Supporting Information

Controlled Synthesis of Diverse Single-Chain Polymeric Nanoparticles Using Polymer Bearing Furan-Protected Maleimide Moieties

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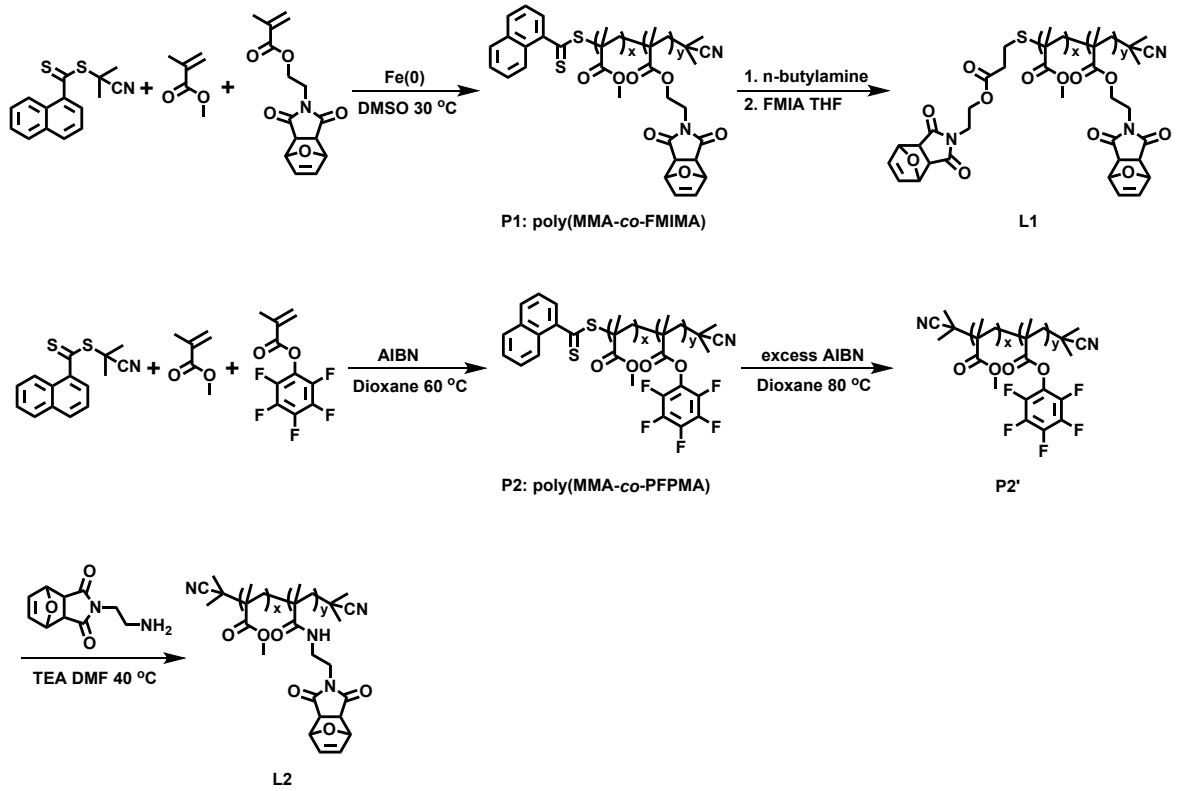
Section A. Results and Discussion



Scheme S1. The synthetic routes of linear precursors

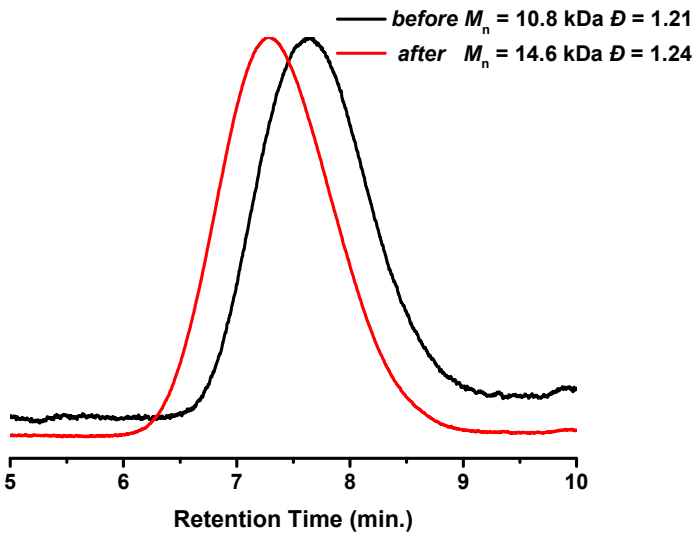


Fig. S1 SEC RI traces of poly(MMA-*co*-FMIMA) and the corresponding precursor L1 after the terminal modification, using THF as the eluent, calibrated with PMMA standards.

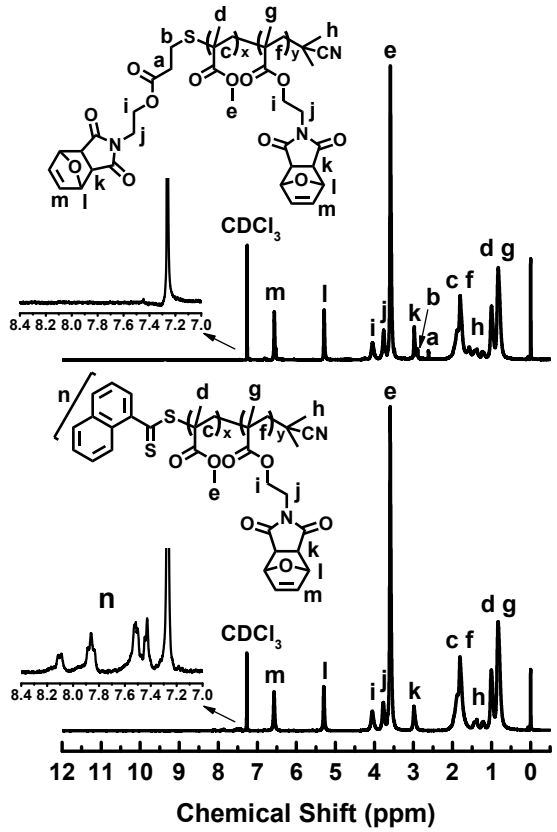


Fig. S2 Comparison of the ^{1}H NMR spectrums of poly(MMA-*co*-FMIMA) and the linear precursor L1 in $CDCl_3$.

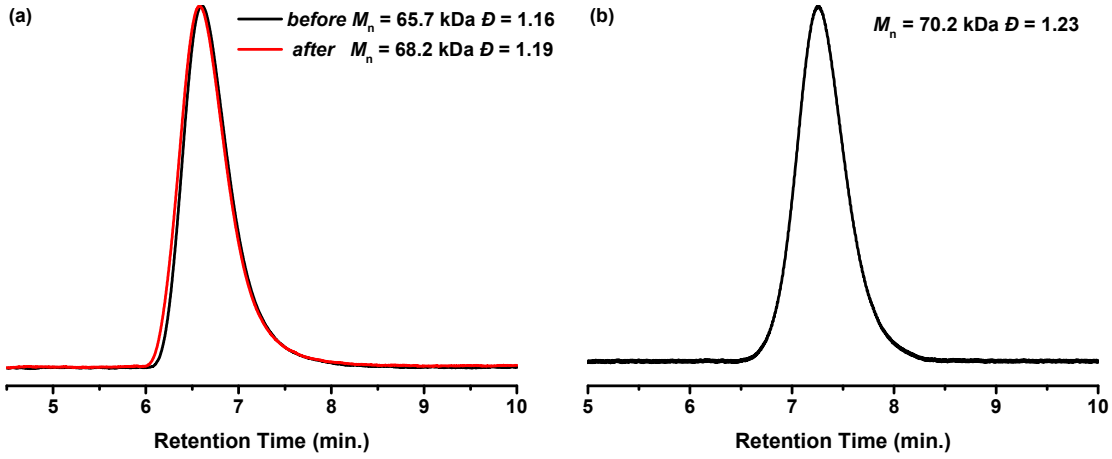


Fig. S3 (a) SEC RI traces of poly(MMA-*co*-FMIMA) and the corresponding post-modified polymer using THF as the eluent, calibrated with PMMA standards, (b) SEC RI trace of the linear precursor L2 using DMF as the eluent, calibrated with PS standards.

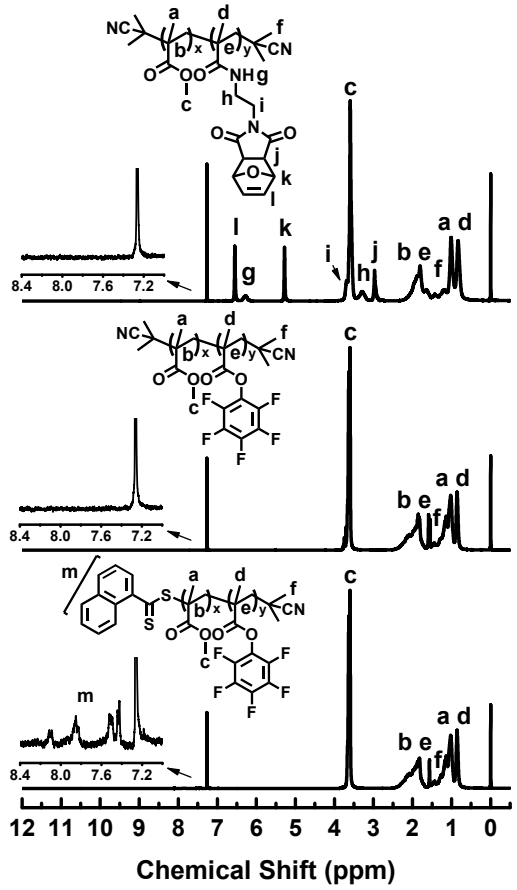


Fig. S4 Comparison of the ^{1}H NMR spectrums of poly(MMA-*co*-PFPMA) and post-modified polymers in $CDCl_3$.

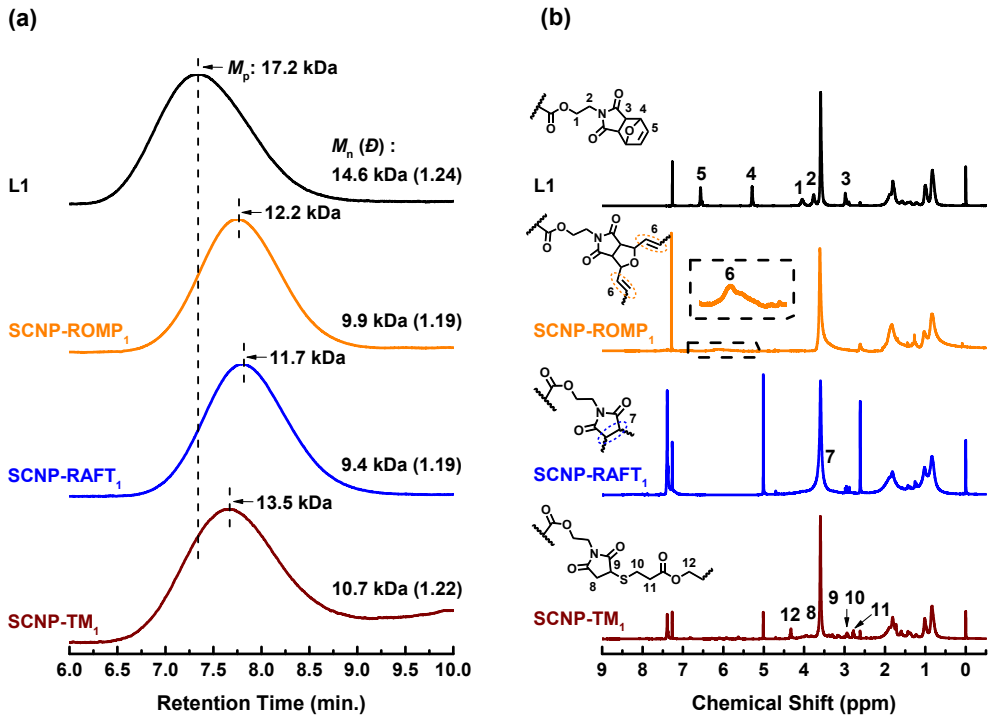


Fig. S5 Intramolecular chain collapse studies (a. SEC RI trace, b. ^{1}H NMR spectrum) of precursor L1 (40.0 mg, FMI units incorporation = 15.6%) and the resulting SCNPs (ROMP$_1$: 21.0 mg Grubbs catalyst; RAFT$_1$: 2.1 mg AIBN, 5.6 mg EXEP; TM$_1$: 6.0 mg EGDMPA).

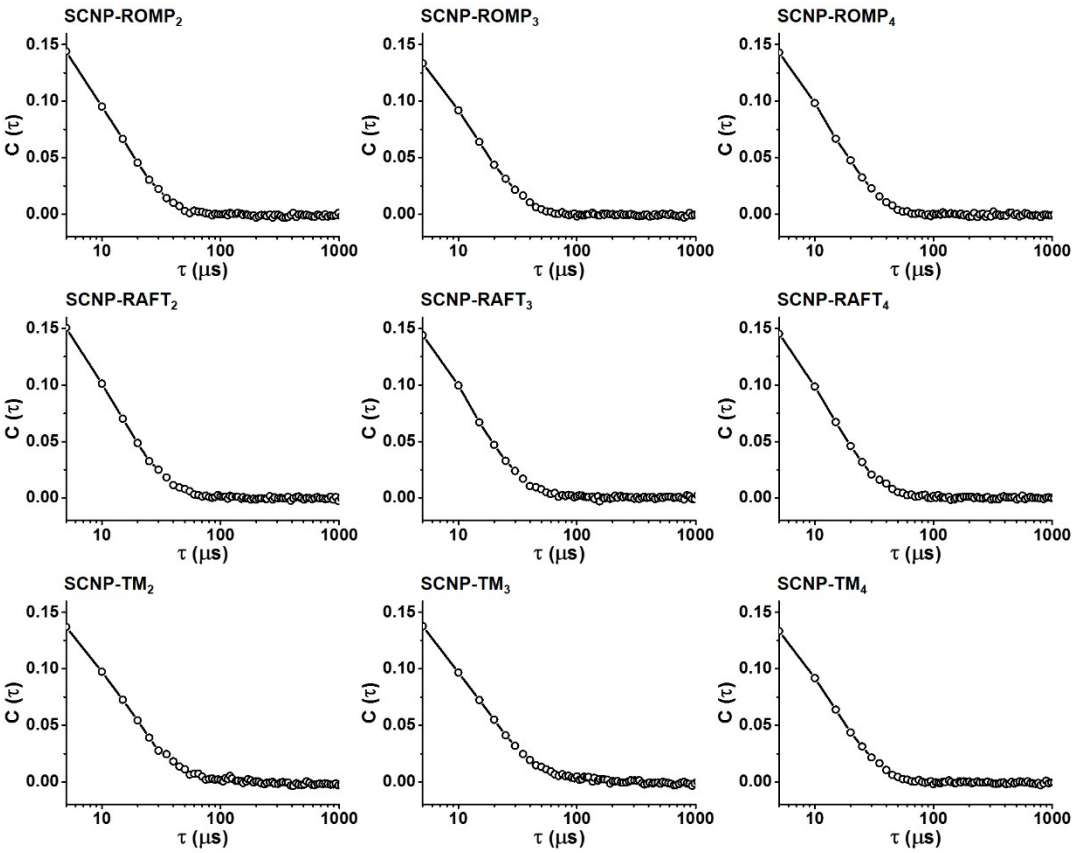


Fig. S6 Correlation functions (solid lines: fitting plots) of DLS analysis.

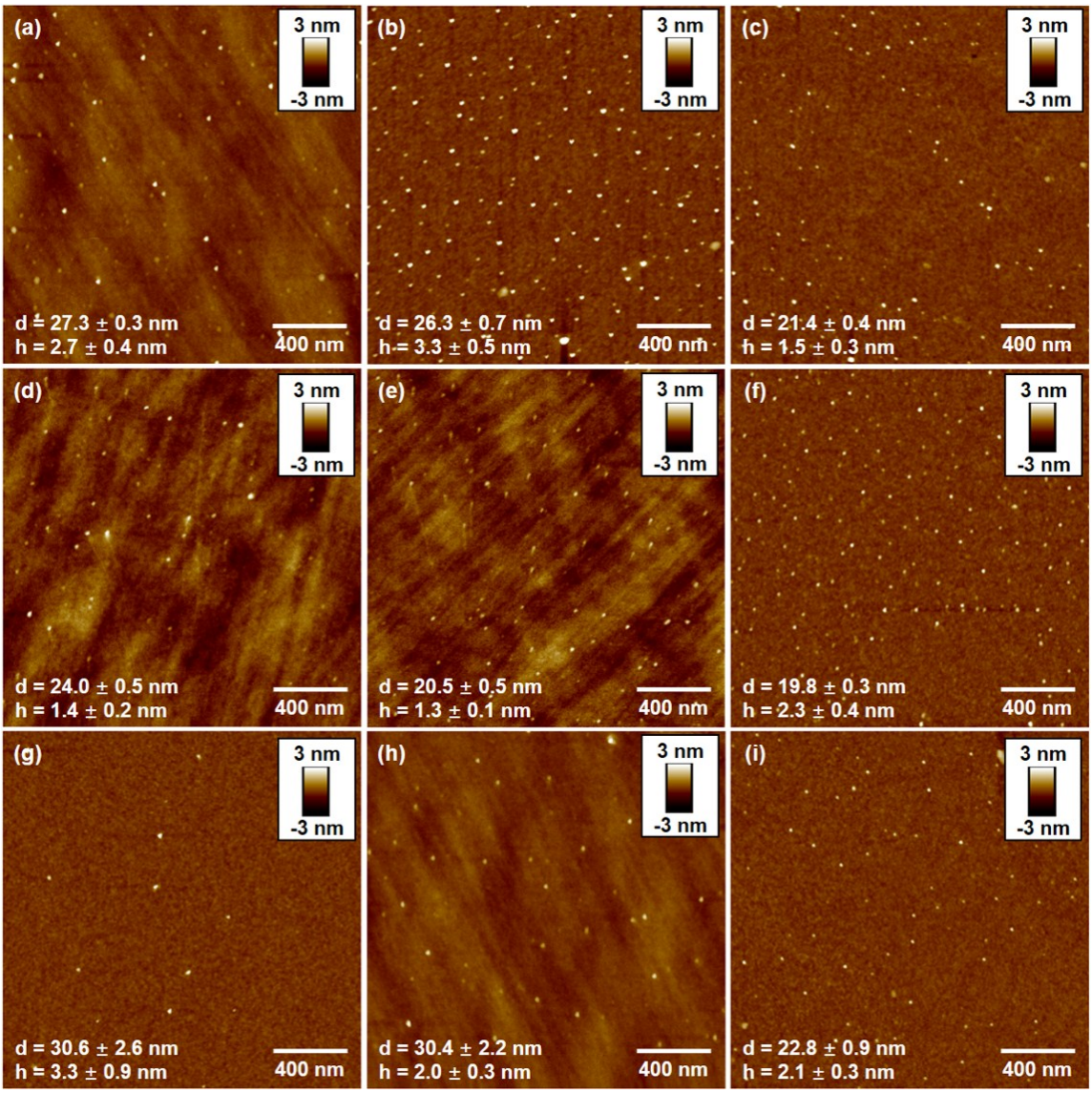


Fig. S7 AFM images of SCNPs on silica wafer [ROMP-induced collapse: a (entry 6), b (entry 7), c (entry 8); RAFT polymerization-induced collapse: d (entry 9), e (entry 10), f (entry 11); TM coupling-mediated collapse: g (entry 12), h (entry 13), i (entry 14); scanning range: 2.0 μm × 2.0 μm].

Theoretical calculation of SCNPs height size by scaling law[2]

linear precursor L2: 70.2 kDa, 16.7% FMI units incorporation.

Equation 1: height (nm) = 5.8 x^0.33 scaling law (on mica substrate, x = molar fraction of reactive groups in the precursor).

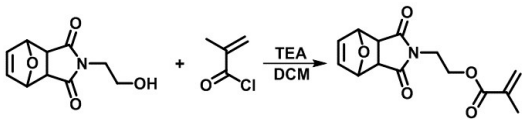
mica substrate (Fig. 5): height = 5.8×0.17^0.33 = 3.1 nm

Equation 2: height (nm) = 0.14 M^0.33 scaling law (on silicon wafer, M = molecular weight of precursor).

silicon substrate (Fig. S7): height = 0.14×70200^0.33 = 5.6 nm

Section B. Synthesis of compound 1-5

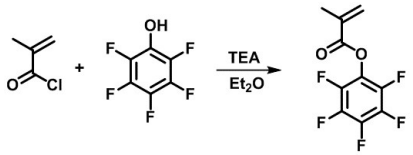
1. Synthesis of FMIMA (compound 1)



Scheme S2. Synthetic route of compound 1

Protected maleimide alcohol (18.4 g, 88.0 mmol) which was synthesized according to the literature, triethylamine (12.6 mL, 90.9 mmol) and 350 mL of dichloromethane were added into a 500 mL round-bottomed flask equipped with a magnetic stirrer. A solution of methacryloyl chloride (8.0 mL, 82.7 mmol) in 10 mL of dichloromethane was added dropwise to the solution within 30 min and the reaction mixture was stirred at 0 ^{o}C for another 2 h. Then the mixture was placed in room temperature with stirring overnight. After filtration, the filtrate was washed with saturated sodium bicarbonate solution and water respectively. The organic phase was dried with anhydrous Na_2SO_4 and thenceforth the solvent was removed by rotary evaporation. The obtained residue was purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate (1/1) to afford white solid (16.0 g, 66.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 2H), 6.07 (d, 1H), 5.56 (dd, 1H), 5.26 (d, 2H), 4.37 – 4.24 (m, 2H), 3.81 (dd, 2H), 2.86 (s, 2H), 1.98 – 1.83 (m, 3H).

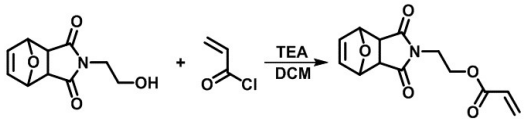
2. Synthesis of PFPMA (compound 2)



Scheme S3. Synthetic route of compound 2

Pentafluorophenol (10.0 g, 54.3 mmol) and triethylamine (7.6 mL, 55.0 mmol) were dissolved in 200 mL anhydrous diethyl ether adequately. The solution was then stirred and cooling to 0 ^{o}C within 30 minutes, to which methacryloyl chloride (5.3 mL, 55.0 mmol) was added. After removing the ice bath the reaction mixture was allowed to stir for 4 h at room temperature. The mixture was filtered and the filtrate was evaporated under reduced pressure. The crude product was purified by silica gel chromatography with petroleum ether as eluent to yield a colorless liquid (12.7 g, 92.9%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.59 – 6.39 (m, 1H), 5.91 (dd, 1H), 2.09 (dd, 3H).

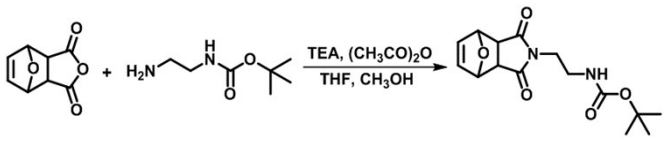
3. Synthesis of FMIA (compound 3)



Scheme S4. Synthetic route of compound 3

Protected maleimide alcohol (10.8 g, 51.6 mmol), triethylamine (7.2 mL, 52.0 mmol) and dried dichloromethane (150 mL) were mixed and stirred until completely dissolved. A solution of acryloyl chloride (4.2 mL, 51.6 mmol) in 4.2 mL of dichloromethane was added dropwise to the mixture which had been cooled to 0 ^{o}C beforehand. Then the reaction mixture was stirred overnight at room temperature. The mixture was washed with saturated sodium bicarbonate solution and water respectively. The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate (1/1) to afford shiny white solid (8.86 g, 65.2%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (s, 2H), 6.38 (dd, 1H), 6.17 – 5.97 (m, 1H), 5.83 (dd, 1H), 5.26 (s, 2H), 4.40 – 4.24 (m, 2H), 3.89 – 3.71 (m, 2H), 2.87 (s, 2H).

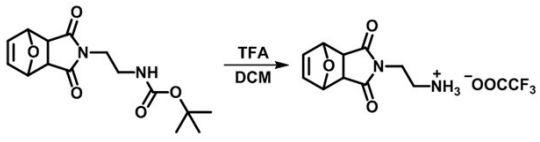
4. Synthesis of BOC-FMI (compound 4)



Scheme S5. Synthetic route of compound 4

Tert-butyl (2-aminoethyl)carbamate (9.61 g, 60.0 mmol) and triethylamine (12.5 mL, 90.1 mmol) were dissolved in a mixture of methanol and THF (40 mL, v/v = 1:1). The system was placed in an ice bath, to which furan-protected maleic anhydride (10.0 g, 60.2 mmol) fully dissolved in a mixture solution of methanol and THF (300 mL, v/v = 1:1) was added dropwise. Then the mixture was warmed up to room time and stirred for an additional 4 hours. The reactor was moved to an oil bath which was preheated to 60 ^{o}C and acetic anhydride (8.5 mL, 89.9 mmol) was added into the mixture. The solution was concentrated by evaporation 20 hours later. The residue was re-dissolved in dichloromethane and was washed with saturated NH_4Cl and brine. The organic phase was dried with anhydrous Na_2SO_4, filtered and concentrated in vacuo. Target product was obtained by flash column chromatography over silica gel eluting with petroleum ether/ethyl acetate (1/2) to yield shaggy solid (9.17 g, 49.6%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.83 (t, 1H), 6.54 (s, 2H), 5.11 (s, 2H), 3.39 (dd, 2H), 3.03 (dd, 2H), 2.88 (s, 2H), 1.36 (s, 9H).

5. Synthesis of NH_2-FMI (compound 5)



Scheme S6. Synthetic route of compound 5

BOC-FMI (6.46 g, 21.0 mmol) and dichloromethane (150 mL) were added to 250 mL round-bottom flask, which was place in an ice bath. Trifluoroacetic acid (32.0 mL, 430.8 mmol) was added to the system slowly and then the reaction mixture was stirred for another 1 h. The solution was concentrated and mixed with cold diethyl ether. The precipitated solid (6.62 g, 98.0%) was triturated and washed with cold diethyl ether without further purification. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.85 (s, 3H), 6.56 (s, 2H), 5.14 (s, 2H), 3.62 (t, 2H), 3.13 – 2.86 (m, 4H).

Section C. References

1. J. F. Zhao, Y. Y. Zhou, Y. Zhou, N. C. Zhou, X. Q. Pan, Z. B. Zhang and X. L. Zhu, Polym. Chem., 2016, 7, 1782-1791.

2. J. De-La-Cuesta, E. González, A. J. Moreno, A. Arbe, J. Colmenero and J. A. Pomposo, Macromolecules, 2017, 50, 6323-6331.