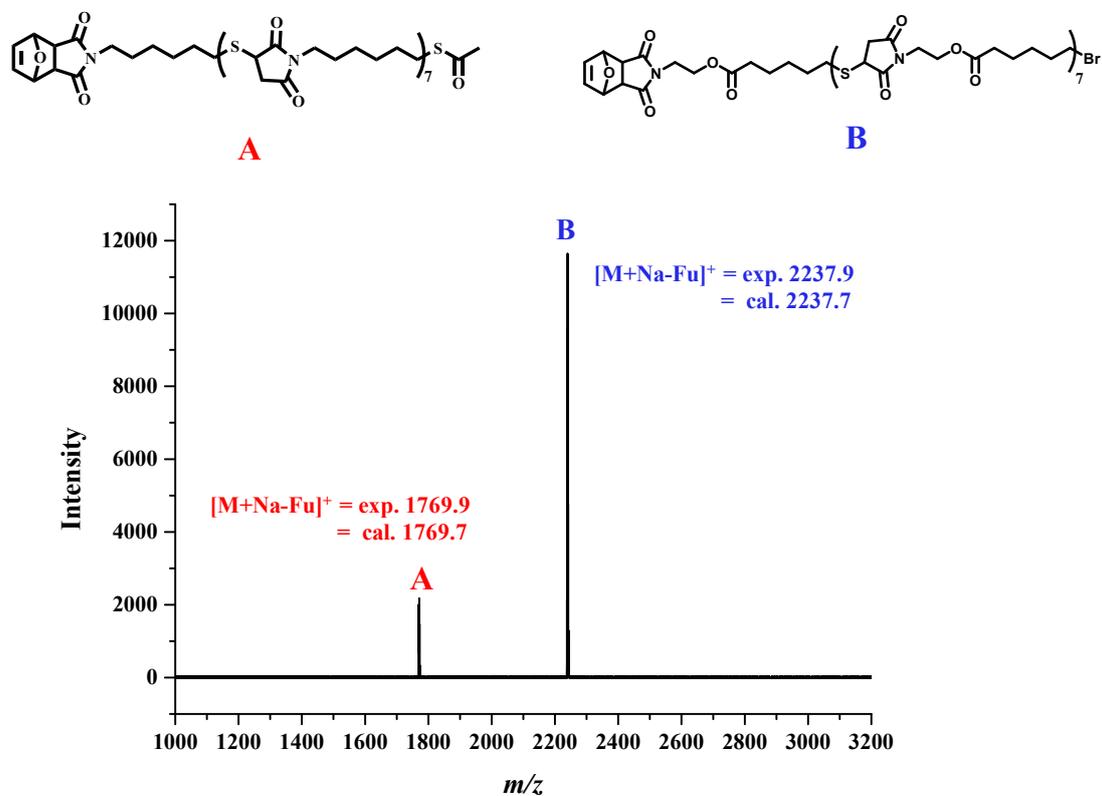
**Figure S34.** (a) MALDI-TOF mass spectrum of  $\text{SO}_2\text{-01010011-Br}$ . The ion at  $m/z$  2349.0 was selected as parent ion and subjected to LIFT cell. (b) MALDI-TOF MS/MS spectrum of parent ion at  $m/z$  2349.0.

**Table S7.** Analysis of structures of secondary fragmentations of  $\text{SO}_2\text{-01010011-Br}$  in MALDI-TOF MS/MS.

Fragmentation Number	$m/z_{\text{cal.}}$ $m/z_{\text{exp.}}$	Structure(+ $\text{Na}^+$ )
* <sub>1</sub>	234.1 234.1	
* <sub>2</sub>	423.1 423.1	
* <sub>3</sub>	537.2 537.2	
* <sub>4</sub>	726.2 726.2	
* <sub>5</sub>	812.2 812.3	
* <sub>6</sub>	904.2 904.3	
* <sub>7</sub>	1001.2 1001.3	

*8	1115.3 1115.4	
*9	1151.2 1151.4	 or 
*10	1304.3 1304.6	
*11	1388.3 1388.6	
*12	1577.3 1577.8	
*13	1663.4 1663.8	
*14	1852.4 1863.1	
*15	2269.5 2270.3	

## SECTION D. Validation Experiment: Ester Group Facilitating Ionization of Oligomer in MALDI Process



**Figure S35.** MALDI-TOF mass spectrum of mixture of a and b with the same quality (Compound b has a higher intensity compared to a).

## SECTION E. References

- 1 Huang, Z. H.; Zhao, J. F.; Wang, Z. M.; Meng, F. Y.; Ding, K. S.; Pan, X. Q.; Zhou, N. C.; Li, X. P.; Zhang, Z. B.; Zhu, X. L., Combining Orthogonal Chain-End Deprotections and Thiol-Maleimide Michael Coupling: Engineering Discrete Oligomers by an Iterative Growth Strategy. *Angewandte Chemie-International Edition* 2017, 56 (44), 13612-13617.
- 2 Bakhtiari, A. B. S.; Hsiao, D.; Jin, G. X.; Gates, B. D.; Branda, N. R., An Efficient Method Based on the Photothermal Effect for the Release of Molecules from Metal Nanoparticle Surfaces. *Angewandte Chemie-International Edition* 2009, 48 (23), 4166-4169.
- 3 Gharakhanian, E. G.; Bahrn, E.; Deming, T. J., Influence of Sulfoxide Group Placement on Polypeptide Conformational Stability. *Journal of the American Chemical Society* 2019, 141 (37), 14530-14533.
- 4 Nielen, M. W. F., Maldi time-of-flight mass spectrometry of synthetic polymers. *Mass Spectrometry Reviews* 1999, 18 (5), 309-344.