Supporting Information to

Quantitatively Monitoring Polymer Chain Growth and Topology Formation Based on Monodisperse Polymers

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Section A. Materials & Analysis Techniques.

Materials: Unless stated otherwise, 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 nitrogen.

Size-exclusion chromatography: Number-average molecular weight (M_n) and polydispersity (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 Mutipore HZ-N (4.6 × 150 mm, 3 μm beads size) columns arranged in series, and it can separate polymers in the molecular weight range of 500-190k Da. THF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. Data acquisition was performed using EcoSEC software, and molecular weights from step polymerization were calculated with the as-prepared monodisperse polymers as standards.

Fluorescence spectra: Fluorescence spectra were obtained on a HITACH F-4600 spectrofluorimeter equipped with a 150-W Xe lamp (EX slit = 5.0 nm, EM slit = 5.0 nm ; λ_{EX} = 366 nm, λ_{EM} = 388 nm; PMT voltage = 400 or 700 V). The test modes include time-scan and wavelength scan.

Preparative size-exclusion chromatography: In order to purify the crude oligomers, a recycling preparative SEC (Japan Analytical Industry Co., Ltd.) system equipped with a manual injector and differential refractive index detector was used. THF was used as the eluent with a flow rate of 6.0 mL/min. The dried crude oligomer was dissolved in THF at 200 mg/mL concentration and filtered through a 0.45 μm PTFE syringe filter prior to injection. The target fraction was collected

manually, and characterized using the TOSOH HLC-8320 SEC equipped with refractive-index and UV detectors as described above.

^{1}H NMR spectroscopy: All ^{1}H NMR spectra were collected using a Bruker nuclear magnetic resonance instrument (300 MHz) at room temperature with tetramethylsilane (TMS) as the internal standard. The ^{1}H NMR spectra were referenced to δ 7.26 ppm in $CDCl_3$.

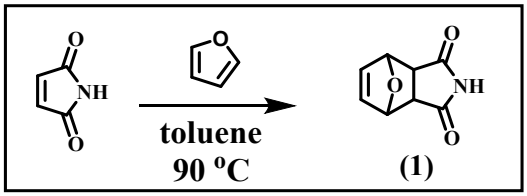
MALDI-TOF-MS analysis: Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectroscopy was acquired on an UltrafleXtreme MALDI TOF mass spectrometer equipped with a 1 kHz smart beam-II laser. The instrument was calibrated prior to each measurement with external PMMA at the molecular weight under consideration. The compound trans-2-[3-(4-tert-butyl-phenyl)-2-methyl-2-propenylidene]-malononitrile (DCTB, Aldrich, >98%) served as the matrix and was prepared in $CHCl_3$ 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 $CHCl_3$ at a concentration of 10 mg/mL. After sample preparation and solvent evaporation, the plate was inserted into the MALDI mass spectrometer. The attenuation of the laser was adjusted to minimize undesired polymer fragmentation and to maximize the sensitivity. Reflection mode was applied to 2mer, 4mer and 8mer. Linear mode was applied for 12mer and 16mer.

Differential scanning calorimetry: DSC was performed with a heating/cooling rate of 10 °C/min with temperature ranging from -50 to 150 °C on a Q200 differential scanning calorimeter (TA Instruments). The glass transition temperature (T_g) was measured on the third cycle of a heat/cool/heat experiment.

Section B. Synthetic Protocols

1. Monomer

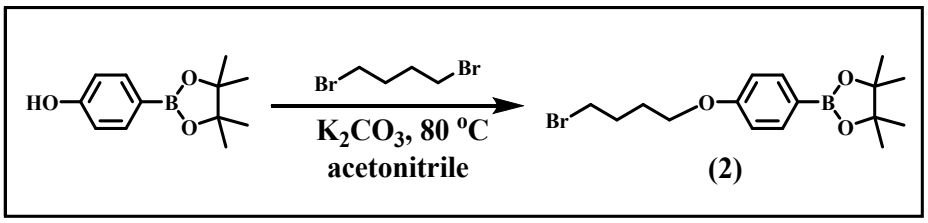
a) furan-protected maleimide (compound 1)



Scheme S1. Synthesis of furan-protected maleimide (compound 1).

A 1.0 L round-bottom flask sealed with a rubber plug were added with maleimide (20.0 g, 0.21 mol) and furan (30.0 mL, 0.42 mol). The mixture was dissolved in 500 mL of toluene. The solution was heated to 90 °C and maintained for 12 h, the product precipitated as a white solid during the process. After cooling the mixture to room temperature, the mixture was filtered and the filter cake was washed with 3×50.0 mL cold toluene. The product was dried under vacuum at 25 °C overnight to afford compound 1 (33.0 g, yield: 95.2%) as a white crystal. ^{1}H NMR (Figure S3, 300 MHz, $CDCl_3$), δ (TMS, ppm): 6.51 (s, 2H), 5.28 (s, 2H), 2.85 (s, 2H).

b) 2-(4-(4-bromobutoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 2)

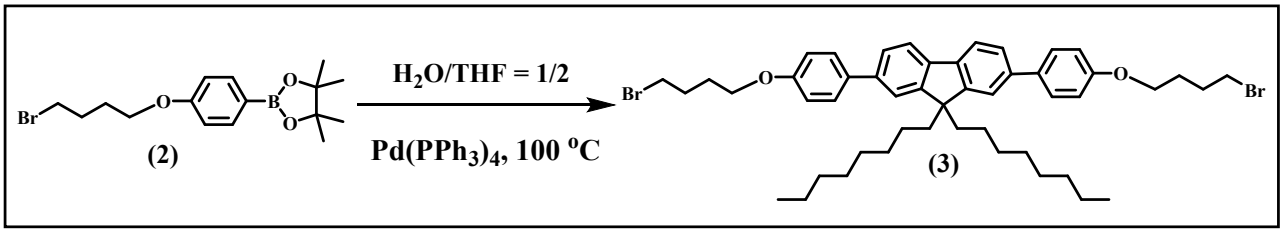


Scheme S2. Synthesis of 2-(4-(4-bromobutoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (compound 2).

4-Hydroxyphenylboronicacidpinacolester (2.2 g, 10.0 mmol), 1,4-butylenedibromide (6.1 mL, 40.0 mmol), potassium carbonate (6.9 g, 50.0 mmol) and 10.0 mg potassium iodide were mixed in

25.0 mL of acetonitrile in an oven-dried 100 mL three-neck round-bottom flask. The resulting mixture was stirred at 25 ^{o}C for 12 h. The acetonitrile was removed under reduced pressure. The residue was re-dissolved in 100 mL $CHCl_3$ and this solution was washed with 3×50.0 mL water, the organic layer was dried with anhydrous Na_2SO_4, and concentrated under vacuum. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (PE/EA, 20/1, v/v) as eluent to afford compound 2 (2.8 g, yield: 79.1%) as a bright white solid. ^{1}H NMR (Figure S4, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 6.86 (d, 2H), 3.98 (t, 2H), 3.42 (t, 2H), 1.87 (m, 4H), 1.33 (S, 12H).

c) fluorene-containing fluorophore (compound 3)

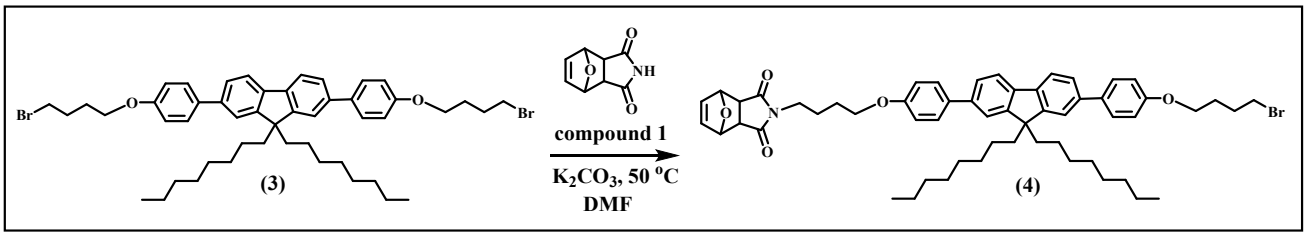


Scheme S3. Synthesis of compound 3.

Compound 2 (2.48 g, 7.0 mmol), 2,7-dibromo-9,9-dioctylfluorene (1.92 g, 3.5 mmol), and $Pd(PPh_3)_4$ (80.0 mg) were added to a 250 mL three-neck round-bottom flask. THF (100 mL) and saturated aqueous sodium carbonate (50.0 mL) was added sequentially to the flask under nitrogen. The mixture was refluxed for 24 h under nitrogen atmosphere. The resulting solution had a strong fluorescence under 365 nm UV light. After cooling to room temperature, the mixture was filtered. The filter cake was washed with 3×100 mL acetone and the combined filtrate was concentrated. The residue was re-dissolved in 100 mL $CHCl_3$ and this solution was washed with 3×50.0 mL water. The organic layer was dried with anhydrous Na_2SO_4, and concentrated under vacuum to afford the crude product which was recrystallized with hexane to obtain compound 3 (2.35 g, yield: 79.7%) as a light

yellow solid. ^{1}H NMR (Figure S5, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.44 (t, 4H),2.02 (m, 4H), 1.54 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

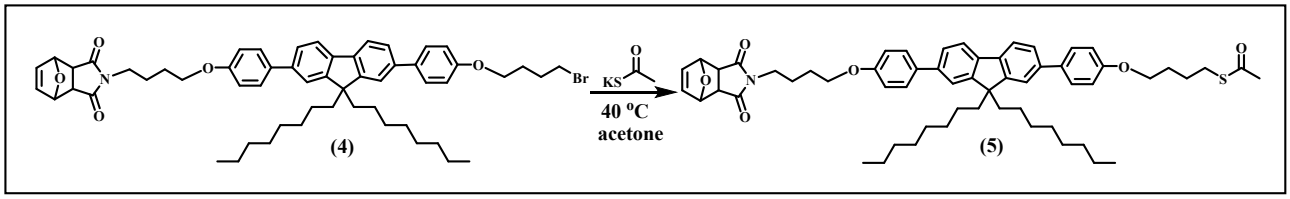
d) maleimide-protected fluorophore (compound 4)



Scheme S4. Synthesis of compound 4.

Compound 3 (0.84 g, 1.0 mmol) was added to dry DMF (50.0 mL) in an oven-dried 250 mL three-neck round-bottom flask. Then potassium carbonate (0.5 g, 2.0 mmol) was added to the mixture, the mixture was stirred under nitrogen flow and heated to 50 ºC for 1 h, then compound 1 (0.16 g, 1.0 mmol) was added and stirred at 50 ºC for 12 h. After cooling to room temperature, the mixture was filtered. The filter cake was washed with 3×100 mL EA. Then the filtrate was combined and washed with 3×100 mL water to remove DMF. The organic layer was then dried with anhydrous Na_2SO_4 and evaporated. The crude product was then purified by flash column chromatography on silica gel. eluting with a mixed solvent of PE/EA (4/1, v/v) and the production was recovered by precipitation in cold methyl alcohol to afford compound 4 (0.58 g, yield: 62.6%) as a light yellow solid. ^{1}H NMR (Figure S6, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 4H), 3.51 (t, 2H), 3.44 (t, 2H), 2.85 (s, 2H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

e) monomer (compound 5)

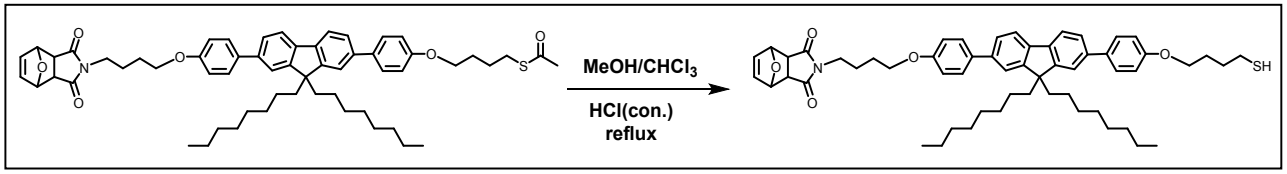


Scheme S5. Synthesis of monomer (compound 5).

Compound 4 (322.8 mg, 0.35 mmol) was dissolved in 50.0 mL of acetone in a 100 mL round-bottom flask. Then potassium thioacetate (38.8 mg, 0.51 mmol) was added. The mixture was heated to 45 ºC and kept under this temperature for 24 h. After cooling to room temperature, the mixture was filtered. The filter cake was washed with 3×100 mL acetone and the combined filtrate was concentrated. The residue was re-dissolved in 100 mL $CHCl_3$ and this solution was washed with 3×100 mL water, the organic layer was dried with anhydrous Na_2SO_4, and concentrated under vacuum to afford a deep yellow oil. The crude product was purified by flash column (neutral alumina) eluting with a mixed solvent of PE/EA (v/v, 1/1) to afford compound 5 (monomer, 322 mg, yield: 99.5%) as a yellow oil. ^{1}H NMR (Figure S7, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 4H), 3.51 (t, 2H), 2.98 (t, 2H), 2.85 (s, 2H), 2.34 (s, 3H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

2. Monodisperse polymers

a) thiol functionalized monomer (Monomer-thiol)

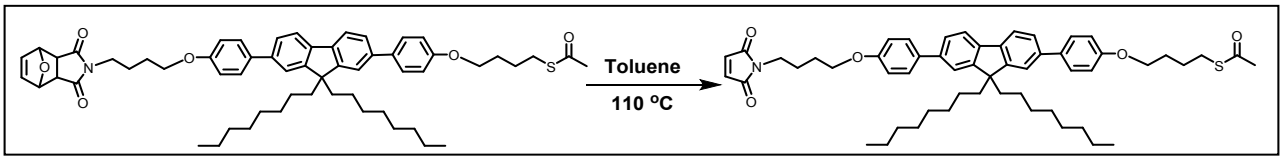


Scheme S6. Synthesis of thiol functionalized monomer (Monomer-thiol).

The monomer (1.0 g, 1.1 mmol) was dissolved in 100 mL of mixed solvent of anhydrous methanol and $CHCl_3$ (1/1, v/v) in a 250 mL three-neck flask equipped with a condenser under nitrogen atmosphere. Then concentrated HCl (1.0 mL, 12 mmol) was added to the solution, and the resulting mixture was refluxed for 8 h. TLC was used to monitor the reaction. After cooling to the room temperature, the mixture was quenched with 100 mL water and extracted with $CHCl_3$ (3×100 mL). The organic layer was combined and washed with 300 mL water and dried with anhydrous Na_2SO_4. $CHCl_3$ was concentrated under vacuum to afford monomer-thiol (0.95 g, yield: 98.0%) as pale yellow solid. ^{1}H NMR (Figure S9, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 4H), 3.51 (t, 2H), 2.85 (s, 2H), 2.53 (t, 2H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

The de-protection of the thiol group for preparations of the monodisperse polymers *via* iterative exponthional growth follows similar approach above.

b) maleimide functionalized monomer (Mal-monomer)



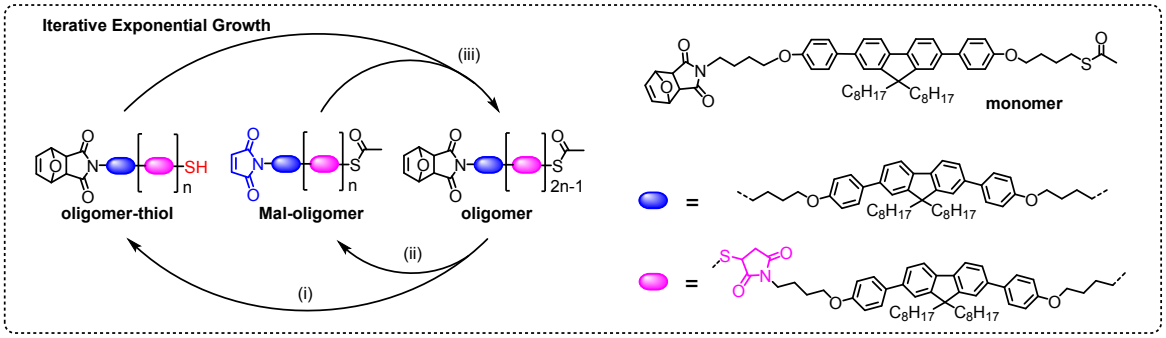
Scheme S7. Synthesis of maleimide de-protected monomer (Mal-monomer).

The monomer (0.94 g, 1.0 mmol) and 50.0 mL of toluene were added to a three-neck flask equipped with a condenser under a nitrogen atmosphere. The reaction mixture was stirred and refluxed at 110 ºC under nitrogen flow for about 6 h. TLC showed that the reaction was complete. After cooling to room temperature, toluene was removed under vacuum. And the residue was dried under vacuum at 25 °C for 24 h to afford Mal-monomer (0.84 g, yield: 97.8%) as a pale yellow solid. ^{1}H NMR (Figure S8, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99

(d, 4H), 6.70 (s, 2H), 4.03 (t, 4H), 3.51 (t, 2H), 2.98 (t, 2H), 2.34 (s, 3H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

The de-protection of the maleimide group for preparations of the monodisperse polymers *via* iterative exponthional growth follows similar approach above.

c) general synthetic routes for monodisperse polymers



Scheme S8. Synthesis of monodisperse polymers.

2mer: The thiol functionalized monomer (Monomer-thiol, 6.9 g, 1.1 mmol) and the maleimide functionalized monomer (Mal-monomer, 6.3 g, 1.0 mmol) were dissolved in 100 mL of $CHCl_3$ in a 250 mL three-neck round-bottom flask under nitrogen atmosphere at 25 °C. TEA (1.0 mL, 7.5 mmol) was added *via* a 1 mL syringe and the mixture was stirred for about 12 h. The reaction mixture was quenched with 100 mL water and washed with 100 mL saturated $NaHCO_3$ (aq.). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product. Then the product was purified by column chromatography over silica gel eluting with PE/EA (2/1, v/v), and concentrated under vacuum to give the pale yellow oil which was recrystallized with cold methanol to afford 2mer as pale yellow solid. 4mer, 8mer and 16mer were obtained *via* the similar procedure as 2mer.

2mer (10.8 g, yield: 85.1 %): ^{1}H NMR (Figure S13, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 4H), 7.60 (d, 8H), 7.51 (d, 8H), 6.99 (d, 8H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 8H), 3.73 (m, 1H),

3.51 (t, 2H), 3.13 (m, 1H), 2.98 (t, 2H), 2.98 (m, 2H), 2.54 (m, 1H) 2.34 (s, 3H), 2.02 (m, 8H), 1.83 (m, 16H), 1.06 (m, 40H), 0.79 (t, 12H), 0.70 (m, 8H).

4mer (6.5g, yield: 74.1%): ^{1}H NMR (Figure S13, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 8H), 7.60 (d, 16H), 7.51 (d, 16H), 6.99 (d, 16H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 16H), 3.73 (m, 3H), 3.51 (t, 2H), 3.13 (m, 3H), 2.98 (t, 2H), 2.98 (m, 6H), 2.54 (m, 3H) 2.34 (s, 3H), 2.02 (m, 16H), 1.83 (m, 16H), 1.06 (m, 80H), 0.79 (t, 32H), 0.70 (m, 16H).

8mer (2.7 g, yield: 56.4%): ^{1}H NMR (Figure S13, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 16H), 7.60 (d, 32H), 7.51 (d, 32H), 6.99 (d, 32H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 32H), 3.73 (m, 7H), 3.51 (t, 2H), 3.13 (m, 7H), 2.98 (t, 2H), 2.98 (m, 14H), 2.54 (m, 7H) 2.34 (s, 3H), 2.02 (m, 32H), 1.83 (m, 32H), 1.06 (m, 160H), 0.79 (t, 64H), 0.70 (m, 32H).

16mer (purified by recycling preparative SEC, 0.4 g, yield: 34.6%) : ^{1}H NMR (Figure S13, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 32H), 7.60 (d, 64H), 7.51 (d, 64H), 6.99 (d, 64H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 64H), 3.73 (m, 15H), 3.51 (t, 2H), 3.13 (m, 15H), 2.98 (t, 2H), 2.98 (m, 30H), 2.54 (m, 15H) 2.34 (s, 3H), 2.02 (m, 64H), 1.83 (m, 64H), 1.06 (m, 320H), 0.79 (t, 128H), 0.70 (m, 64H).

12mer: The thiol functionalized 8mer (8mer-thiol, 131.0 mg, 0.02 mmol) and the maleimide functionalized 4mer (Mal-4mer, 66.0 mg, 0.02 mmol) were dissolved in 20.0 mL of $CHCl_3$ in a 100 mL three-neck round-bottom flask under nitrogen atmosphere at 25 ^{o}C. TEA (0.1 mL, 0.75 mmol) was added *via* a 1 mL syringe and the mixture was stirred for about 12 h. The reaction mixture was quenched with 20.0 mL water and washed with 20.0 mL saturated $NaHCO_3$ (aq.). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product which was purified by recycling preparative SEC. Then, THF was concentrated under

vacuum to afford yellow solid which was recrystallized with cold methanol to obtain 12mer as a pale yellow solid.

12mer (154.0 mg, yield:78.1%): ^{1}H NMR (Figure S13, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 24H), 7.60 (d, 48H), 7.51 (d, 48H), 6.99 (d, 48H), 6.51 (s, 2H), 5.28 (s, 2H), 4.03 (t, 48H), 3.73 (m, 11H), 3.51 (t, 2H), 3.13 (m, 11H), 2.98 (t, 2H), 2.98 (m, 22H), 2.54 (m, 11H) 2.34 (s, 3H), 2.02 (m, 48H), 1.83 (m, 48H), 1.06 (m, 240H), 0.79 (t, 96H), 0.70 (m, 48H).

3. Step-growth polymerization *via* Thiol-Maleimide Michael addition

The Mal-monomer (92.4 mg, 0.1 mmol) were dissolved in 50.0 mL of mixed solvent of anhydrous methanol and $CHCl_3$ (1/1, v/v) in a 100 mL three-neck flask equipped with a condenser under nitrogen atmosphere. Concentrated HCl (2.0 mL, 23.8 mmol) was added to the solution, and the resulting mixture was refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, then the reaction mixture was evaporated and re-dissolved in $CHCl_3$. The organic solution was then washed with saturated $NaHCO_3$ (aq.) and water. The organic layer was combined and dried with anhydrous Na_2SO_4, then $CHCl_3$ was removed. Immediately after adding 10.0 mL of THF (the monomer concentration = 10^{-2} mol/L) followed by 14.0 μL of TEA (10^{-4} mmol) under nitrogen atmosphere, the mixture was stirred at room temperature. Meanwhile, at the certain points of time, an aliquot of the reaction solution was withdrawn and quenched by addition of excess N-propylmaleimide (1.0 mg/mL in THF), and subjected to SEC measurement calibrated with the as-prepared monodisperse polymers as standard samples. Meanwhile, the resulting mixture was monitored by fluorescence spectrophotometer.

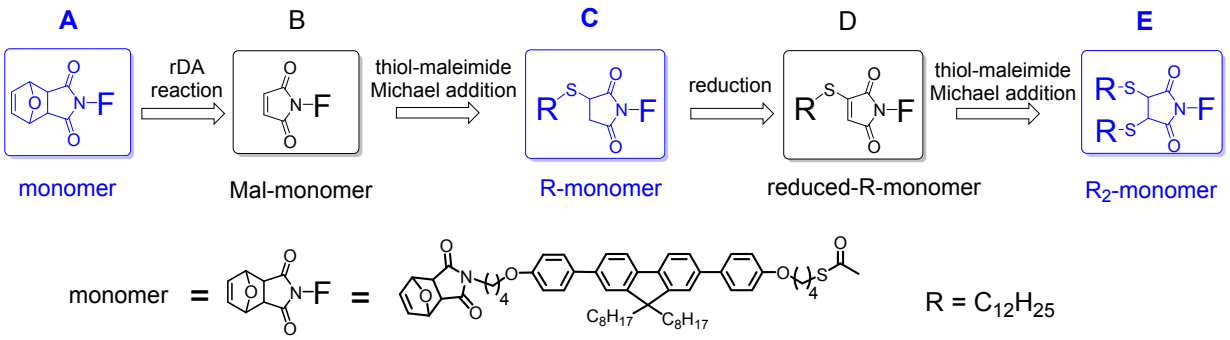
4. Cyclic monodisperse polymers

***cyclic*-2mer**: The maleimide de-protected 2mer (167.0 mg, 0.1 mmol) were dissolved in 50.0 mL of mixed solvent of anhydrous methanol and $CHCl_3$ (1/1, v/v) in a 100 mL three-neck flask equipped with a condenser under nitrogen atmosphere. Concentrated HCl (2.0 mL, 23.8 mmol) was added to the solution, and the resulting mixture was refluxed for 24 h under nitrogen atmosphere. Then the organic layer was washed with water. The combined organic layer was dried with anhydrous Na_2SO_4 and filtered under nitrogen atmosphere. The solvent was removed, and the residue was re-dissolved in 20.0 mL THF and diluted to 1000 mL (the monomer concentration = 10^{-4} mol/L). TEA (2.0 mL, 15.0 mmol) was added *via* a 2 mL syringe over 5 min. The mixture was stirred at room temperature for 24 h. The fluorescence intensity was monitored online. Meanwhile, at certain points of time, an aliquot of the reaction solution was withdrawn and quenched by addition of excess N-propylmaleimide (1.0 mg/mL in THF), and subjected to SEC measurement calibrated with the as-prepared monodisperse polymers as standard samples. In the last, most of the solvent was evaporated and the residue was re-dissolved in 100 mL of $CHCl_3$, and then washed with saturated $NaHCO_3$ (aq.) and water, respectively. The combined organic layer was dried with anhydrous Na_2SO_4, the $CHCl_3$ was evaporated and the crude product was purified by preparative SEC to give *cyclic*-2mer as a yellow solid. Using the similar procedure, *cyclic*-4mer and *cyclic*-8mer were sucessfully obtained.

cyclic-2mer (133.3 mg, yield: 81.1%). ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.73 (m, 1H), 3.51 (t, 2H), 3.13 (m, 1H), 2.98 (t, 2H), 2.98 (m, 2H), 2.54 (m, 1H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H). *cyclic*-4mer (117.1 mg, yield: 40.2%): ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm):

7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.73 (m, 1H), 3.51 (t, 2H), 3.13 (m, 1H), 2.98 (t, 2H), 2.98 (m, 2H), 2.54 (m, 1H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).*cyclic*-8mer (81.7 mg, yield: 31.7%): ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.73 (m, 1H), 3.51 (t, 2H), 3.13 (m, 1H), 2.98 (t, 2H), 2.98 (m, 2H), 2.54 (m, 1H), 2.02 (m, 4H), 1.83 (m, 8H), 1.06 (m, 20H), 0.79 (t, 6H), 0.70 (m, 4H).

5. Model reactions on maleimide group



Scheme S9. Illustration of the model reactions on maleimide group.

a) R-monomer

Mal-monomer (942.1 mg, 1.1 mmol) and dodecyl mercaptan (1.3 mL, 5.5 mmol) were dissolved in 50.0 mL of $CHCl_3$ in a 50 mL three-neck flask under nitrogen atmosphere at room temperature. TEA (1.0 mL, 7.5 mmol) was added to the solution, and the mixture was stirred under nitrogen atmosphere until complete consumption of starting material as monitored by TLC. The reaction mixture was quenched with water (50.0 mL) and washed with saturated $NaHCO_3$ (aq.). The organic layer was combined and dried with anhydrous Na_2SO_4. $CHCl_3$ was evaporated and the crude product was purified by column chromatography over silica gel eluting with PE/EA (2/1, v/v) to afford a yellow oil. And the oil was precipitated with cold methanol to obtain R-monomer (1.08 g, yield: 94.0%) as a pale yellow oil. ^{1}H NMR (Figure S10, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d,

2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.73 (m, 1H), 3.51 (t, 2H), 3.13 (m, 1H), 2.98 (t, 2H), 2.89 (t, 2H), 2.54 (m, 1H), 2.34 (s, 3H), 2.02 (m, 4H), 1.83 (m, 8H), 1.69-1.25 (m, 20H), 1.06 (m, 20H), 0.88 (t, 3H), 0.79 (t, 6H), 0.70 (m, 4H).

b) reduced-R-monomer

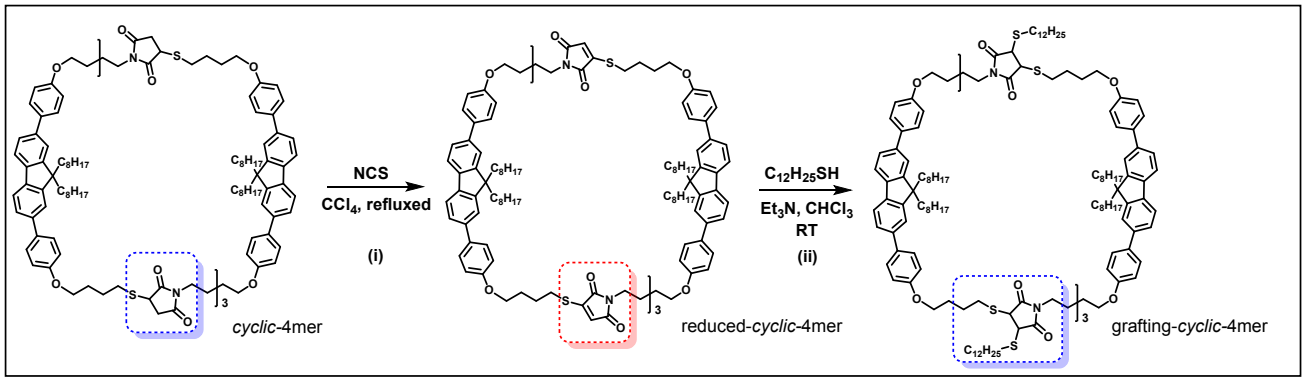
The solution of R-monomer (1.05 g, 1.0 mmol) and carbon tetrachloride (100 mL) were added to a 250 mL three-neck flask equipped with a condenser. Then, N-chlorosuccinimide (140.0 mg, 1.05 mmol) was added in one portion to the stirring solution. The mixture was allowed to reflux at 80 ºC under nitrogen atmosphere for about 6 h. TLC showed that the reaction was complete. After cooling to room temperature, the reaction mixture was concentrated. The residue was re-dissolved in 50.0 mL of dichloromethane and washed with saturated $NaHCO_3$ (aq.) (20.0 mL) and water (20.0 mL). The combined organic layer was dried with anhydrous Na_2SO_4 and the solvent was evaporated to afford the crude product which was purified by column chromatography on silica gel eluting with PE/EA (2/1, v/v) to give the reduced-R-monomer (0.99 g, yield: 95.1%) as a yellow solid. ^{1}H NMR (Figure S11, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 6.03 (s, 1H), 4.03 (t, 4H), 3.51 (t, 2H), 2.98 (t, 2H), 2.89 (t, 2H), 2.34 (s, 3H), 2.02 (m, 4H), 1.83 (m, 8H), 1.69-1.25 (m, 20H), 1.06 (m, 20H), 0.88 (t, 3H), 0.79 (t, 6H), 0.70 (m, 4H).

c) R_2-monomer

The reduced-R-monomer (0.53 g, 0.5 mmol) and dodecyl mercaptan (0.59 mL, 2.5 mmol) were dissolved in 50.0 mL of $CHCl_3$ in a 100 mL three-neck flask under nitrogen atmosphere at room temperature. TEA (0.5 mL, 3.7 mmol) was added to the solution, and the mixture was stirred under nitrogen atmosphere until complete consumption of starting material as monitored by TLC. The reaction mixture was quenched with water (50.0 mL) and washed with saturated $NaHCO_3$ (aq.). The

organic layer was combined and dried with anhydrous Na_2SO_4. $CHCl_3$ was evaporated and the crude product was purified by column chromatography over silica gel eluting with PE/EA (10/1, v/v) to give R_2-monomer (0.51 g, yield: 90%) as pale yellow oil. ^1H NMR (Figure S12, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.51 (t, 2H), 2.98 (t, 2H), 2.89-2.70 (t, 4H), 2.61 (d, 2H), 2.34 (s, 3H), 2.02 (m, 4H), 1.83 (m, 8H), 1.69-1.25 (m, 40H), 1.06 (m, 20H), 0.88 (t, 6H), 0.79 (t, 6H), 0.70 (m, 4H).

6. Grafting-*cyclic*-4mer



Scheme S10. Synthetic route of grafting-*cyclic*-4mer

The synthsis of reduced-*cyclic*-4mer was similar as that of R-reduced monomer as described above. Reduced-*cyclic*-4mer (32.4 mg, 0.01 mmol) and dodecyl mercaptan (24.0 μL, 0.1 mmol) were added in a NMR tube with 1.0 mL of $CDCl_3$ at room temperature. A parallel rection with same reactants was conducted in a cuvette independently to monitor the reaction by fluoresence emission. Immediately, TEA (0.1 mL, 0.75 mmol) was added to the solution in NMR tube and cuvette, respectively. The fluorescence intensity of reaction solution was online measured by fluorometer. Meanwhile, the reaction was also maonitored by real-time NMR spectroscopy. After determined time 10.0 mL $CHCl_3$ was added, then the reaction mixture was quenched with 10.0 mL water. The organic layer was washed with saturated $NaHCO_3$ (aq.) and water. The combined organic layer was

dried with anhydrous Na_2SO_4, the $CHCl_3$ was concentrated and precipitated in ice methanol to give grafting-*cyclic*-4mer (30.1 mg, yield: 70.9%) as pale yellow solid. ^1H NMR (Figure S14, 300 MHz, $CDCl_3$), δ (TMS, ppm): 7.72 (d, 2H), 7.60 (d, 4H), 7.51 (d, 4H), 6.99 (d, 4H), 4.03 (t, 4H), 3.73 (m, 2H), 3.57 (t, 2H), 3.49 (m, 2H) 2.98 (t, 2H), 2.98 (m, 2H), 2.70 (m, 2H), 2.02 (m, 4H), 1.83 (m, 8H), 1.69-1.25 (m, 20H), 1.06 (m, 20H), 0.88 (t, 3H), 0.79 (t, 6H), 0.70 (m, 4H).

Section C. Fluorescence Emission

1. Fluorescence emission of monomer, Mal-monomer, R-monomer, Reduced-R-monomer, R_2-monomer in model reaction

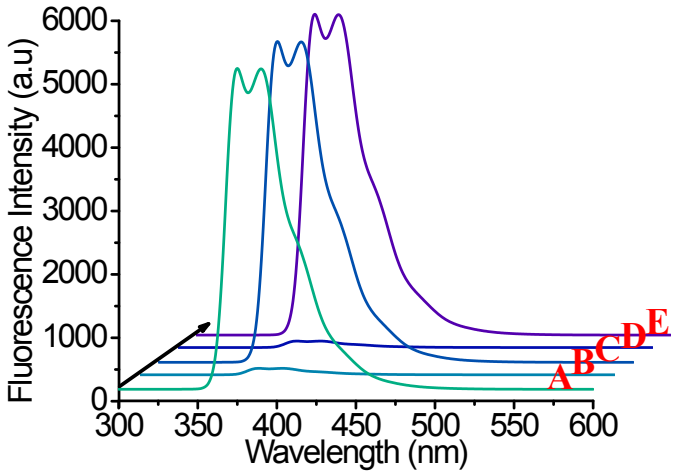


Figure S1. Fluorescence emission spectra of A: monomer, B: Mal-monomer, C: R-monomer, D: reduced-R-monomer, E: R_2-monomer (The fluorophotometer was set at λ_{EX} = 366 nm, λ_{EM} = 388 nm, EX Slit = 5.0 nm, EM Slit = 5.0 nm and PMT Voltage = 400 V, fluorophore = 10^{-4} mol/L).

2. Fluorescence emission of monodisperse polymers (2mer, 4mer and 8mer)

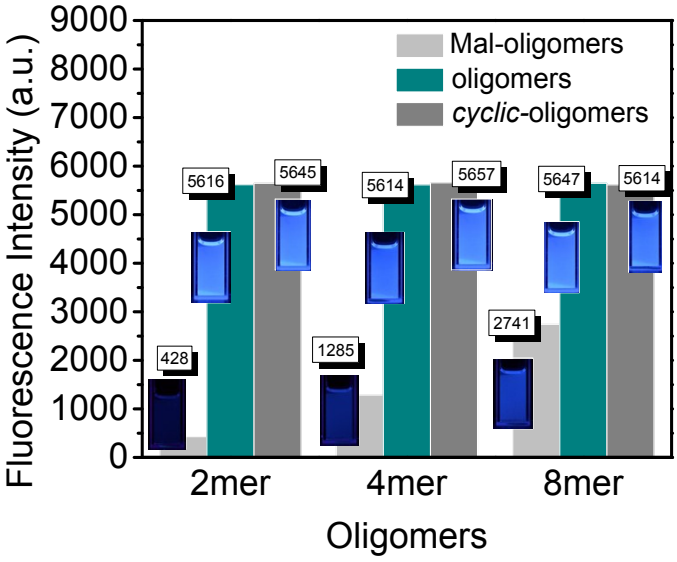


Figure S2. The fluorescence intensities of monodisperse polymers oligomers, Mal-oligomers and relevant cyclic oligomers (The fluorophotometer was set at λ_{EX} = 366 nm, λ_{EM} = 388 nm, EX Slit = 5.0 nm, EM Slit = 5.0 nm and PMT Voltage = 400 V, fluorophore = 10^{-4} mol/L).

3. Fluorescence emission models (equation 1-5)

In the case of step polymerization of Mal-monomer-thiol, Perrin-model was applied as demonstrated in equation (1), which describes the relationship between the emission intensities and the concentration of the quencher.

$$\ln(\frac{I_0}{I}) = V \cdot N_0 \cdot [Q] \quad (1)$$

where I_o and I are the fluorescence intensities in the absence and presence of quencher, respectively; V is the volume of quenching sphere in cubic centimeters; N_0 is Avogadro's number; [Q] is the concentration of quencher.

The MWs of Mal-oligomers can be calculated from equation (2),

$$MW = \frac{n_F}{n_Q} \cdot m = \frac{[F]}{[Q]} \cdot m \quad (2)$$

where n_F/n_Q is molar ratio of fluorophore and quencher moieties in the polymer; m is molecular weight of monomer; [F] and [Q] is molar concentration of fluorophore and quencher, respectively.

Combining Eq(1) and Eq(2) leads to a linear relationship between the ln$I$ and MW^{-1} of Mal-oligomers, as shown in equation (3).

$$\ln I = \ln I_0 - \frac{V \cdot N_0 \cdot m \cdot [F]}{MW} \quad (3)$$

As for monitoring cyclic-brush-like topology formation, the degree of grafting at prescribed time can be deduced by the fluorescence intensity (R_{FL}, equation 4). Meanwhile, the grafting ratio

can be calculated based on the decreases of integration value of the double bond protons at δ = 6.09 ppm (R_{NMR}) arising from the reduced-*cyclic*-4mer, according to equation (5).

$$R_{FL} = \frac{I_{exp.} - I_{red.}}{I_{max} - I_{red.}} \quad (4)$$

$$R_{NMR} = \frac{V_{red.} - V_{exp.}}{V_{red.}} \quad (5)$$

R_{FL} is the grafting ratio based on fluorescence calculation by equation (1); R_{NMR} is the grafting ratio based on ^{1}H NMR calculation by equation (2). $I_{exp.}$ = fluorescence intensity of reaction solution at determined time; $I_{red.}$ = fluorescence intensity of reduced-cyclic-4mer; I_{max} is maximum fluorescence intensity of grafting reaction solution; $V_{red.}$ = ^{1}H NMR integration value of the double bond protons (δ = 6.09 ppm) arising from the reduced-*cyclic*-4mer before grafting process; $V_{exp.}$ = ^{1}H NMR integration value of the double bond protons (δ = 6.09 ppm) arising from the reduced-*cyclic*-4mer at determined time.

Section D. ^{1}H NMR Spectra

1. furan-protected maleimide (compound 1)

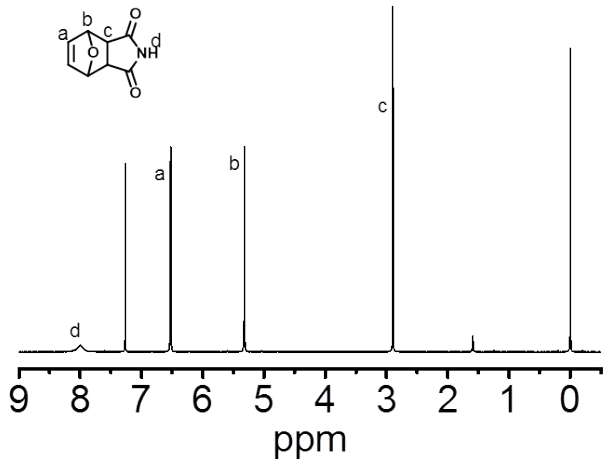


Figure S3. ^{1}H NMR spectrum of compound 1 in $CDCl_3$ (Bruker, 300 MHz, TMS).

2. 2-(4-(4-bromobutoxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (Compound 2)

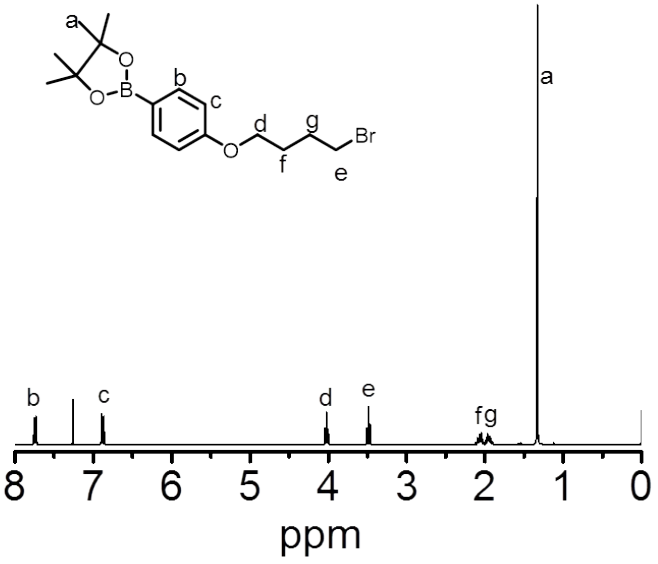


Figure S4. ^{1}H NMR spectrum of compound 2 in $CDCl_3$ (Bruker, 300 MHz, TMS).

3. fluorene-containing fluorophore (compound 3)

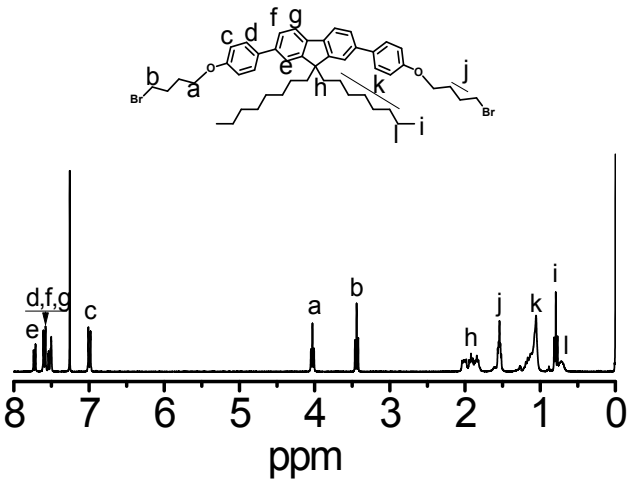


Figure S5. ^{1}H NMR spectrum of compound 3 in $CDCl_3$ (Bruker, 300 MHz, TMS).

4. maleimide-protected fluorophore (compound 4)

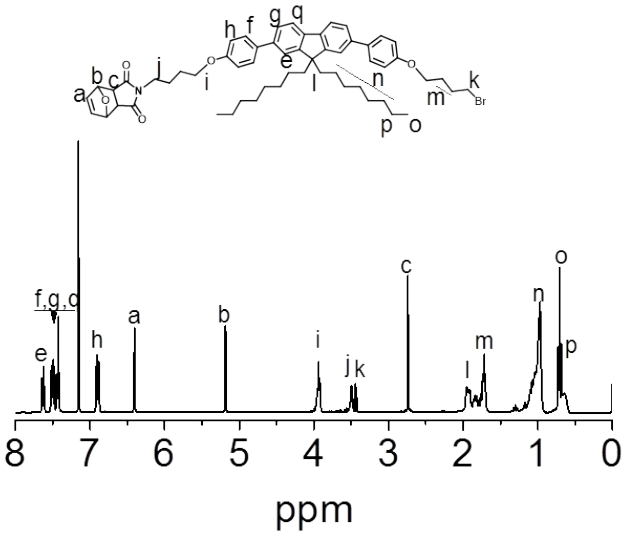


Figure S6. ^{1}H NMR spectrum of compound 4 in $CDCl_3$ (Bruker, 300 MHz, TMS).

5. monomer (compound 5)

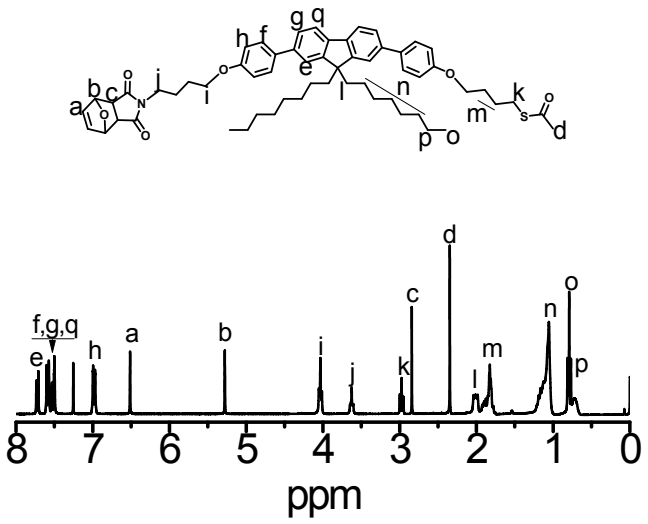


Figure S7. ^{1}H NMR spectrum of compound 5 (monomer) in $CDCl_3$ (Bruker, 300MHz, TMS).

6. Mal-monomer

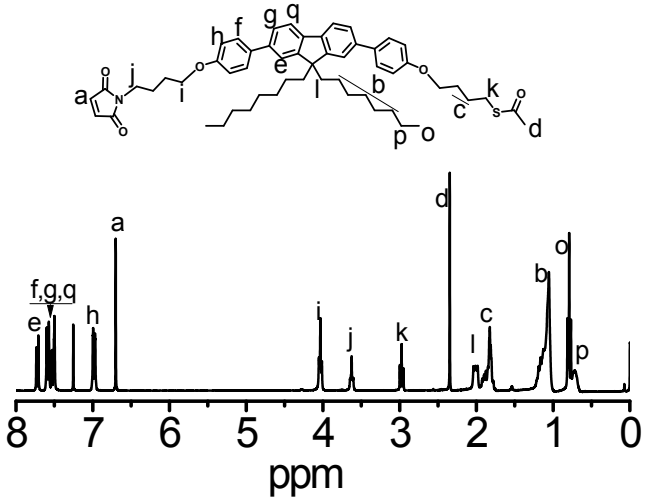


Figure S8. ^{1}H NMR spectrum of Mal-monomer in $CDCl_3$ (Bruker, 300MHz, TMS).

7. monomer-thiol

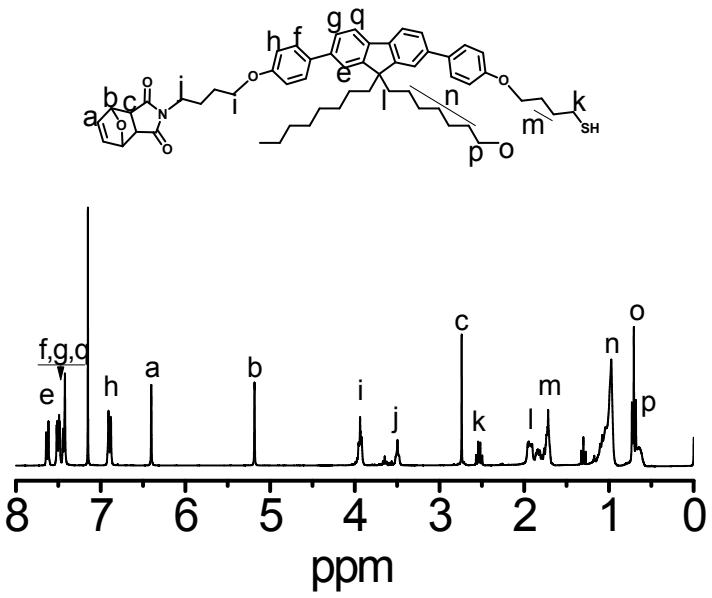


Figure S9. ^{1}H NMR spectrum of monomer-thiol in $CDCl_3$ (Bruker, 300MHz, TMS).

8. R-monomer

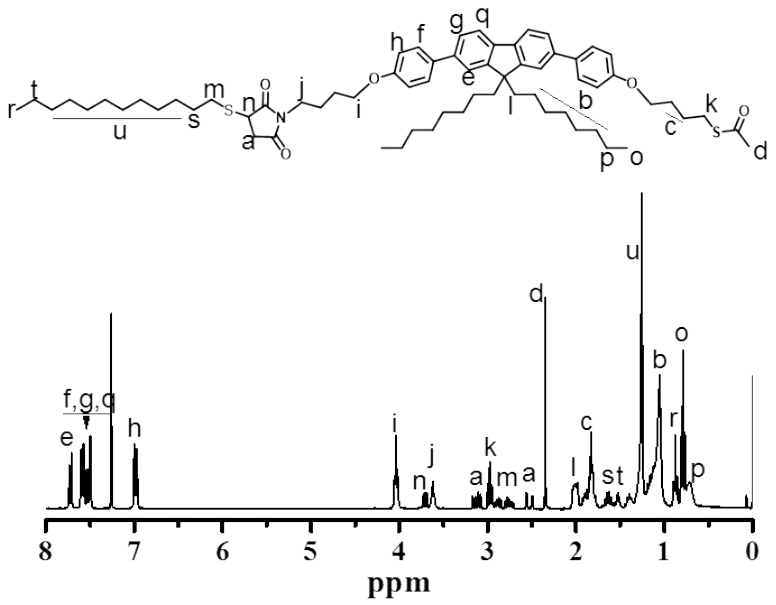


Figure S10. ^{1}H NMR spectrum of R-monomer in $CDCl_3$ (Bruker, 300 MHz, TMS).

9. reduced-R-monomer

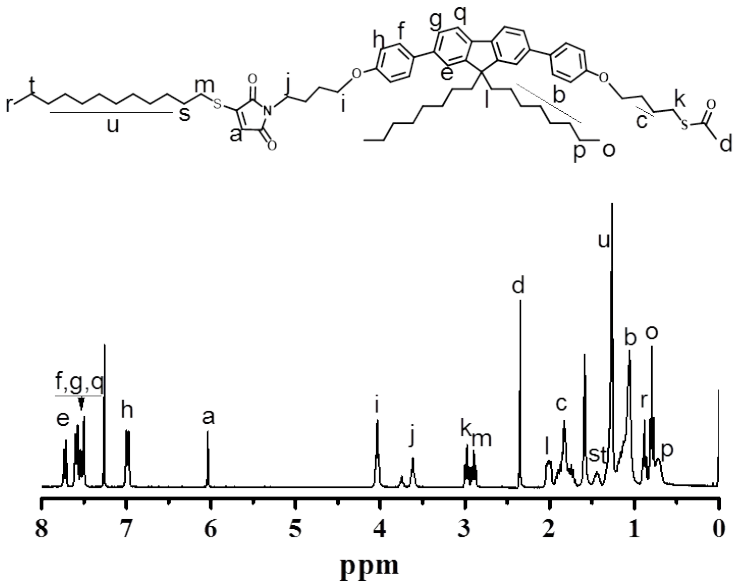


Figure S11. ^{1}H NMR spectrum of reduced-R-monomer in $CDCl_3$ (Bruker, 300MHz, TMS).

10. R_2-monomer

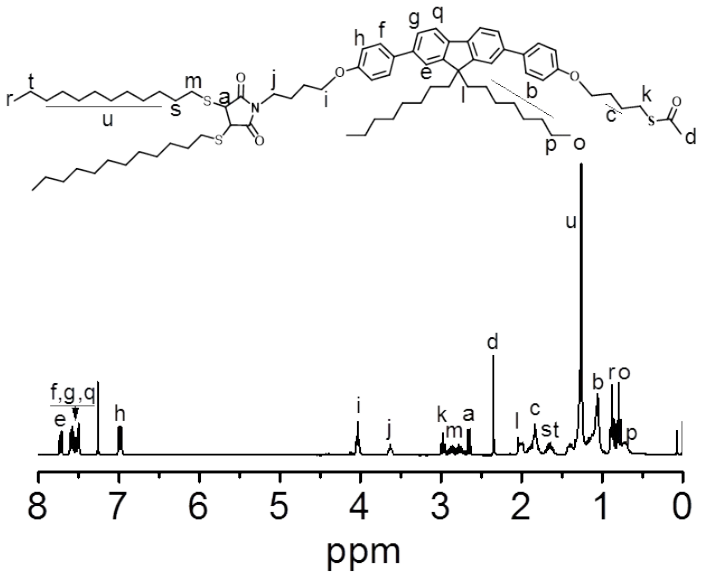


Figure S12. ^{1}H NMR spectrum of R_2-monomer in $CDCl_3$ (Bruker, 300MHz, TMS).

11. 2mer, 4mer, 8mer, 12mer and 16mer

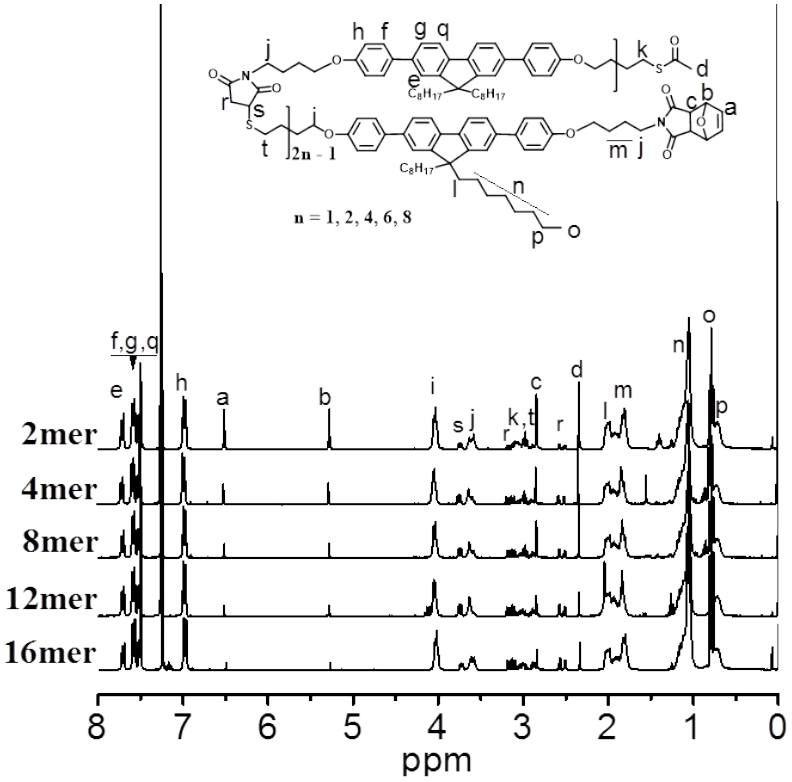


Figure S13. ^{1}H NMR spectra of monodisperse polymers in $CDCl_3$ (Bruker, 300MHz, TMS).

12. *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer

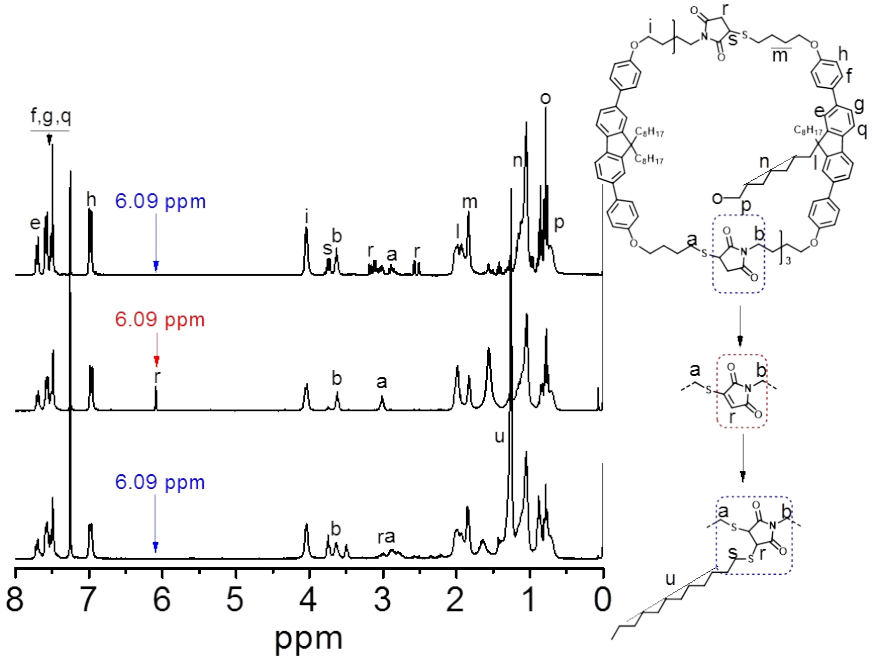


Figure S14. ^{1}H NMR spectra of *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer in $CDCl_3$ (Bruker, 300 MHz, TMS).

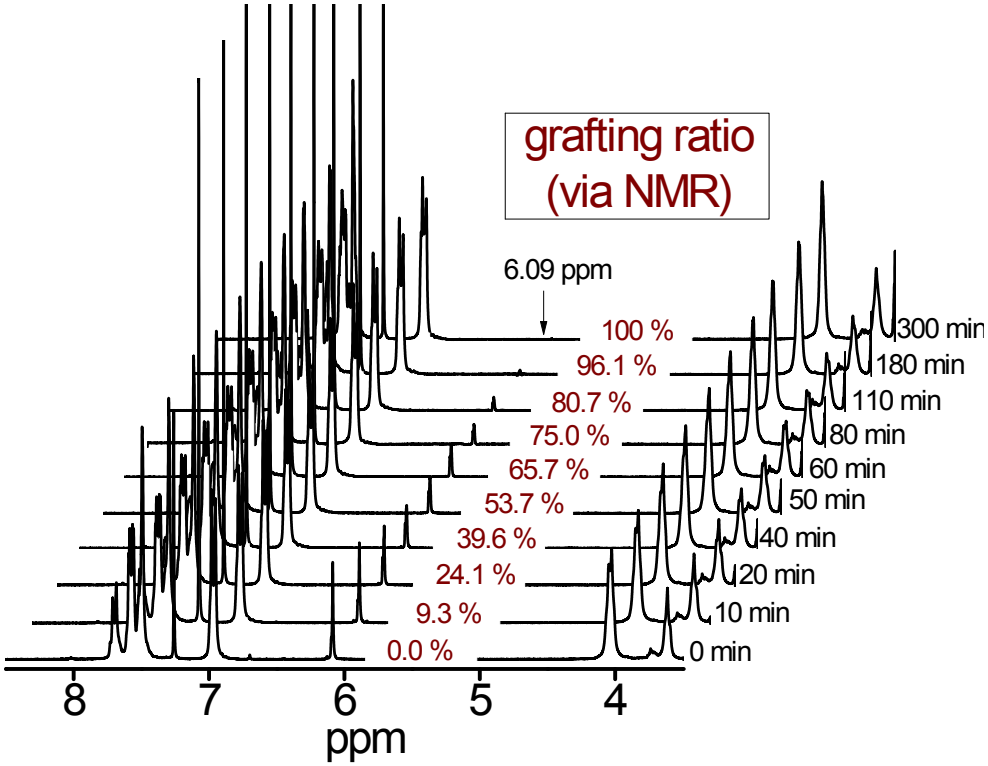


Figure S15. *In situ* ^{1}H NMR spetra of real-time monitoring the grafting reaction process and the fluorophore concentrations = 10^{-2} mol/L (Bruker, 300 MHz, $CDCl_3$, TMS as internal standard).

Section E. Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS)

1. R-monomer, reduced-R-monomer and R_2-monomer

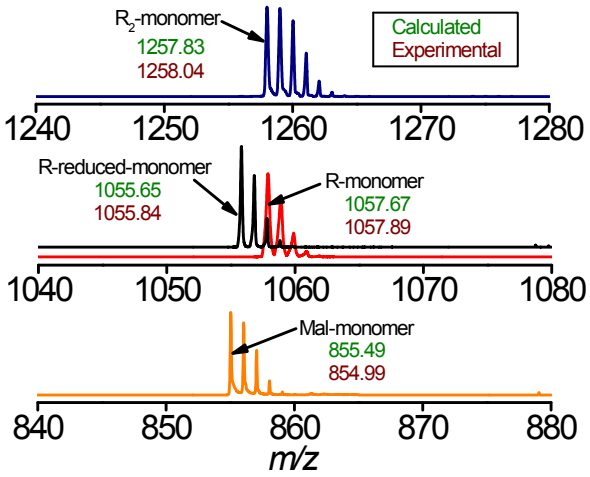


Figure S16. MALDI-TOF mass spectra of the small molecules in model reaction (Mal-monomer, R-monomer and R_2-monomer, DCTB as the matrix, reflection mode).

2. *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer

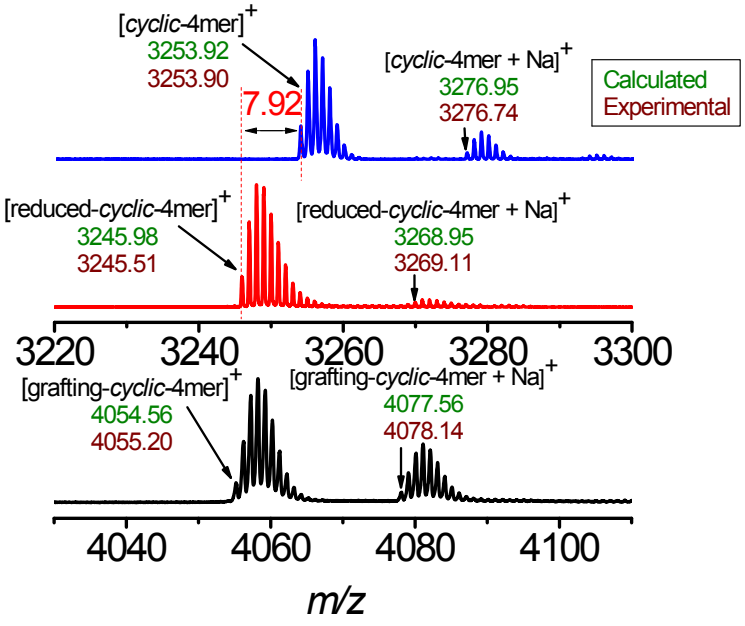


Figure S17. MALDI-TOF mass spectra of *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer (DCTB as the matrix, reflection mode).

Section F. Differential Scanning Calorimetry

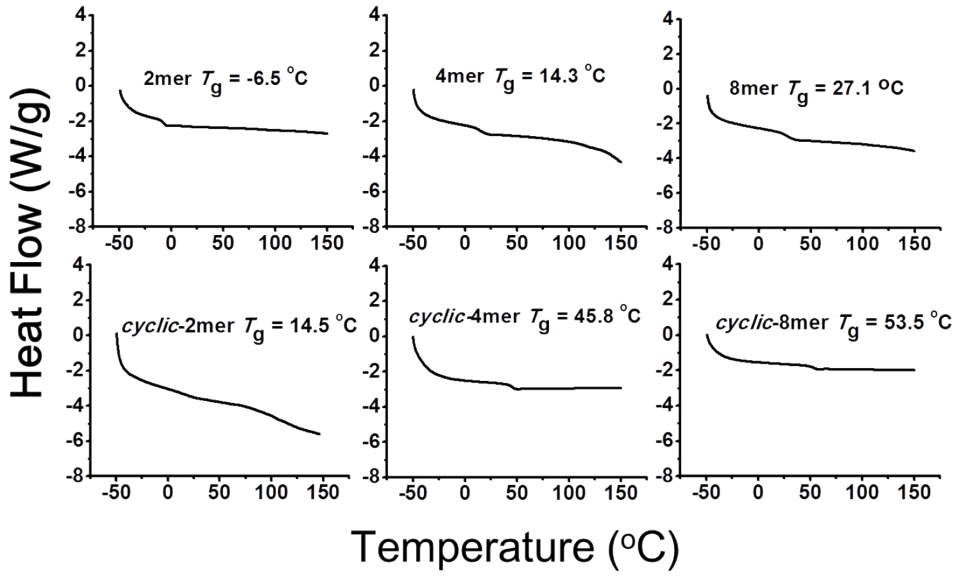


Figure S18. DSC traces of 2mer, 4mer, 8mer and relevant cyclic oligomers. (-50 °C – 150 °C, and the glass transition temperature T_g was measured on the third cycle of a heat/cool/heat experiment).

Section G. Size Exclusion Chromatography

1. 2mer, 4mer, 8mer, 12mer and 16mer

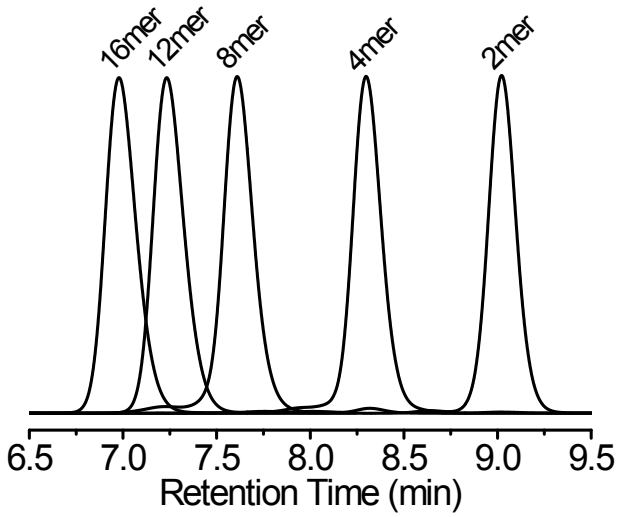


Figure S19. SEC traces of the monodisperse polymers.

2. polymers from step-growth polymerization *via* thiol-maleimide Michael addition

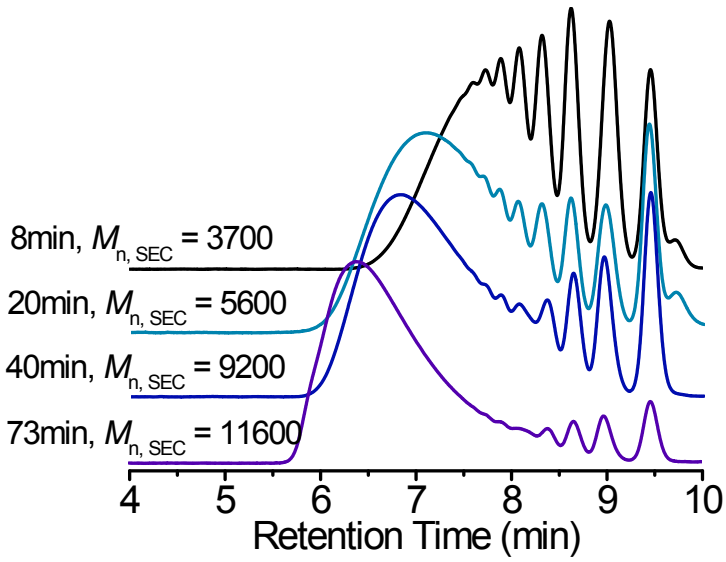


Figure S20. SEC traces of the thiol-Michael step-growth polymer.

3. R-monomer, reduced-R-monomer and R_2-monomer

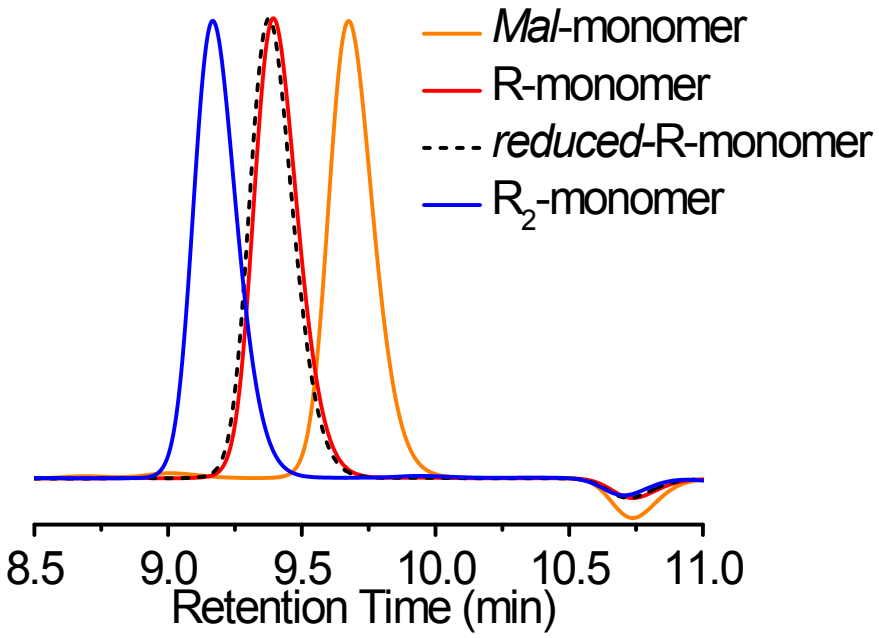


Figure S21. SEC traces of Mal-monomer, R-monomer, reduced-R-monomer and R_2-monomer.

4. 2mer, 4mer, 8mer and relevant cyclic oligomers

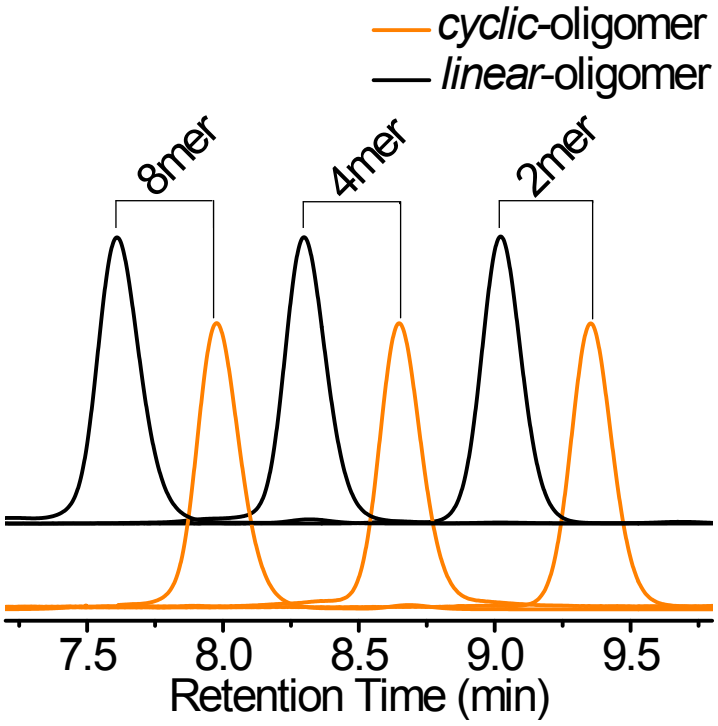


Figure S22. SEC traces of 2mer, 4mer, 8mer and relevant cyclic oligomers.

5. *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer

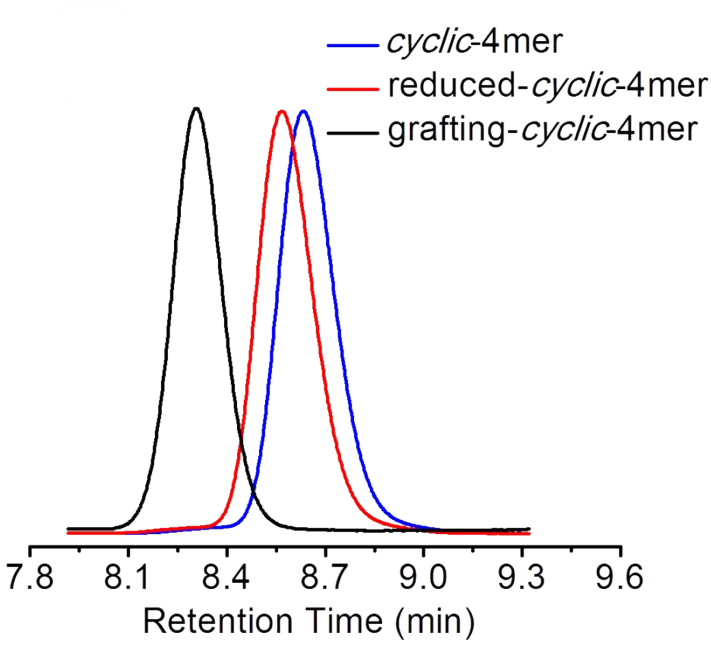


Figure S23. SEC traces of *cyclic*-4mer, reduced-*cyclic*-4mer and grafting-*cyclic*-4mer.

6. Monitoring intramolecular cyclization

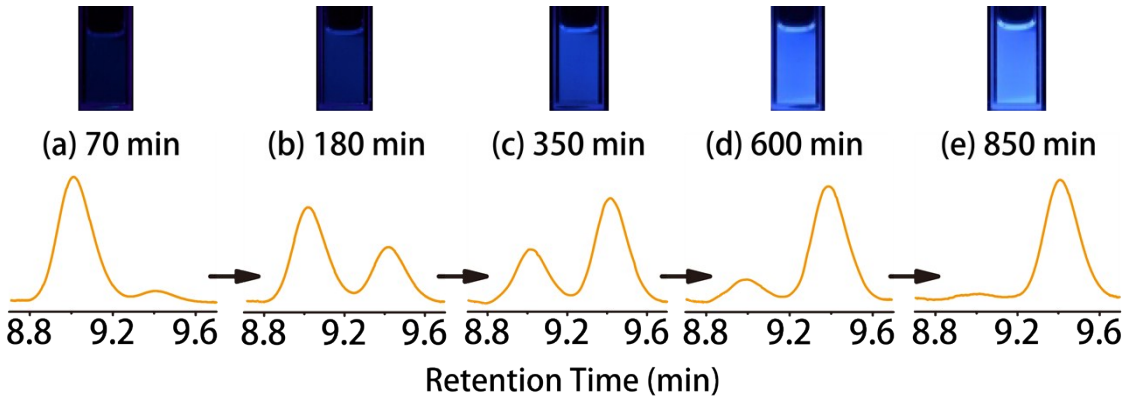


Figure S24. SEC traces of polymers from cyclization process.

Table S1. The molar percentage of *cyclic*-2mer from intramolecular reaction, side product from intermolecular reaction, and *linear*-2mer precursor during cyclization reaction.

Reaction Time	70 min	180 min	350 min	600 min	850 min
cyclic-2mer	8.9%[a]	36.7%	66.1%	83.9%	96.0%
linear-2mer	90.9%	62.0%	30.2%	12.7%	2.2%
side product	0.2%	1.3%	3.7%	3.4%	1.8%

[a]calculated by Gaussian multiple peak deconvolution of the number distribution chromatogram

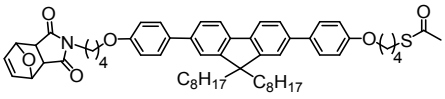
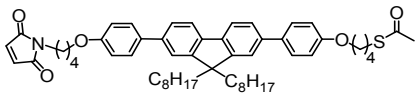
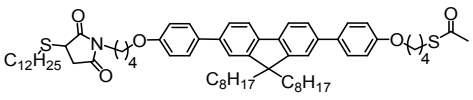
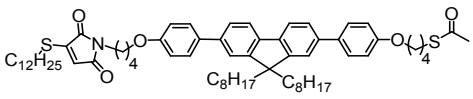
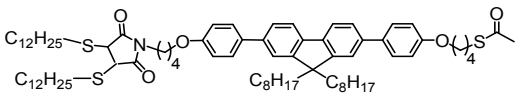
Section H. General calculation method for quantum yield of fluorescence

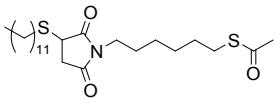
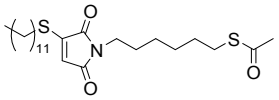
The quantum yield of fluorescence was determined relative to quinine sulfate in 0.5 M H_2SO_4 solutions with a quantum yield of 0.546, excited at 365 nm. The quantum efficiency of a sample was calculated by using the following equation:

$$\phi_f = \phi_r(A_r / A_s)(F_s / F_r)(n_s^2 / n_r^2)$$

Here ϕ_f and ϕ_r are quantum efficiencies of the sample and reference compound; A_r and A_s are the absorbances of the sample and reference solutions at the excitation wavelength; F_s and F_r are the corresponding emission intensity areas, respectively; and n_s and n_r are refractive indices of the sample and standard solutions, respectively. The experiments were repeated three times and the final value of the quantum yields were reported as the average within a deviation of ± 0.01. Details of measurement can be found in *J. Mater. Chem*. **1998,** 8, 1687.

Table S2. Fluorescence quantum yields of Model molecules.

Model molecule	solvent	$\lambda_{EX}/\lambda_{EM}$ (nm)	Φ_f/%
A: 	THF	366/388	65.1
B: 	THF	366/388	5.5
C: 	THF	366/388	66.0
D: 	THF	366/388	2.7
E: 	THF	366/388	65.9

Control sample 1: 	THF	366/388	0.01
Control sample 2: 	THF	366/388	0.24
	THF	280/306	1.12
	$CHCl_3$	366/388	0.06
	$CHCl_3$	255/300	1.55
	Toluene	366/388	0.12
	Toluene	300/404	0.37

* The sample concentration is 10^{-4} mg/mL.

Table S3. Quantum yields of fluorescence data of monodisperse polymers and derivates.

Sample name	refractive indices	FL intensity	UV Abs.	Φ_f/%
monomer	1.4961	5593	0.93	65.1
2mer	1.4961	5619	0.93	65.4
4mer	1.4962	5612	0.93	65.3
8mer	1.4961	5646	0.93	65.7
12mer	1.4962	5599	0.93	65.2
16mer	1.4963	5617	0.92	66.1
Mal-monomer	1.4965	484	0.95	5.5
Mal-2mer	1.4964	1353	0.95	15.4
Mal-4mer	1.4961	2769	0.93	32.2
Mal-8mer	1.4961	3863	0.93	45.0
Mal-12mer	1.4963	5281	0.95	60.2
Mal-16mer	1.4962	5536	0.94	63.8
cyclic-2mer	1.4964	5581	0.92	65.7
cyclic-4mer	1.4964	5611	0.92	66.0
cyclic-8mer	1.4963	5612	0.93	65.3
reduced-*cyclic*-4mer	1.4964	120	0.86	1.5
grafting-*cyclic*-4mer	1.4965	5660	0.92	66.6

* The solvent was toluene, and the sample concentration is 10^{-4} mg/mL. The maximum UV-Vis absorption of quinine sulfate was 0.11 (a.u.), and the maximum fluorescence emission intensity of the quinine sulfate was 663 (a.u.) in 0.5 M H_2SO_4 solutions, and the refractive indice of the quinine sulfate was 1.3387.

Section I. References

[1] K. Hu, Y.-j. Qi, J. Zhao, H.-f. Jiang, X. Chen, J. Ren, *Eur. J. Med. Chem.* **2013**, *64*, 529-539.

[2] T. Barton, *J. Mater. Chem.* **1998**, *8*, 1687-1690.