Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting Information

Folding-Directed Catalytic Microenvironment in Helical Dynamic Covalent Polymers Formed by Spontaneous Configuration Control

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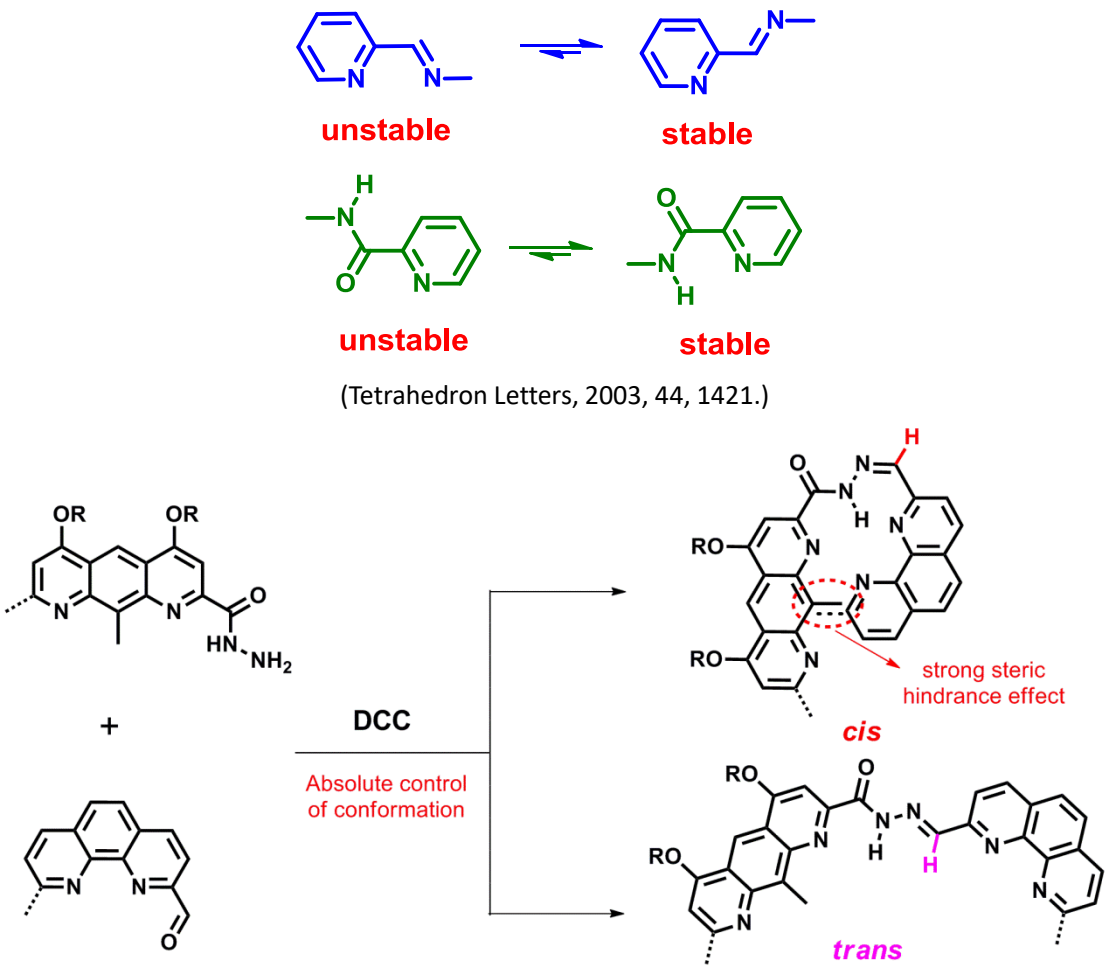


Figure S1. The stable conformation analyses of structural motifs and polymer **1** formed by dynamic covalent reaction including *cis* and *trans* conformations.

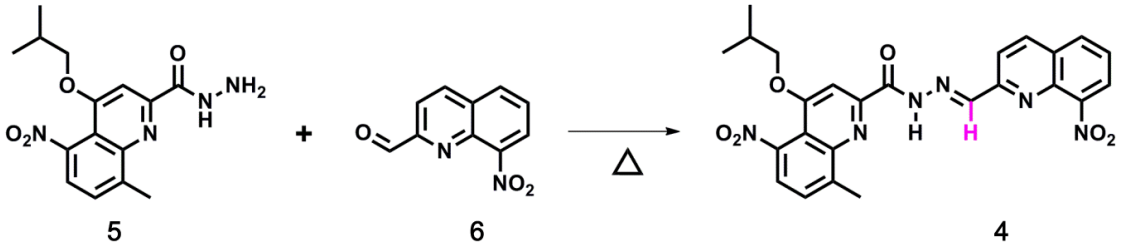


Figure S2. An experiment whose structure of product (compound 4) is the same with the skeleton of polymer **1**.

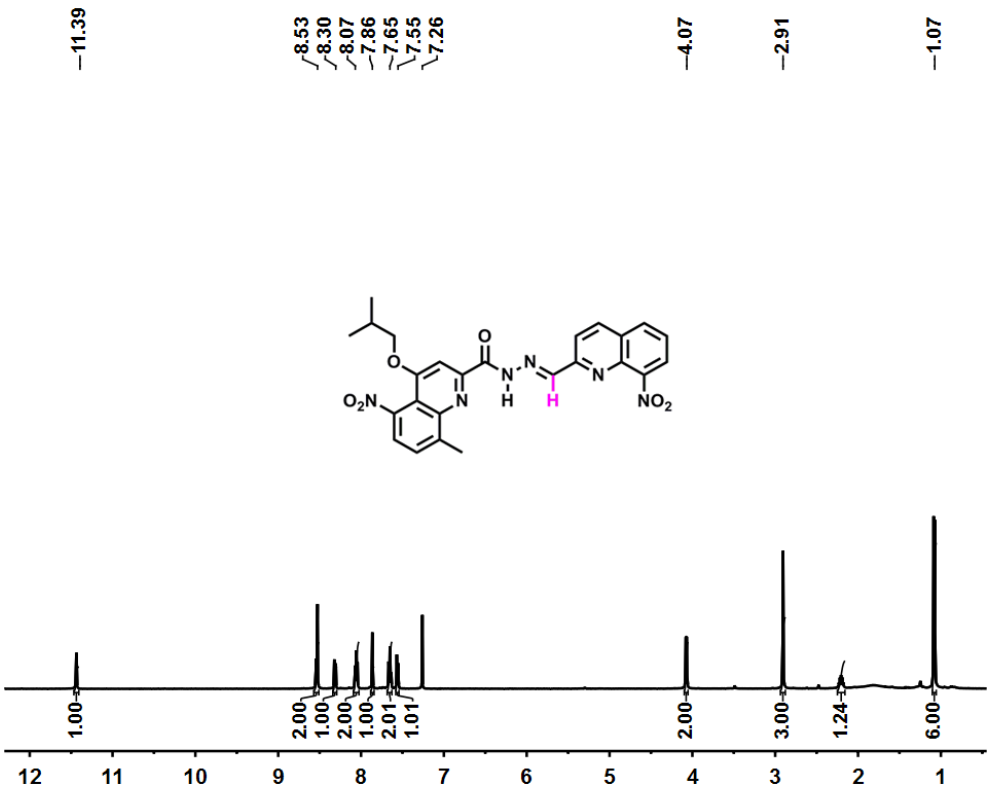


Figure S3. ^{1}H NMR spectrum of compound **4**.

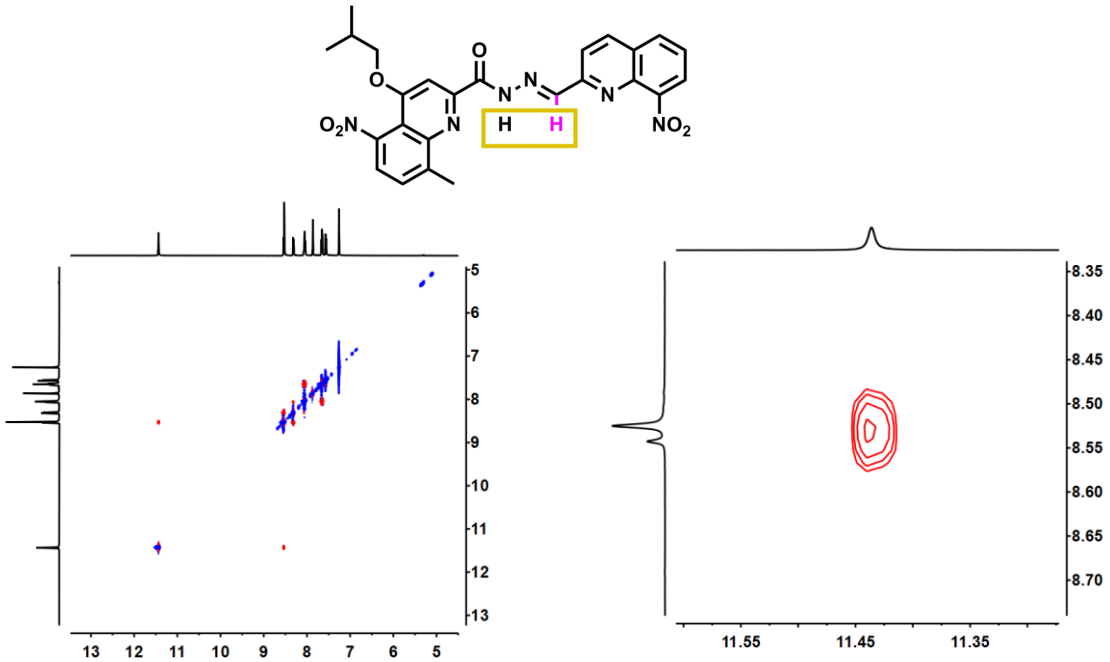


Figure S4. 2D NMR spectra of the compound above (15 mM) in $CDCl_3$ at 298 K. The yellow border indicates the NOE interactions present between the protons in the structure.

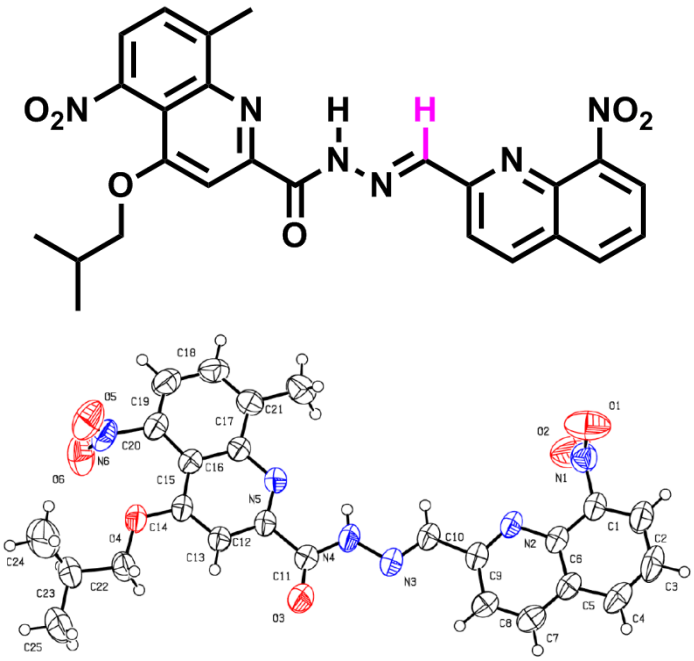
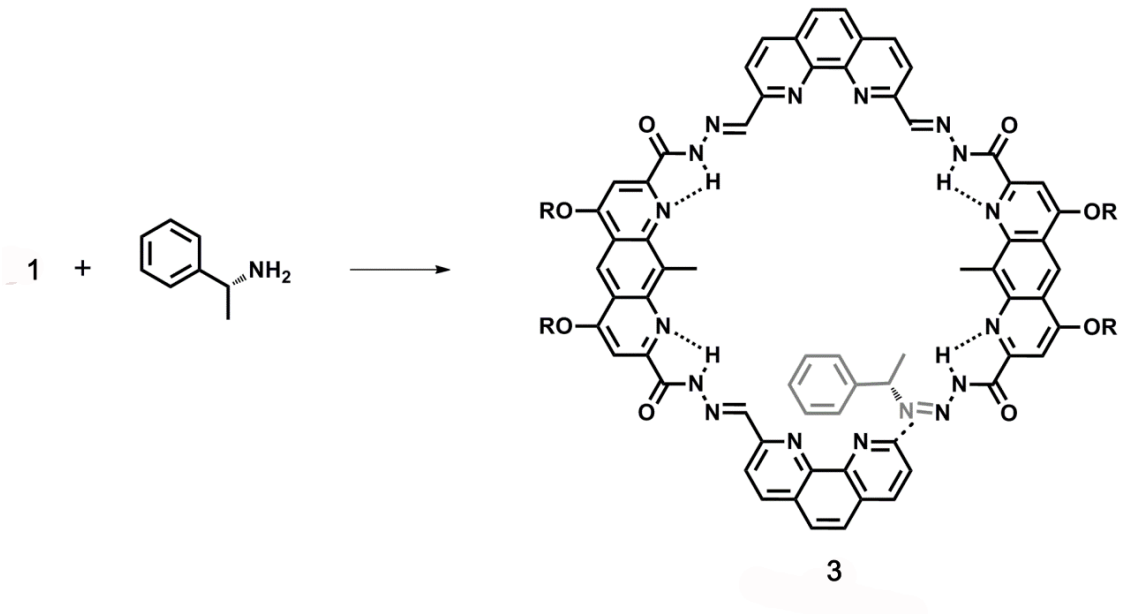


Figure S5. The crystal structure of the compound **4**.



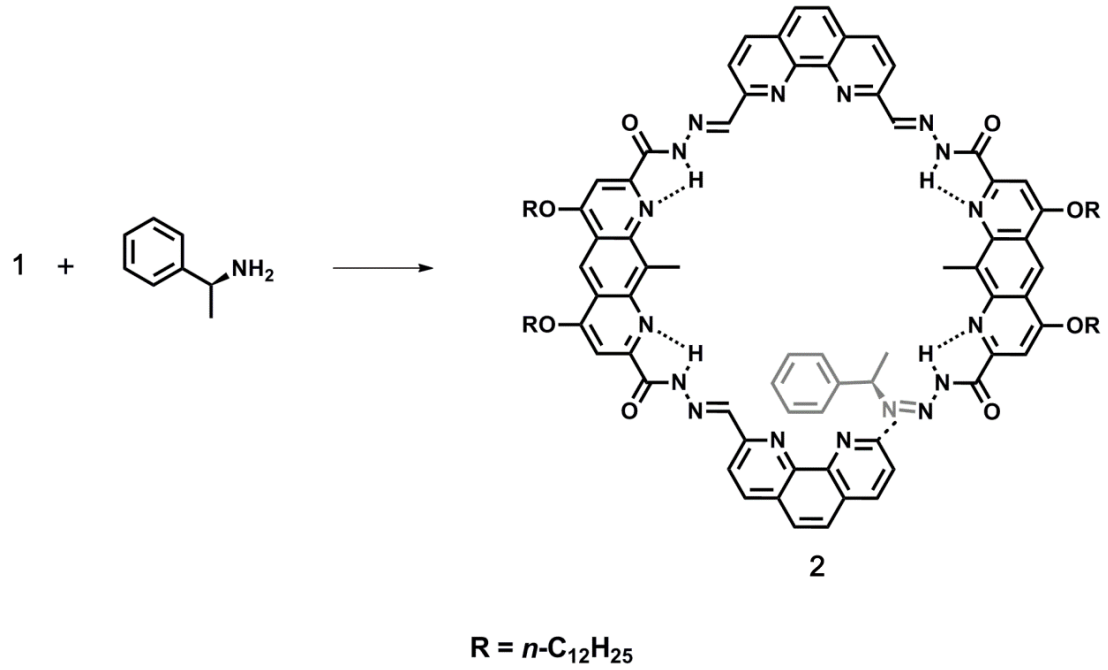


Figure S6. The synthetic procedure of the chiral dynamic covalent helical polymer **2** and **3**.

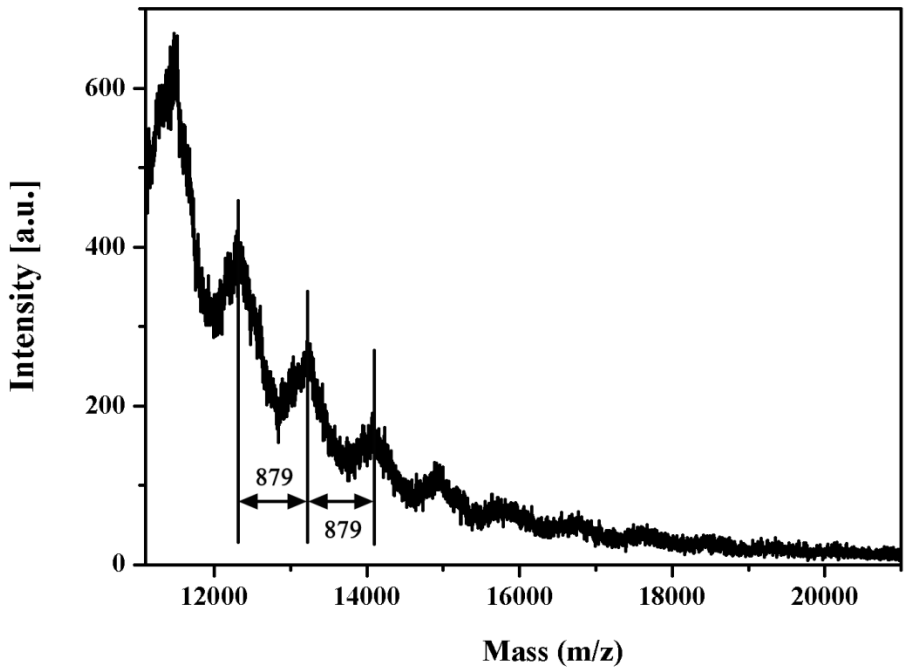


Figure S7. MALDI-TOF MS of polymer **1**. The mass difference between neighboring peaks is 879 g/mol that is consistent with the actual molecular weight of repeating units.

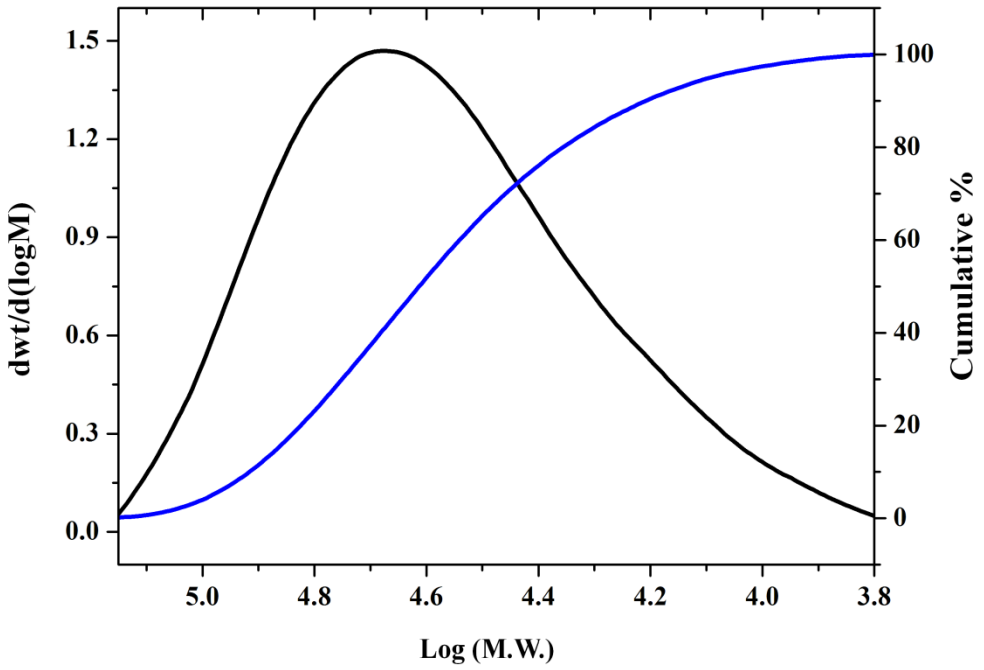


Figure S8. The GPC curve of polymer **1**.

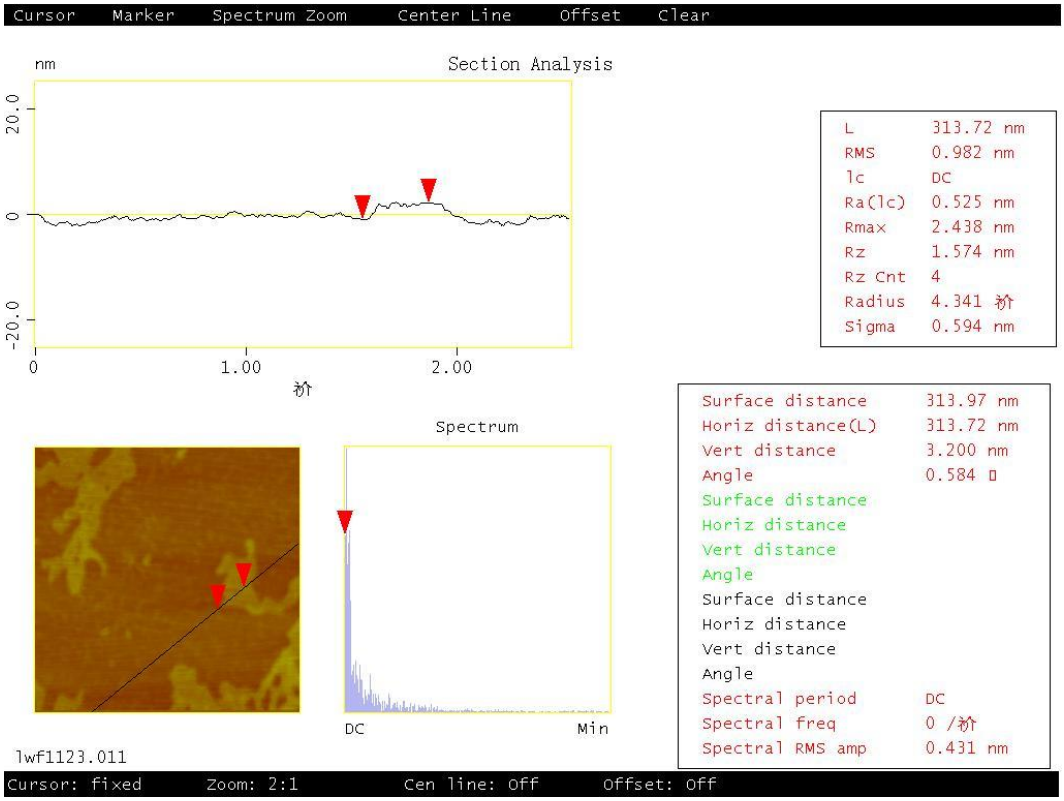


Figure S9. AFM image and height profile of aggregates from polymer **1**.

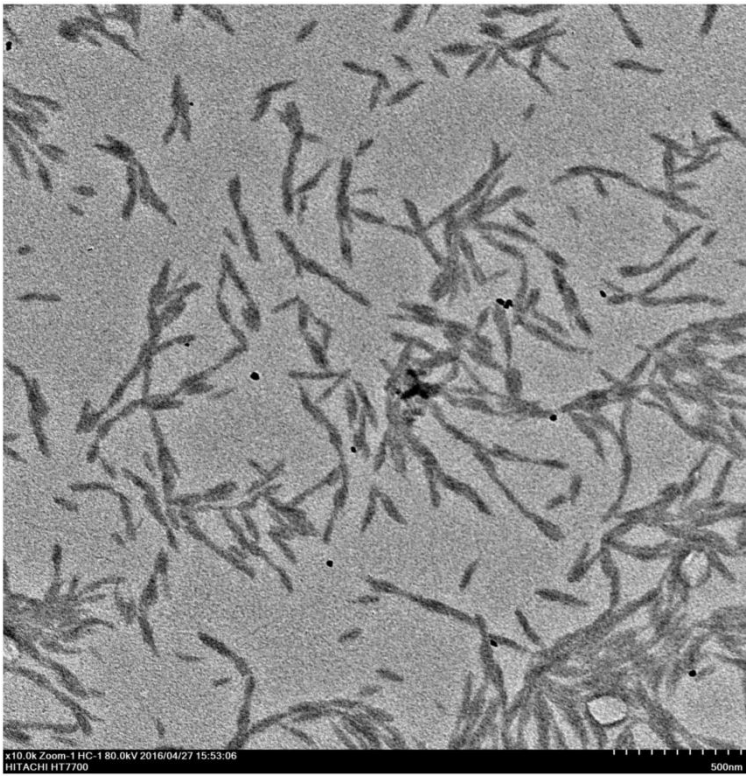


Figure S10. TEM image of aggregates formed by self-assembly of polymer **1**.

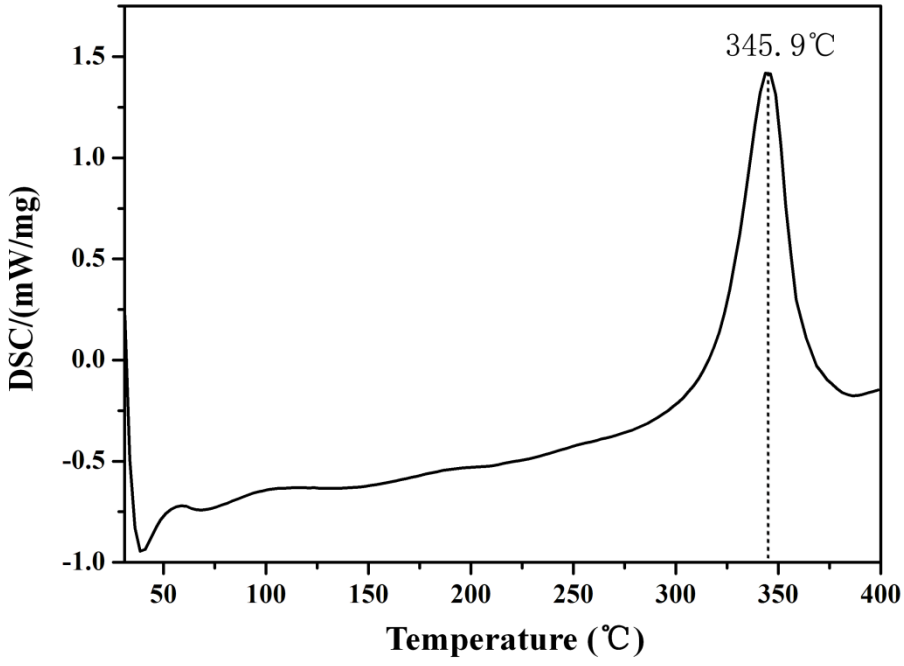


Figure S11. DSC spectrum of polymer **1**.

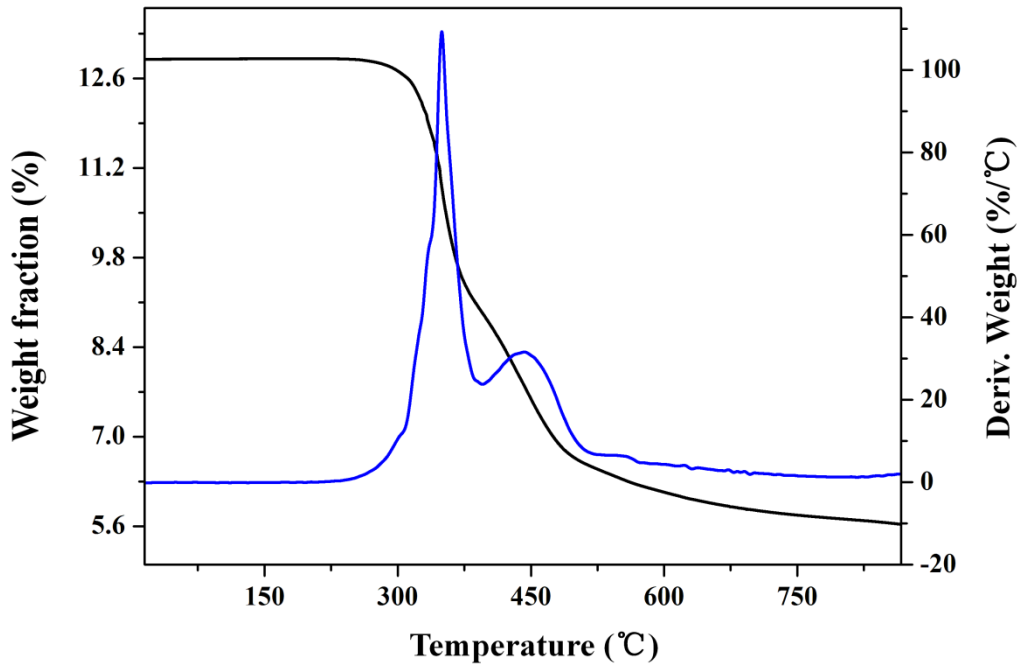


Figure S12. TGA and DTG profiles of polymer **1**.

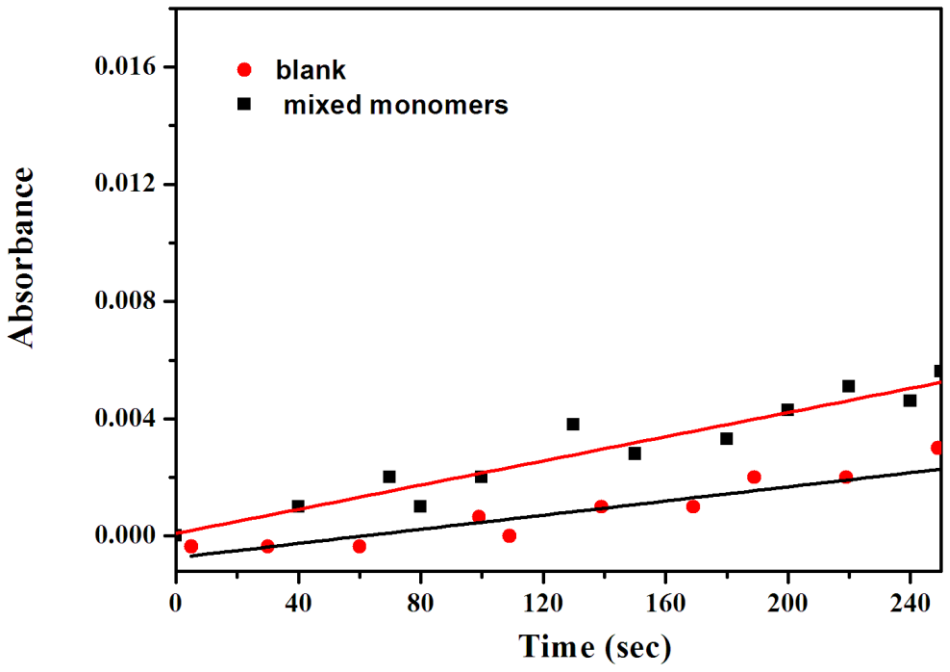


Figure S13. Mixed monomers (monomer **8** and monomer **9**, 1 μM) in solvent of 3:1 chloroform/ methanol at 37 ˚C without obvious catalytic ability compared with the blank under the same conditions.

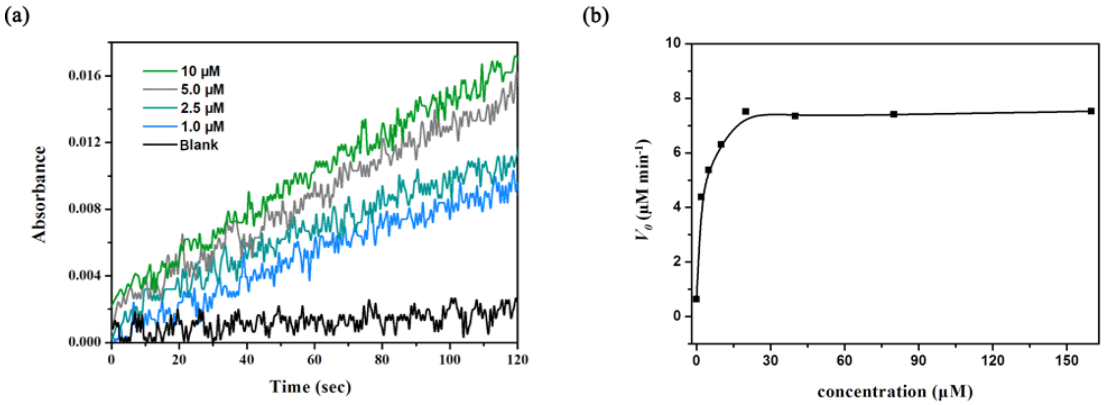
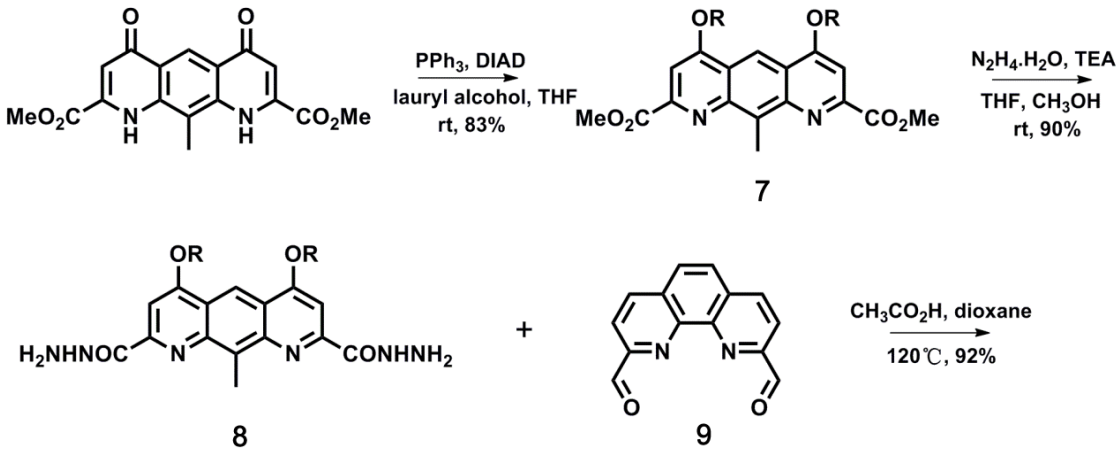


Figure S14. a) Plots of absorbance vs time during the oxidation of different concentration of PhSH by H_2O_2 (200 μM) with catalyst DCHP (1 μM) in mixed solvent of 3:1 chloroform/ hexane with 1% acetonitrile at 37 ℃. Blank: PhSH: 100 μM, H_2O_2: 200 μM, DCHP: none at 37 ℃. b) Plot of initial oxidation rates V_0 vs different concentration of PhSH with same conditions of plot a) at 37 ℃, the concentration were 0 μM, 1 μM, 2.5 μM, 5 μM, 10 μM, 20μM, 40μM, 80μM, respectively.



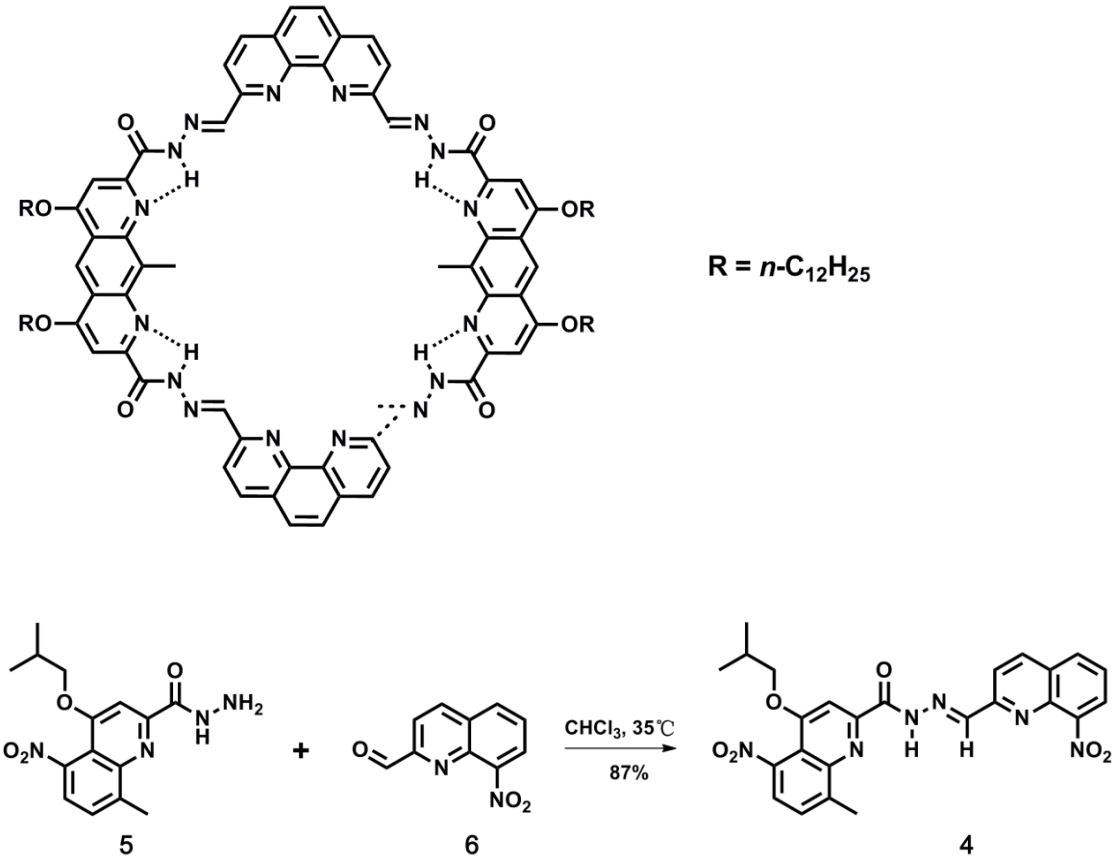


Figure S15. The synthetic procedure of the dynamic covalent helical polymer **1** and compound **4**.

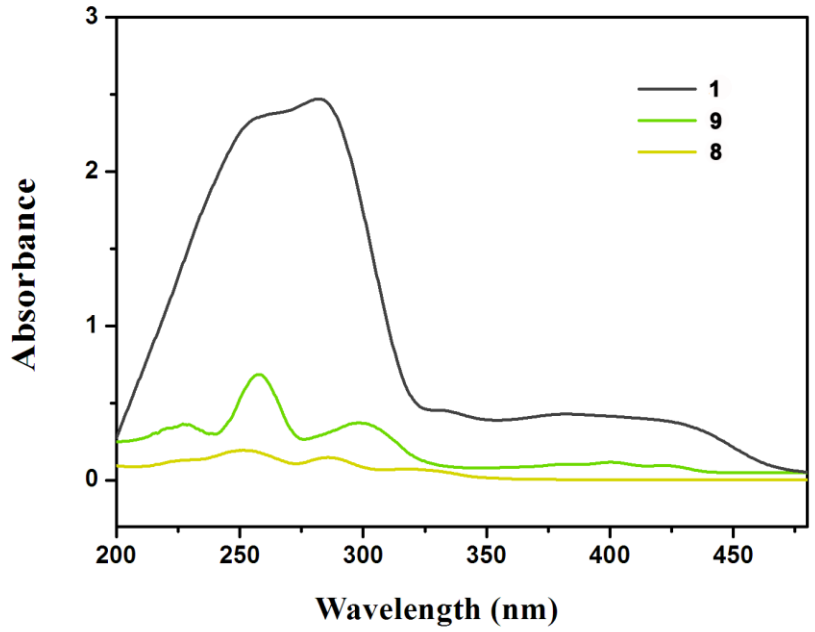


Figure S16. UV spectrum of monomer **8**, **9** and polymer **1**.

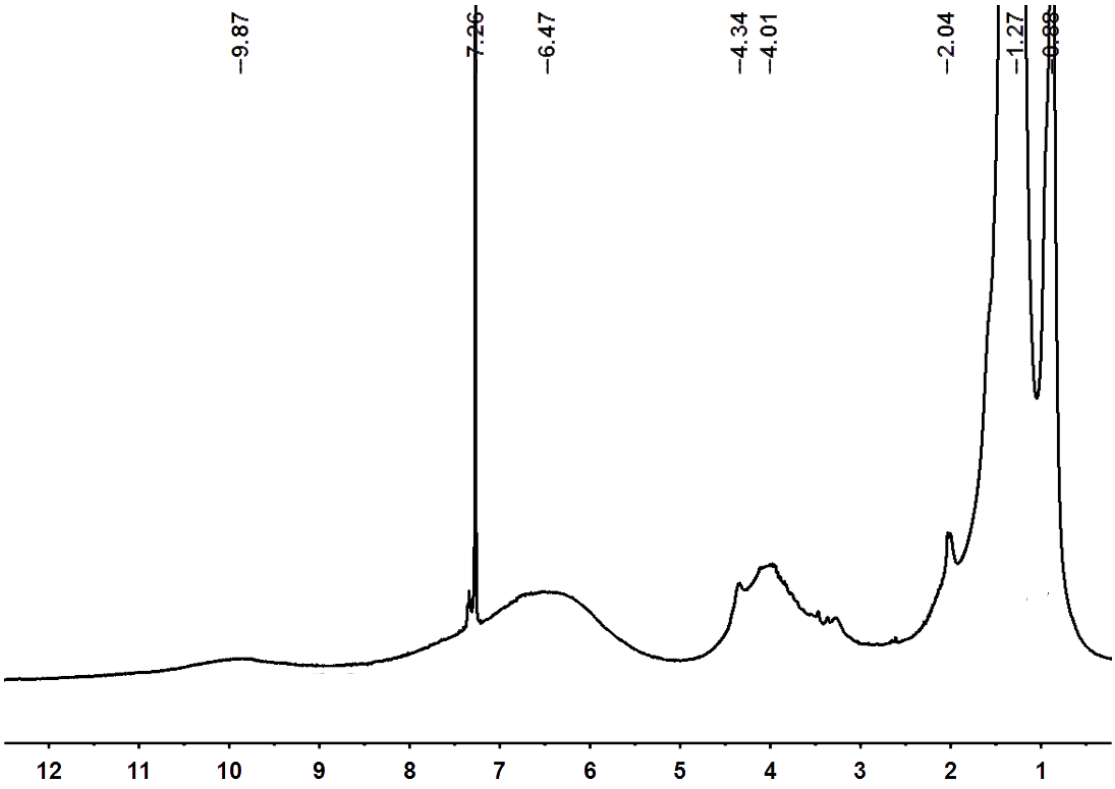


Figure S17. ^{1}H NMR spectrum of polymer **1** (Mn 31000 g/mol, PDI 1.46) in $CDCl_3$.

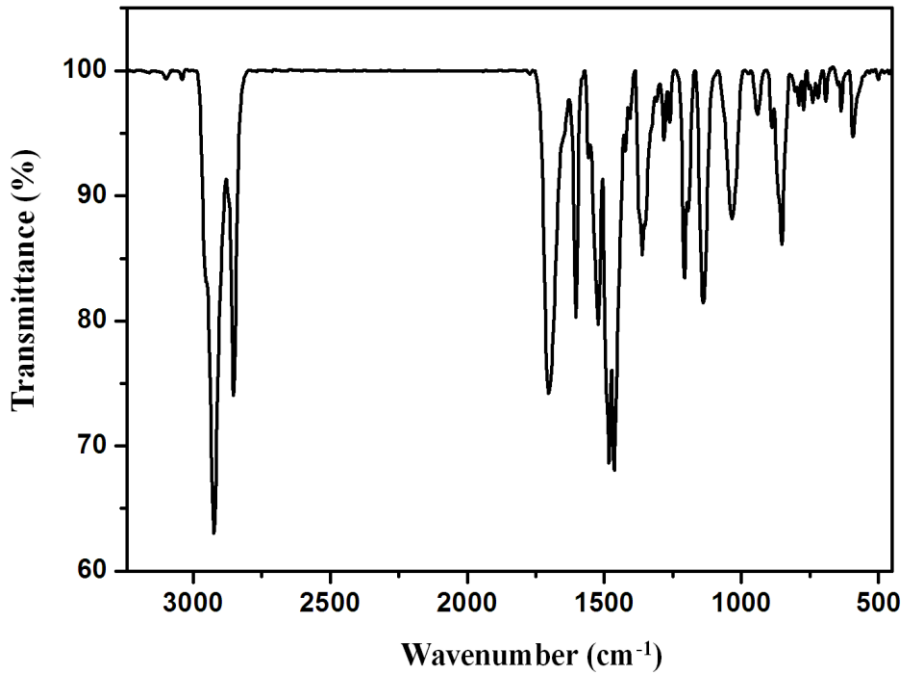


Figure S18. IR spectrum of polymer **1**.

Experimental Procedures and Compound Characterizations

Synthesis of compound **7**

To a mixed solution of triphenylphosphine (21.4g, 81.6mmol), lauryl alcohol (13.9ml, 61.2mmol) and dimethyl-10-methyl-4,6-dioxo-1,4,6,9-tetrahydropyrido[3,2-g] quinoline-2,8-dicarboxylate (7.0g, 20.5mmol) in dry tetrahydrofuran (300ml) under N_2 atmosphere and ice bath condition was added diisopropyl azodiformate (16.1ml, 81.6mmol). The reaction was stirred overnight at room temperature, and the solvent was removed in vacuo. The crude mixture was purified by recrystallization in methanol to provide the desired product **1** (11.5g, 16.9mmol) as yellow powder, yield 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.08 (s, 1H), 7.51 (s, 2H), 4.36 (t, J=6.4, 4H), 4.09 (s, 6H), 3.50 (s, 3H), 2.07 – 2.00 (m, 4H), 1.66 – 1.59 (m, 4H), 1.48 – 1.41 (m, 4H), 1.39 – 1.24 (m, 28H), 0.87 (t, J=6.9, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 166.55, 163.46, 149.77, 145.95, 139.18, 121.60, 113.52, 98.78, 77.41, 77.16, 76.91, 69.22, 53.26, 32.04, 29.83, 29.79, 29.50, 29.48, 28.97, 26.25, 22.80, 14.20, 13.19. MS (TOF MS ES+): calcd for $[C_{41}H_{62}N_2O_6H+H]^+$: 679.46; found: 679.36.

Synthesis of compound **8**

Hydrazine hydrate (2.14ml, 44.2mmol) was added to a solution of compound 7 (1.5g, 2.21mmol) in a mixture of tetrahydrofuran (3 mL) and trichloromethane (3ml), then triethylamine (6.2ml, 44.2mmol) was added and the solution was stirred at room temperature , Then the solvents were evaporated to dryness, the residue was washed with water and the pure product was obtained by filtration as a yellow powder, Yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 9.29 (s, 2H), 9.01 (s, 1H), 7.56 (s, 2H), 4.37 (t, J=6.5, 4H), 4.18 (d, J=4.6, 4H), 3.26 (s, 3H), 2.07 – 2.00 (m, 4H), 1.65 – 1.59 (m, 4H), 1.48 – 1.41 (m, 4H), 1.39 – 1.24 (m, 28H), 0.87 (t, J=6.9, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 165.32, 164.01, 151.03, 145.12, 136.14, 121.39, 120.17, 114.12, 96.63, 77.41, 77.16, 76.91, 69.48, 32.07, 29.85, 29.82, 29.81, 29.53, 29.51, 29.02, 26.27, 22.82, 14.22, 12.91. MS (TOF MS ES+): calcd for $[C_{39}H_{62}N_6O_4+H]^+$: 679.48; found: 679.25.

Synthesis of compound **1**

Catalytic amount of acetic acid (0.2ml) was added to a mixture of 8 (0.72g, 1.06mmol) and 9 (0.25g, 1.06mmol) in 1,4-dioxane (10ml) under nitrogen condition, the mixture was sealed and refluxed at 120℃ without disturbance for 4 days. The solvent was removed in vacuo and the crude product was obtained as brown powder, which was washed by dioxane for 3 times and recrystallized by methanol, then dried under vacuum at 50 °C for 4 h to afford a red-brown powder (0.89g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.39 – 9.05 (m, 2H), 8.79 – 5.22 (m, 9H), 4.81 – 2.94 (m, 7H), 2.53 – 0.30 (m, 46H). Elemental analysis calculated for $[C_{53}H_{66}N_8O_4]_n$: C 72.41, H 7.57, N 12.75; found: C 67.81, H 7.42, N 11.47. IR [cm^{-1}]: 3279, 3059, 2925, 2851, 1704, 1602, 1522, 1483, 1462, 1362, 1311, 1283, 1260, 1208, 1195, 1136, 1033, 940, 891, 849, 803,

790, 772,720. Decomposition temperature > 300℃.

Synthesis of compound **2** and **3**

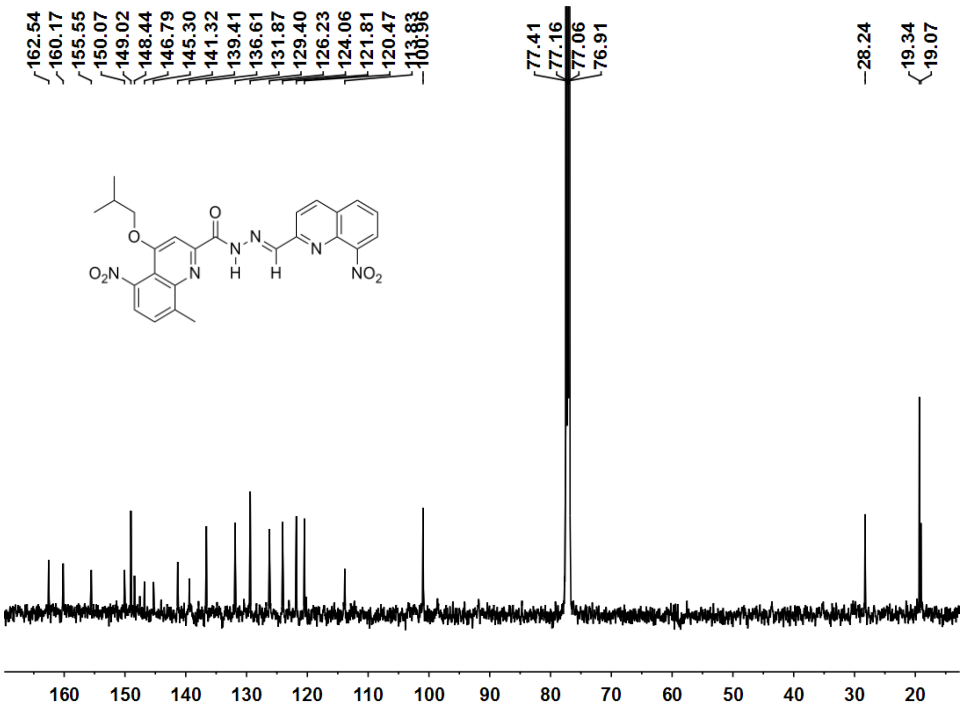
(S)-(-)-α-methylbenzylamine (0.012mmol) was added to the mixture of polymer **1** (100 mg) in chloroform under anhydrous atmosphere. The sealed reaction mixture was stirred for 6h at 35℃, the solvent was removed in vacuo and the residue was dispersed into methanol. The precipitation was filtered and collected, and the residue was washed with methanol three times to afford a brown solid (90 mg, 90%). Decomposition temperature > 300℃.

Compound **3** (88mg) was also prepared by using (R)-(+)-α-methylbenzylamine in the same way as mentioned above. The characterization is the same as compound **2**.

Synthesis of compound **4**

To a mixture of compound 5 (0.24g, 0.75mmol) and 6 (0.10g, 0.50mmol), added 6 ml of dry chloroform, the mixture was stirred at 35℃ overnight, then the solvent was removed in vacuo and the pure white product was obtained (0.21g, 87%) by column chromatography (silica gel, dichloromethane/ methanol =100/1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.53 (d, J = 8.7 Hz, 2H), 8.31 (d, J = 8.7 Hz, 1H), 8.06 (t, J = 6.7 Hz, 2H), 7.86 (s, 1H), 7.65 (t, J = 7.7 Hz, 2H), 7.56 (d, J = 7.6 Hz, 1H), 4.07 (d, J = 6.2 Hz, 2H), 2.91 (s, 3H), 2.20 (m, J = 13.3, 6.7 Hz, 1H), 1.08 (d, J = 6.7 Hz, 6H). ^{13}C NMR (500 MHz, $CDCl_3$) δ = 162.54, 160.17, 155.55, 150.07, 149.02, 148.44, 147.56, 146.79, 145.30, 141.32, 139.41, 136.61, 131.87, 129.40, 126.23, 124.06, 121.81, 120.47, 113.83 , 100.96, 77.41, 77.16, 77.06, 76.91, 28.24, 19.34, 19.07. MS (TOF MS ES+): calcd for $[C_{25}H_{22}N_6O_6+H]^+$: 503.16; found: 503.16.

NMR data



Crystal data block

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Calculated Reported
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Hall group                -P 2yn                    -P 2yn
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