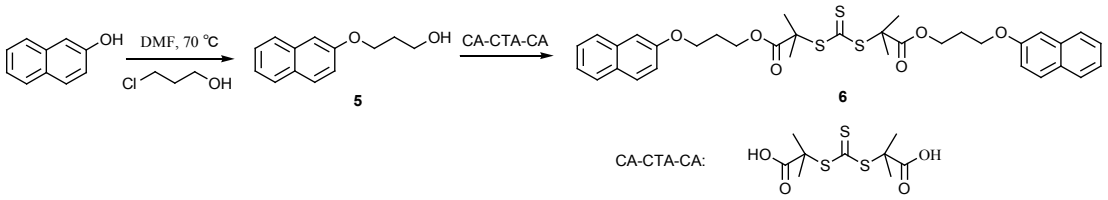
Experimental Section

Materials. *N*,*N*-Dimethylacrylamide (DMA, distilled under reduced pressure before polymerization) and *N*-Isopropylacrylamide (NIPAM, recrystallized three times from benzene/hexane (65:35 v/v) prior to use) were purchased from Tokyo Kasei Kagyo Co. Azodiisobutyronitrile (AIBN, CP, recrystallized from ethanol before use) were supplied by Sinopharm Chemical Reagent Co. N,N-dimethylformamide (DMF) and dichloromethane (CH_2Cl_2) were dried by calcium hydride and distilled before use. S,S'-Bis(α,α'-dimethyl-α''-acetic acid)-trithiocarbonate was synthesized according to the literature[1]. Cucurbit[8]uril was prepared by following reported procedure[2]. Unless specially mentioned, all other chemicals were used as received.

Characterizations. ^{1}H NMR spectra were recorded with a JEOL ECA-400 spectrometer or a Bruker DMX500 spectrometer. ^{13}C NMR (126 MHz) spectra were performed on a Bruker DMX500 spectrometer. MALDI-TOF experiments were performed on Voyager DE-STR MALDI-TOF MS from the Applied Biosystems (USA). Gel permeation chromatography (GPC) analysis was carried out with a Waters Breeze 1525 GPC analysis system with two TSK-gel column, using DMF with 0.5 M LiBr as eluents at the flow rate of 1 mL/min at 80 ºC, PEO calibration kit (purchased from TOSOH) was used as the calibration standard. To confirm the desired telechelic structure of **P1** and **P2**, aminolysis of the polymers was carried out with treatment of excess hydrazine for 20 min. The ITC experiments were carried out on a MicroCal VP-ITC system at 25.00 ± 0.01 ºC. Experimental titration curves were analyzed with the Origin LLC ITC 7.0 program. UV-vis spectra were recorded in a conventional quartz cell (light path 10 mm) on a spectrophotometer (Shimadzu UV-2550) equipped with a temperature controller. Optical transmittance of aqueous sample solutions was measured at 800 nm to avoid the absorbance caused by HSCT. The solutions were heated at the rate of 0.2 °C/min in LCST test. Dynamic light scattering studies were conducted by using ALV/5000E laser light scattering (LLS) spectrometer at scattering angle of 90°, CONTIN analysis was used for the extraction of R_h data. Samples were filtered through 450 nm PVDF filters before test.

Viscometry. Viscosities were measured in an Ubbelohde semi-micro dilution viscometer immersed in a thermostatic water bath (± 0.01 °C) with a 0.63 mm inner diameter capillary (ZONWON IVS300). Samples were filtered over 450 nm PVDF filters and stand at 20 °C (15 °C for samples containg **P2** to avoid aggregation) for 20 min before test. Flowing time was recorded by a laser timer automatically. Every sample was tested at least three times and the error was kept less than 0.1 second.

TEM sample preparation. TEM observations were conducted on a Philips CM120 electron microscope at an acceleration voltage of 80 kV. Samples for TEM observation were prepared in the following way: one drop of solution after 1 h incubation at 4 °C freezer was loaded onto carbon-coated copper grids and kept at 4 °C for further 15 minutes. Then excess liquid was removed by a filter paper and the copper grid was quickly transferred into a vaccum.



Scheme S1. Synthetic procedure of Np functionalized RAFT CTA

Synthesis of CA-CTA-CA. S,S'-Bis(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (CA-CTA-CA) was synthesized according to the procedure described in the literature[1].

Synthesis of compound 5. Typically**,** to the solution of 2-naphthol (8.7 g, 60 mmol), potassium carbonate (16.6 g, 120 mmol) and catalytic amount of potassium iodide in anhydrous DMF (300 mL) was added 6.5 mL 3-Chloropropanol (7.4 g, 78 mmol). The reaction mixture were kept at 70 °C for 24 h under N_2. After cooled to room temperature, most solvent was removed under reduced pressure and the resulting mixture was precipitated in water. The precipitate was dissolved in DMF and precipitated again into an excess of H_2O. Then the crude product was purified by column chromatography, using dichloromethane as eluent. The obtained white solid (9.2 g, 76%) was characterized by ^{1}H NMR (Fig. S1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.72 (dd, 3H), 7.46-7.42 (t, 1H), 7.36-7.32 (t, 1H), 7.16-7.13 (m, 2H), 4.26-4.23 (t, 2H), 3.94-3.90 (q, 2H), 2.15-2.09 (m, 2H).

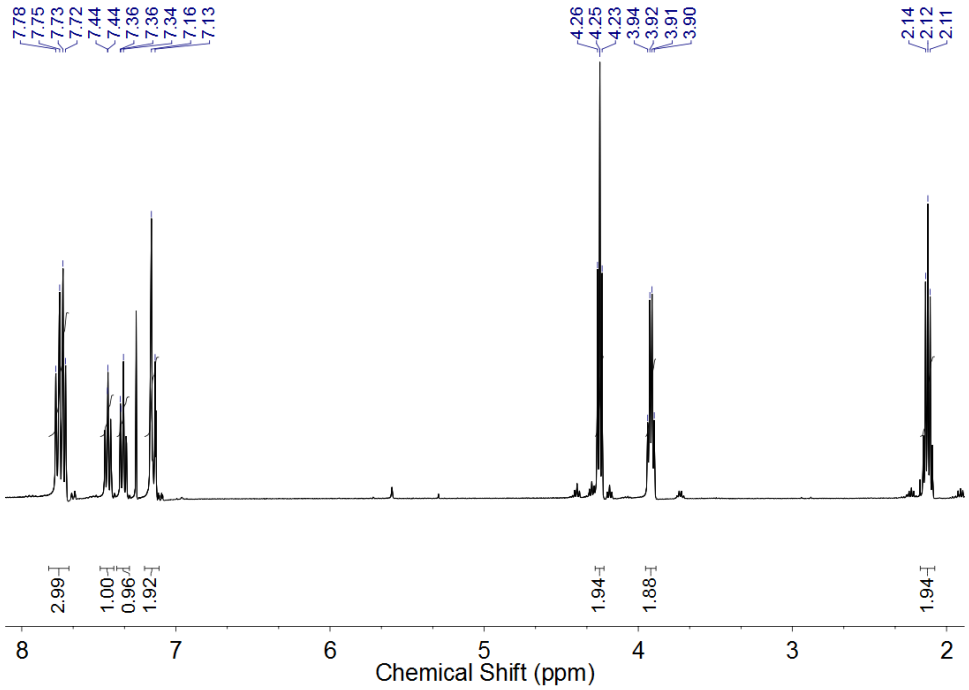


Fig. S1. ^{1}H NMR spectrum of compound **5**

Synthesis of compound Np-CTA-Np 6. Np-CTA-Np (**6**) was synthesized according to the literature[3] with some modification. Firstly, CA-CTA-CA (0.51 g, 1.81 mmol), compound **5** (0.8 g, 3.98 mmol) and triphenylphosphine (PPh_3) (1.04 g,

3.97 mmol) were dissolved in distilled CH_2Cl_2. Diisopropyl azodicarboxylate (DIAD) (0.81 g, 4.01 mmol) diluted with distilled CH_2Cl_2 was then added dropwise at 0 °C under Ar atmosphere. After stirred at room temperature overnight, the solution was heated to 40 °C during 3 h. Then the reaction mixture was cooled to room temperature, diluted with dichloromethane (150 mL) and washed with distilled water (2×200 mL). The organic layer was collected and dried with $MgSO_4$. The solvent was removed under reduced pressure and the resulting yellow oil was purified by column chromatography using dichloromethane: hexane (*v*:*v* = 2:1) as eluent. The combined fractions were concentrated to dryness and the resulting yellow oil crystallized slowly at room temperature (0.6 g, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.71 (dd, 6H), 7.45-7.41 (t, 2H), 7.35-7.31 (t, 2H), 7.13-7.11 (m, 4H), 4.31-4.28 (t, 4H), 4.11-4.08 (t, 4H), 2.17-2.10 (m, 4H), 1.62 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 218.9, 172.8, 156.9, 134.7, 129.6, 127.8, 126.9, 126.5, 123.8, 119.1, 106.8, 64.5, 63.0, 56.3, 28.6, 25.3. MALDI.-TOF MS: $(C_{35}H_{38}O_6S_3+Na)^+$: 673.22 (Calculated: 673.87).

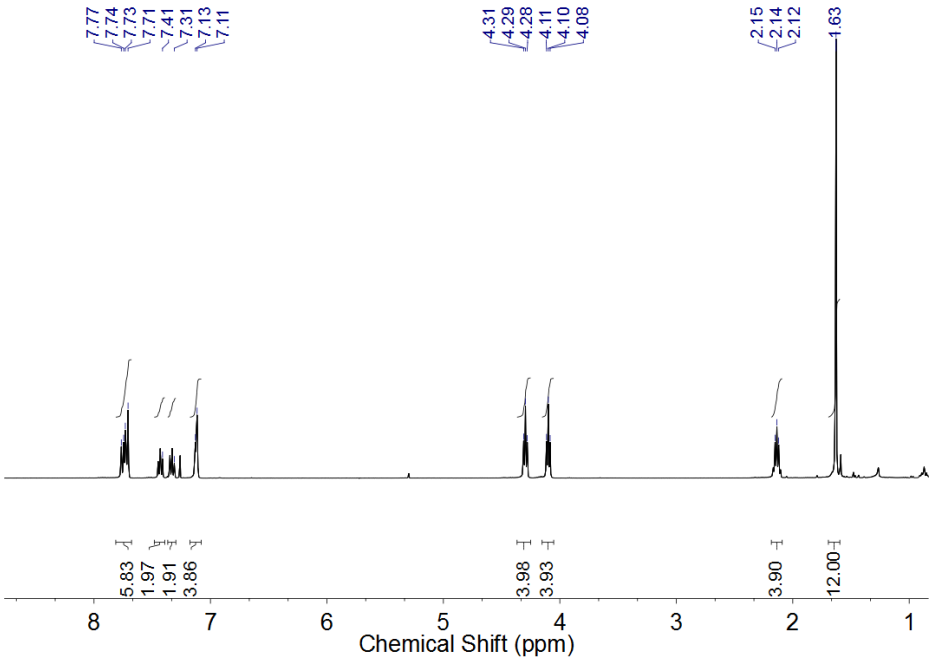


Fig. S2. ^{1}H NMR spectrum of Np-CTA-Np (**6**)

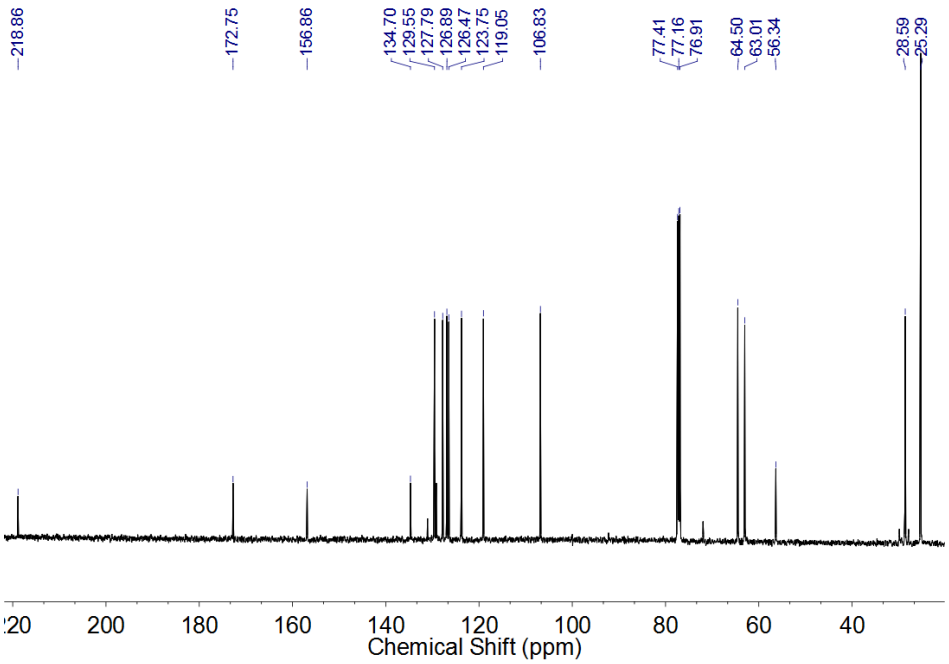


Fig. S3. ^{13}C NMR spectrum of Np-CTA-Np (**6**)

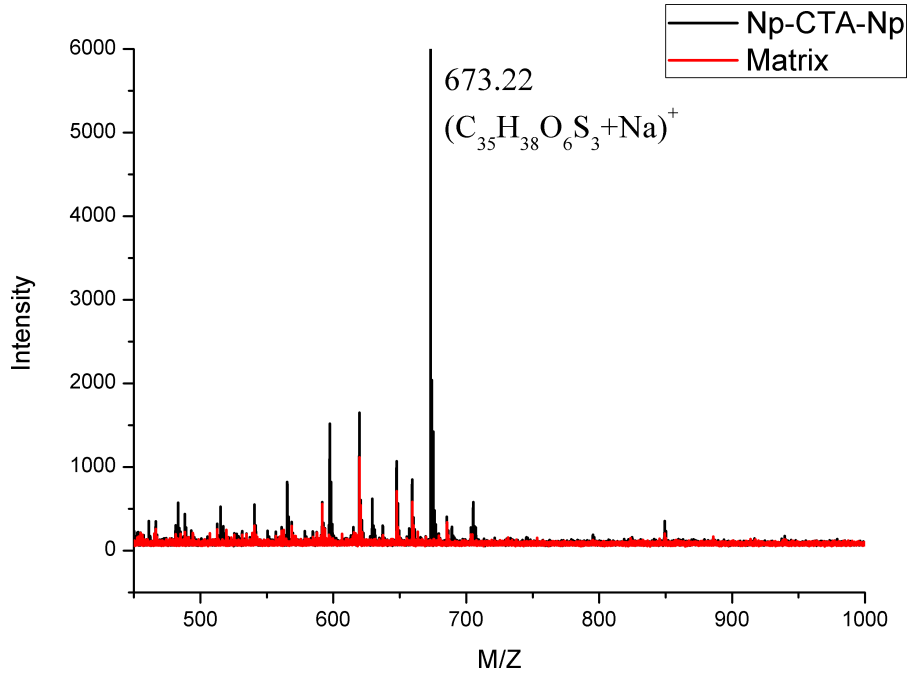
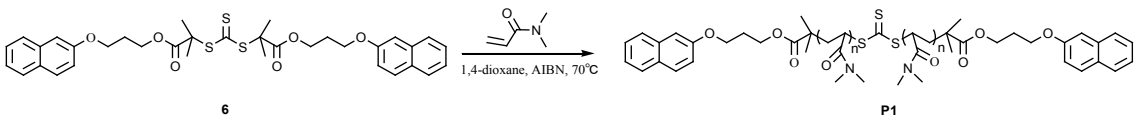
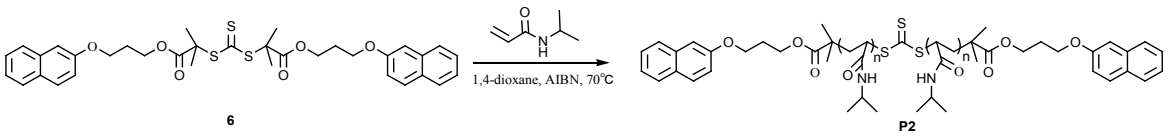


Fig. S4. MALDI-TOF MS of Np-CTA-Np (**6**) and the Matrix used in the characterization.



Scheme S2. Synthetic procedure of **P1** from **6**.



Scheme S3. Synthetic procedure of **P2** from **6**.

Synthesis of Np-PDMA-Np (P1) by RAFT polymerization. Typically, Np-CTA-Np (0.345 g, 0.53 mmol), N,N-dimethylacrylamide (2.63 g, 26.5 mmol), AIBN (0.0174 g, 0.106 mmol) and 7 mL 1,4-dioxane were sealed in a flask equipped with a magnetic stir bar, followed by three freezeethaw cycles. The reaction flask filled with argon was placed in a preheated oil bath at 70 °C. After 4 h, the polymerization was quenched by liquid N_2, and the resulting mixture was precipitated in diethyl ether. The precipitate was dissolved in THF and then precipitated again into diethyl ether. The above dissolution-precipitation cycle was repeated five times. The polymer was obtained as light-yellow powder (2.47 g, 83%) after drying under vacuum at room temperature for 12 h and characterized by GPC ($M_{n,GPC}$=1.47×10^3, PDI=1.17) and ^{1}H NMR ($M_{n,NMR}$=5.87×10^3, calculated based on the integrals of signals corresponding to naphthalene at δ 7.76-7.71 and DMA block at δ 2.86-2.95).

Synthesis of polymer Np-PNIPAm-Np (P2) by RAFT polymerization. Typically, Np-CTA-Np (0.345 g, 0.53 mmol), N-Isopropylacrylamide (3 g, 26.5 mmol), AIBN (0.0174 g, 0.106 mmol) and 7 mL 1,4-dioxane were sealed in a flask equipped with a magnetic stir bar, followed by three freeze-thaw cycles. The reaction flask filled with Ar atmosphere was placed in a preheated oil bath at 70 °C. After 6 h, the polymerization was quenched by liquid N_2, and the resulting mixture was precipitated in diethyl ether. The precipitate was dissolved in THF and then precipitated again into diethyl ether. The above solvation-precipitation cycle was repeated five times. The polymer was obtained as light-yellow powder (2.68 g, 80%) after drying under vacuum at room temperature for 12 h and characterized by GPC ($M_{n,GPC}$ = 2.75×10^3, PDI = 1.09) and ^{1}H NMR ($M_{n,NMR}$ = 6.97×10^3, calculated based on the integrals of signals corresponding to naphthalene at δ 7.76-7.71 and NIPAm block at δ 3.98).

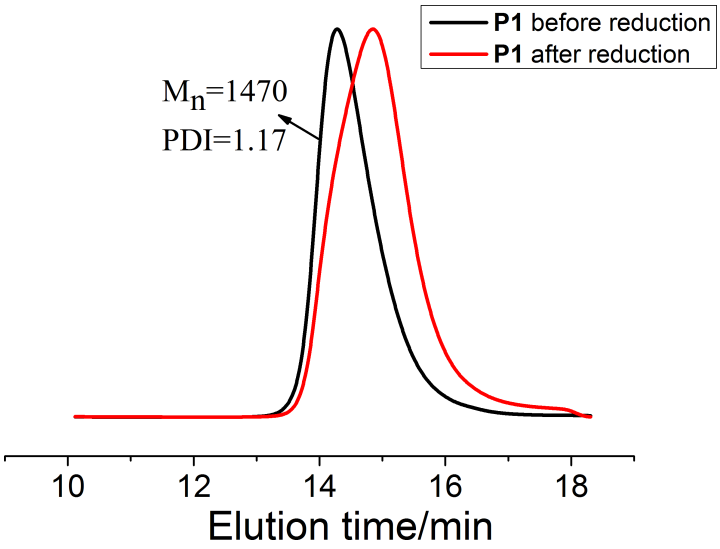


Fig. S5. GPC result of Np-PDMA-Np (**P1**) and its chain-cleavage product after reduction.

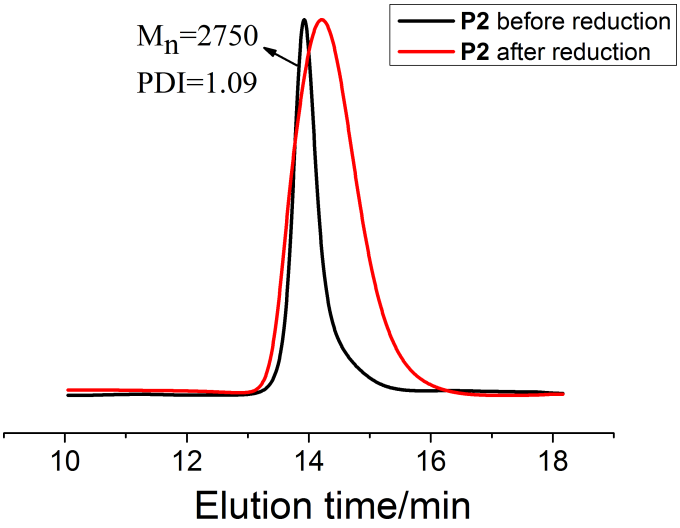


Fig. S6. GPC result of Np-PNIPAm-Np (**P2**) and its chain-cleavage product after reduction.

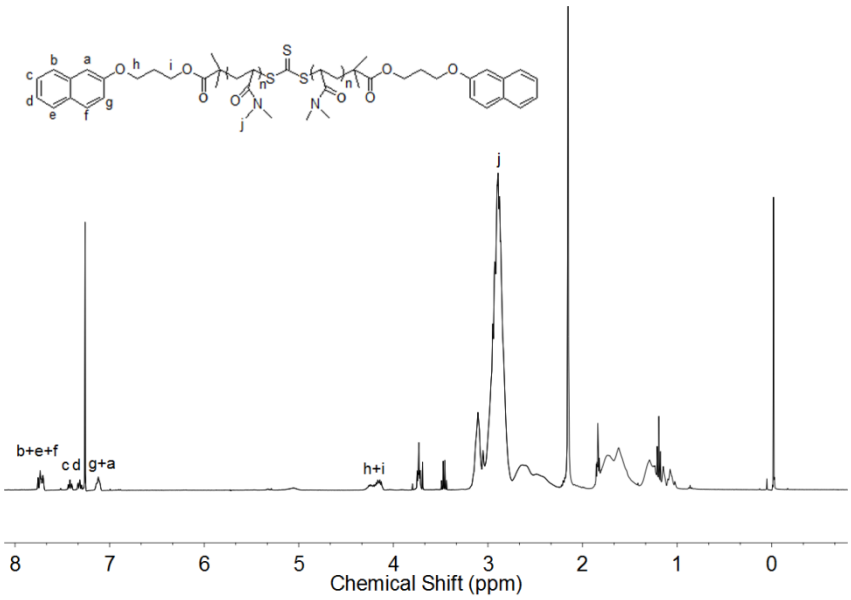


Fig. S7. ^{1}H NMR spectrum of Np-PDMA-Np (**P1**)

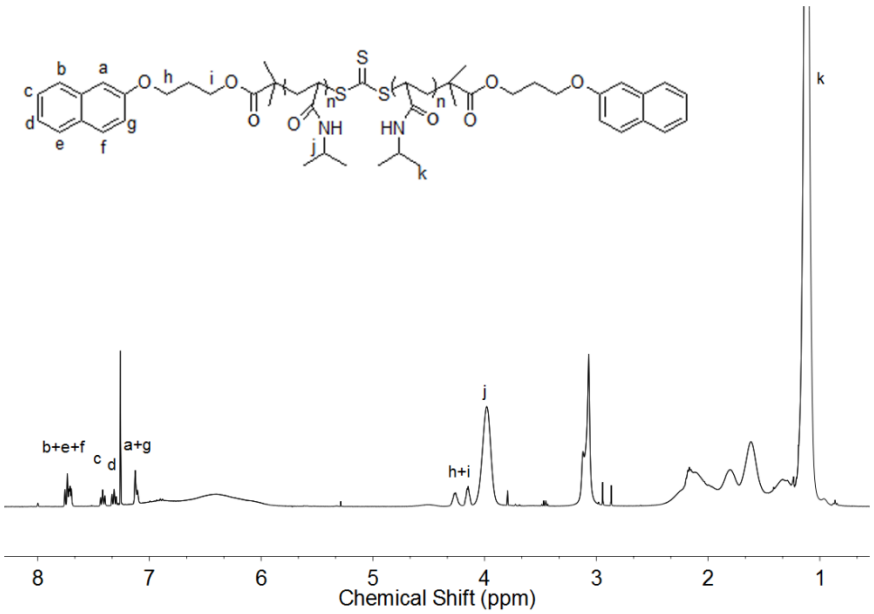
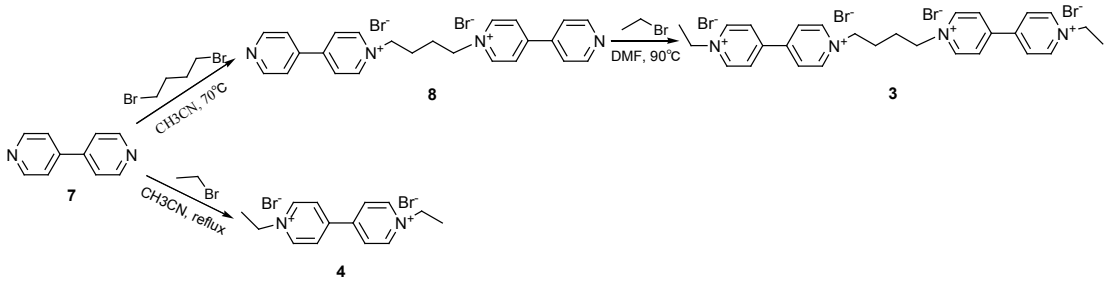


Fig. S8. ^{1}H NMR spectrum of Np-PNIPAm-Np (**P2**).



Scheme S4. Synthetic procedures of **3** and **4**.

Synthesis of ditopic guest molecule 3. Compound **8** was synthesized according to the procedure described in the literature[4] with some modifications. Briefly, excess 4,4'-bipyridine (6.256 g, 40 mmol) and 1,4-dibromobutane (2.878 g, 13.3 mmol) were mixed in a three-neck round-bottom flask equipped with a magnetic stir bar and condenser. The reaction mixture was heated at 70 °C for 24 h to produce a precipitate. After filtration, the precipitate was washed with CH_3CN and then diethyl ether to yield **8** (6.4 g, 91%).

Compound **8** (3.3 g, 6.25 mmol), bromoethane (1.361 g, 12.5 mmol) were reacted in DMF at 90 °C overnight. The obtained precipitate was filtered and washed with hot DMF several times and then CH_3CN to get a brown solid **3** (2.9 g, 63%). ^{1}H NMR (500 MHz, DMSO) δ 9.53-9.44 (dd, 8H), 8.88-8.84 (dd, 8H), 4.85 (s, 4H), 4.78-4.73 (q, 4H), 2.12 (s, 4H), 1.63-1.60 (t, 6H).

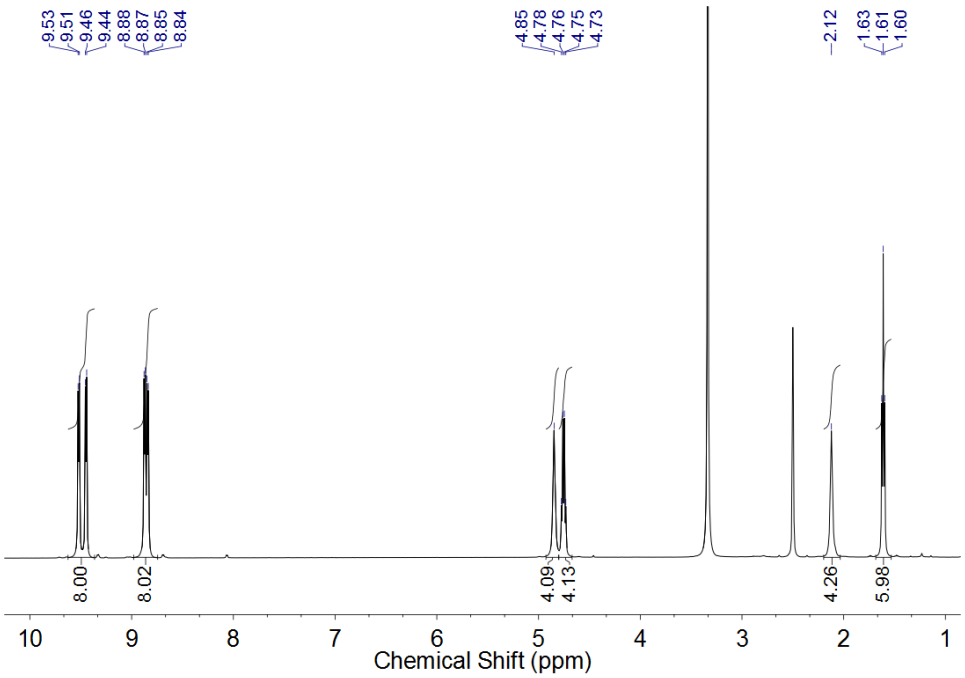


Fig. S9. ^{1}H NMR spectrum of ditopic guest molecule **3**.

Synthesis of mono-topic guest 4. Compound **4** was prepared according to the previous paper[5] with some modifications. Briefly, 4,4'-dipyridyl (3.128 g, 20 mmol), bromoethane (4.79 g, 44 mmol) and 50 mL CH_3CN were mixed in a flask under N_2. After refluxed for 24 h, the solution was cooled to room temperature and then the solvent was removed under reduced pressure. The obtained yellow solid was suspended in 100 mL of hot DMF, filtered, washed with hot DMF several times and then diethyl ether to get the final product (3.1 g, 42%). ^{1}H NMR (400 MHz, CD_3OD) δ 9.32-9.30 (d, 4H), 8.71-8.70 (d, 4H), 4.85-4.79 (q, 4H), 1.76-1.72 (t, 6H).

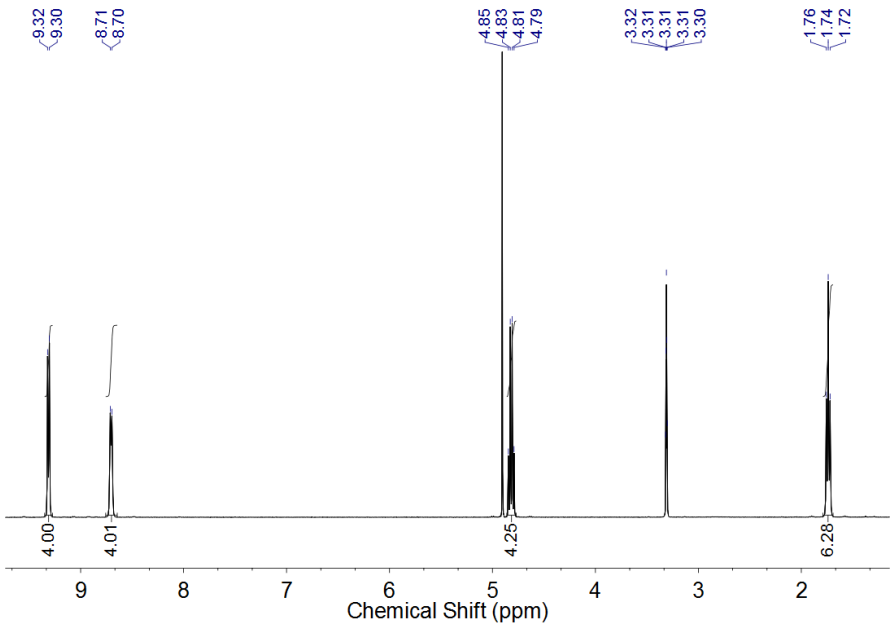


Fig. S10. ^{1}H NMR spectrum of mono-topic guest **4**.

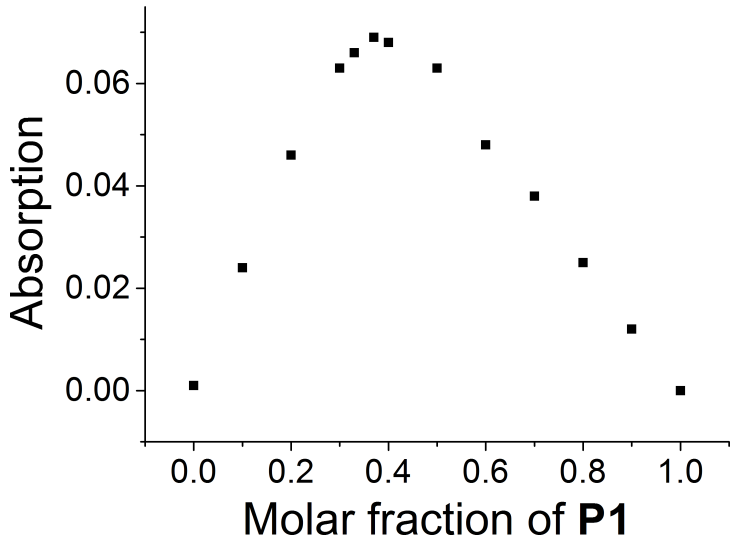


Fig. S11. Job's plot of **P1** and **4**⊂CB[8] (total concentration of **P1** and **4**⊂CB[8] fixed at 0.5 mM, absorption intensity measured at 495 nm).

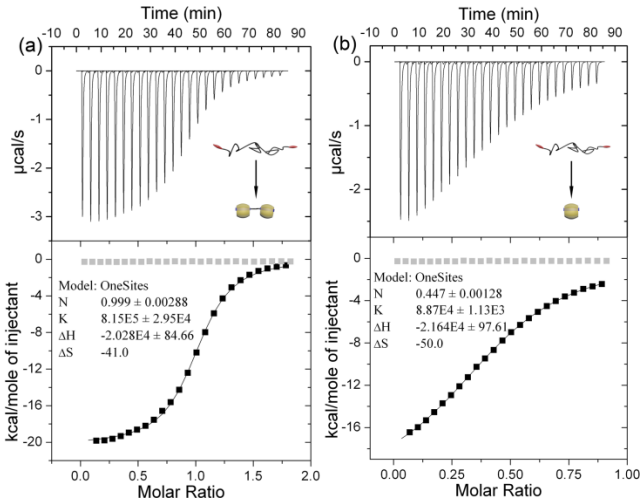


Fig. S12. Raw and integrated data for titration of (a) **3**⊂CB[8] (0.05 mM) with **P1** (0.5 mM) (b) **4**⊂CB[8] (0.1 mM) with **P1** (0.5 mM) in water at 25 °C.

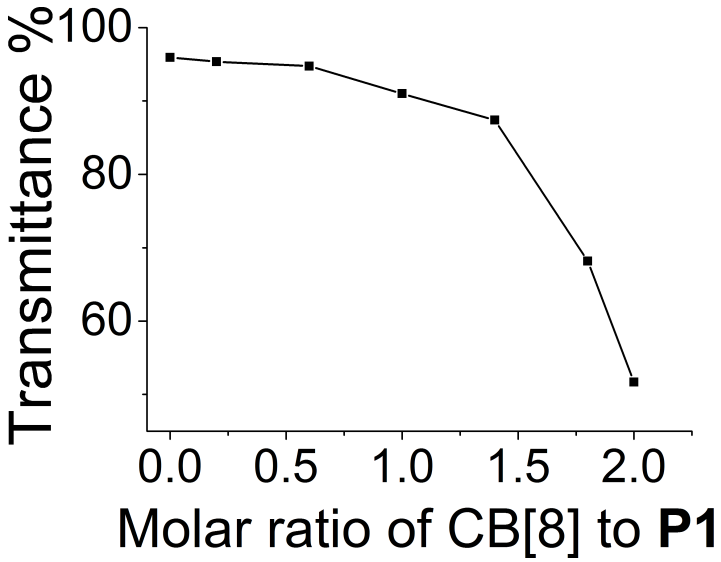


Fig. S13. Transmittance of the mixture of **P1** and **3** (4 mM) with different molar ratios of CB[8] to **P1** (20 °C in H_2O).

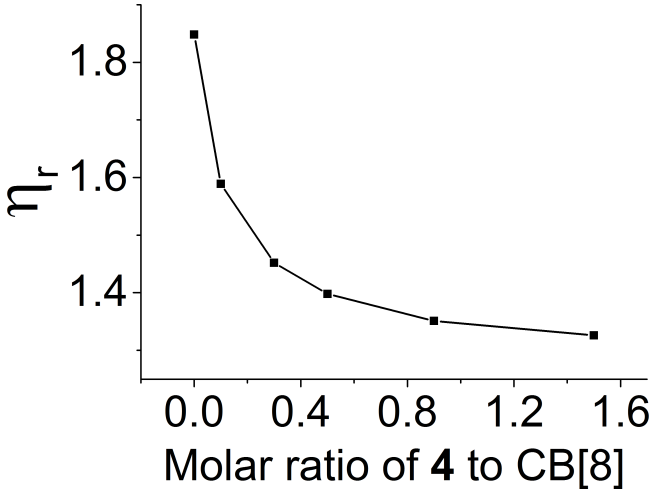


Fig. S14. Relative viscosity of **P1**+**3**⊂CB[8] (4 mM, calculated as **P1**) with excess competitive guest **4**. (20 °C in H_2O).

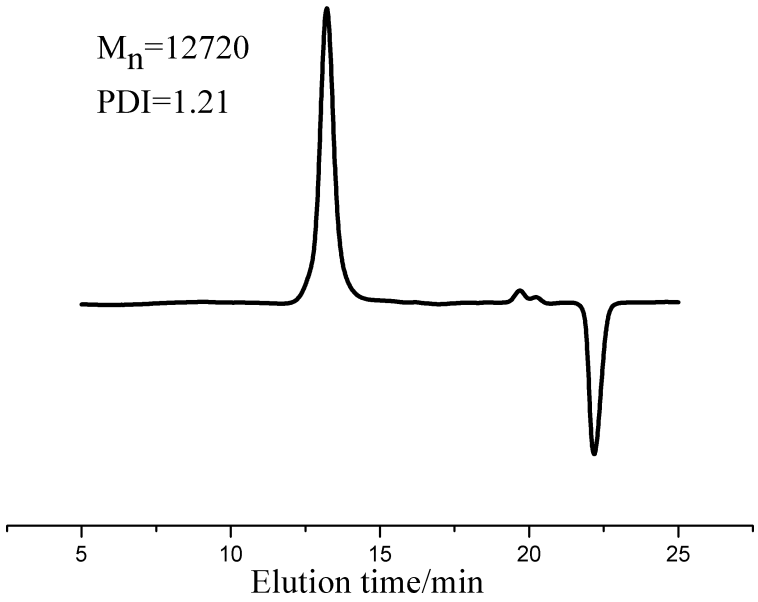


Fig. S15. GPC of DMA_{300} prepared by RAFT polymerization.

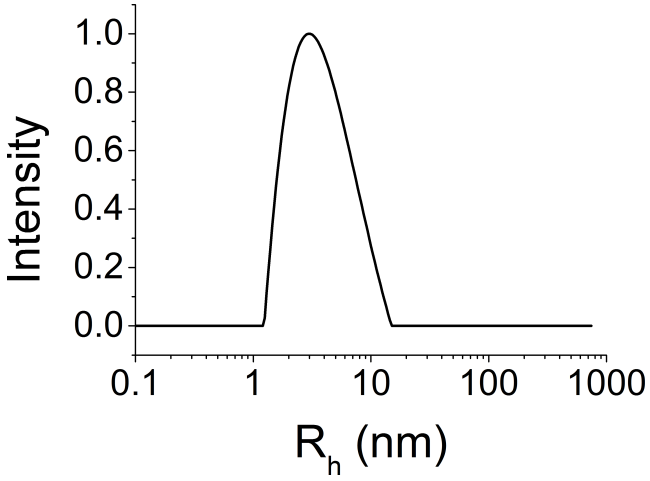


Fig. S16. Hydrodynamic radius distribution of **P1** (4 mM) and **3** (4 mM) without addition of CB[8].

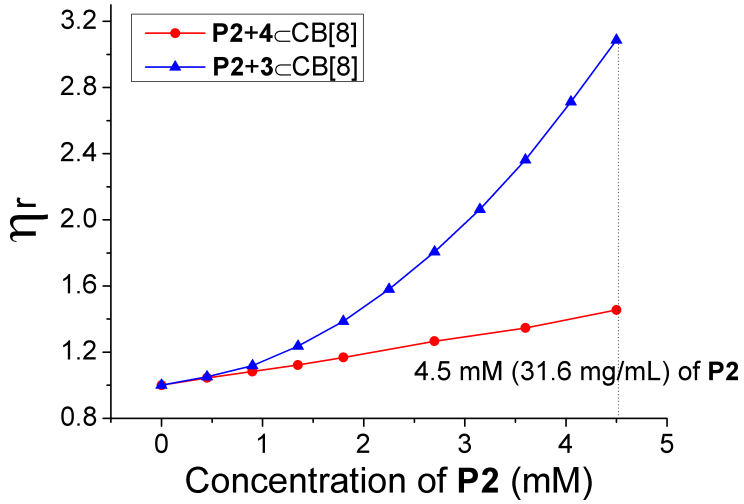


Fig. S17. Relative viscosity of **P2**+**4**⊂CB[8] and **P2**+**3**⊂CB[8] *vs* concentration in H_2O at 15 °C.

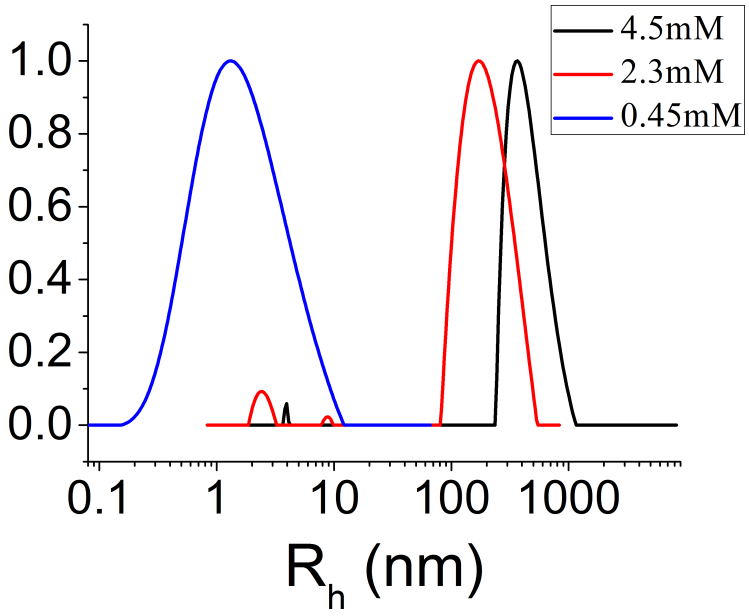


Fig. S18. Hydrodynamic radius distribution of the **P2**+ **3**⊂CB[8] at various concentrations at 15 °C.

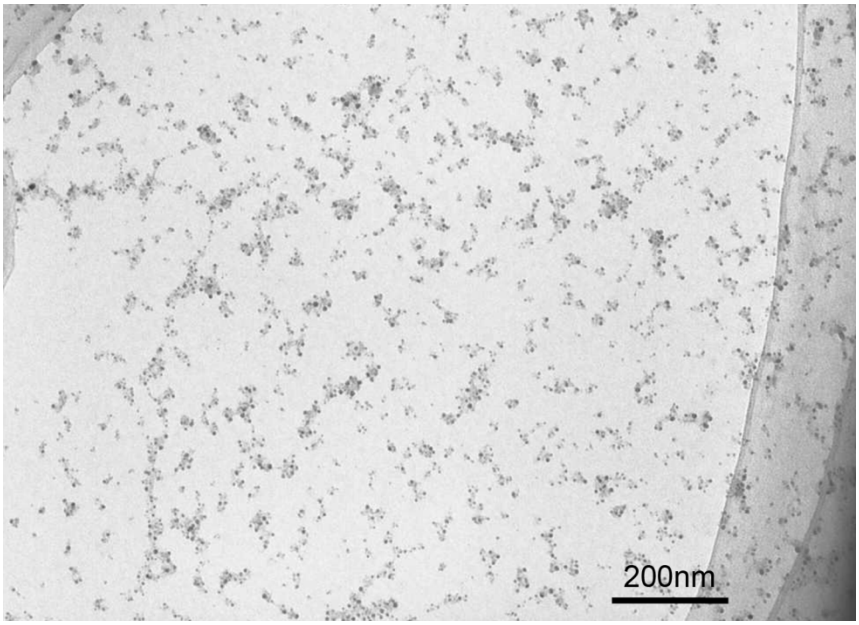


Fig. S19. TEM image of **P2**+ **3**⊂CB[8] (0.5 mg/mL, calculated as **P2**).

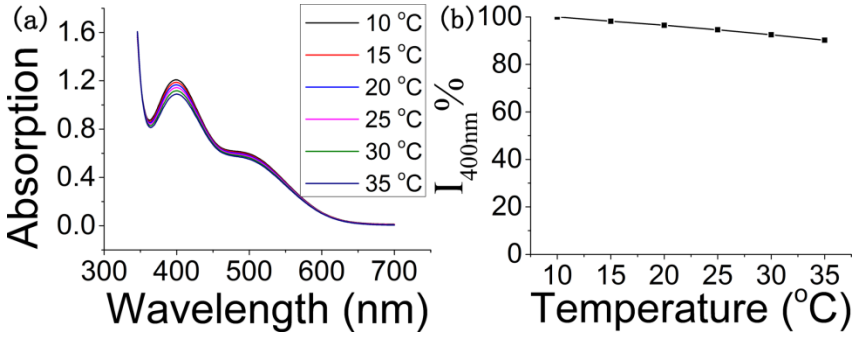


Fig.20. (a) UV-Vis spectra of **P1**+**3**⊂CB[8] (1.2 mM, calculated as **P1**) at different temperatures. (b) Absorption intensity (400 nm) vs temperature.

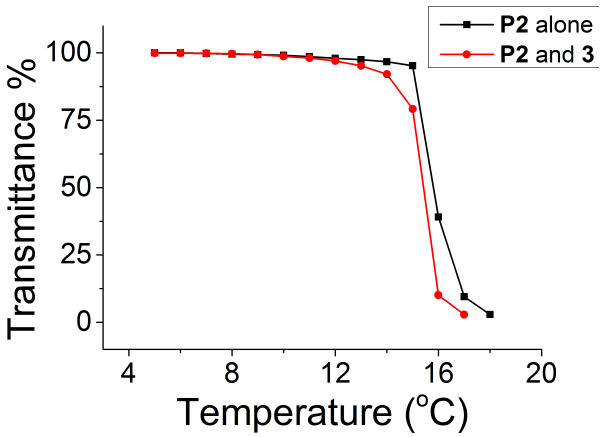


Fig.21. Temperature dependence of optical transmittance at 800 nm obtained for **P2** (2 mg/mL) alone and **P2** with **3** (2.8 mM).

Reference

(1) J. T. Lai, D. Filla, R. Shea, *Macromolecules* 2002, **35**, 6754.

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(3) A. Bertrand, S. Chen, G. G. Souharce, C. Ladavière, E. Fleury, J. Bernard, *Macromolecules* 2011, **44**, 3694.

(4) Y. Liu, Y. Yu, J. Gao, Z. Wang, X. Zhang, *Angew. Chem. Int. Ed.* 2010, **49**, 6576.

(5) M. F. Pepitone, G. G. Jernigan, J. S. Melinger, O. K. Kim, *Org. Lett.* 2007, **9**, 801.