Dual-responsive crown ether-based supramolecular chain extended polymers

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Electronic Supplementary Information (14 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compounds **2**[S1] and **7**[S2] were prepared according to the published procedures. NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. Low-resolution electrospray ionization mass spectra were recorded with a Bruker Esquire 3000 Plus spectrometer. High-resolution mass spectrometry experiments were performed with a Bruker Daltonics Apex III spectrometer. Viscosity measurements were carried out with a Cannon-Ubbelohde semi-micro dilution viscometer at 25 °C in chloroform. The optical photographs were taken with an Olympus BX-51 optical microscope. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) with a Waters 1515 pump and Waters 2414 differential refractive index detector relative to linear PS standards. GPC was performed at 40 °C using THF as eluent at a flow rate of 1.0 mL/min. Fourier Transform Infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. Differential Scanning Calorimetry (DSC) measurements were conducted on a DSC TA Q100 thermal analysis instrument (TA Instruments, US). Samples were first heated from 40 to 90 °C at a heating rate of 30 °C/min under nitrogen atmosphere, followed by cooling to –70 °C at a scan rate of 2 °C/min and reheating to 90 °C at 2 °C/min.

*2. Synthesis of macromonomer **1***

*2.1 Synthesis of compound **3***

Compound **2** (8.00 g, 20.8 mmol) was dissolved in anhydrous THF (100 mL) and then added to a mixture of $LiAlH_4$ (1.20 g, 31.2 mmol) and THF (50 mL) dropwise over 1 h at 0 °C. The mixture was stirred for 24 hours at room temperature and the reaction mixture was quenched with methanol. The solvent was evaporated and the residue was partitioned between water and dichloromethane. The water layer was extracted with dichloromethane three times. The combined dichloromethane solution was washed with saturated NaCl solution and water, dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated to give a white solid **3** (6.2 g, 78%). mp 39.5–40.5 °C. The ^{1}H NMR spectrum of **3** is shown in Figure S1. ^{1}H NMR (400 MHz, chloroform-*d*, room temperature) δ (ppm): 6.92 (s, 1H), 6.81–6.90 (m, 2H), 4.59 (s, 2H), 4.13–4.20 (m, 4H), 3.89–3.95 (m, 4H), 3.76–3.83 (m, 4H), 3.70–3.75 (m, 4H), 3.62–3.69 (m, 8H). The ^{13}C NMR spectrum of **3** is shown in Figure S2. ^{13}C NMR (125 MHz, chloroform-*d*, room temperature) δ (ppm): 65.06, 69.11, 69.29, 69.77, 70.54, 70.97, 70.99, 71.03, 71.08, 113.14, 114.10, 119.94, 134.37, 148.30, and 148.97. LRESIMS is shown in Figure S3: *m*/*z* 409.3 [M + Na]$^+$ (100%). HRESIMS: *m*/*z* calcd for [M]$^+$ $C_{19}H_{30}O_8$, 386.1941; found 386.1942, error 0.3 ppm.

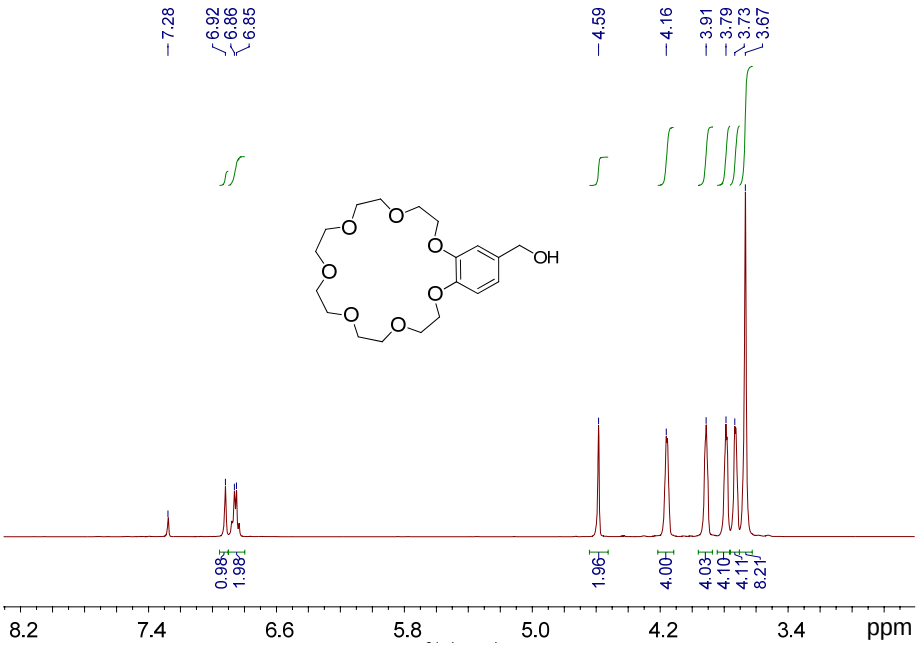

Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **3**.

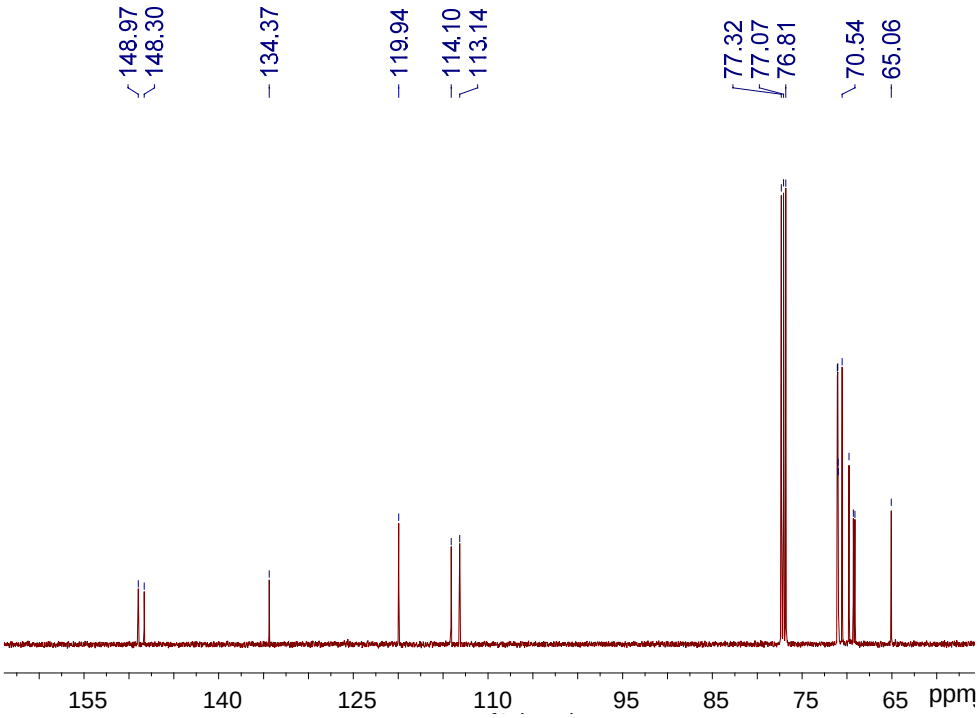

Figure S2. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 20 °C) of **3**.

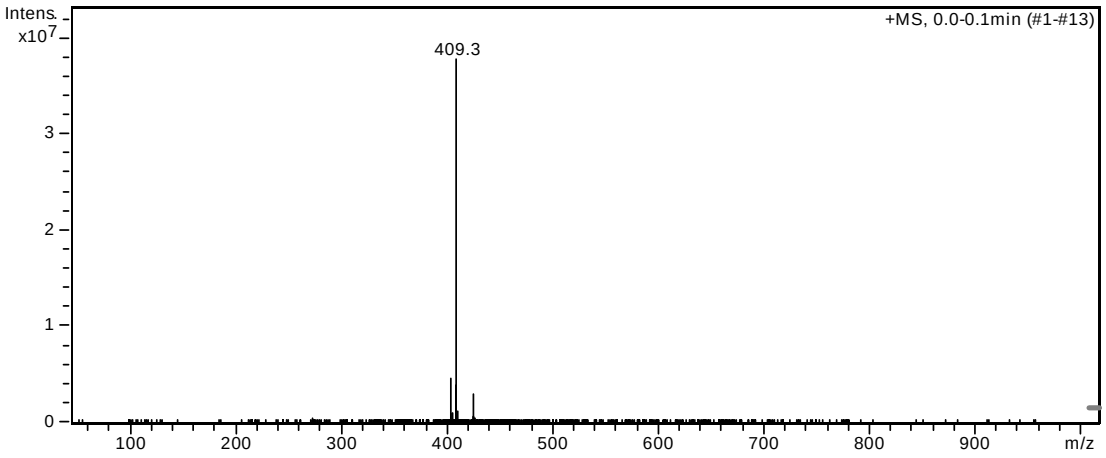

Figure S3. Electrospray ionization mass spectrum of **3**.

*2.2 Synthesis of polymer **4***

To a previously flamed Schlenk tube equipped with a magnetic stirring bar, **3** (2.65 g, 6.8 mmol), $Sn(Oct)_2$ in toluene (0.62 mol/L, 0.55 mL), ε-CL (12.0 mL, 108 mmol), and dry toluene (30 mL) were added. After removal of ~10 mL of toluene under reduced pressure, the tube was sealed under nitrogen gas, and placed in an oil bath thermostated at 100 °C. After 24 h, the reaction mixture was dissolved in THF and precipitated into an excess of cold methanol. After filtration, the sediment was dissolved in THF and precipitated into an excess of cold methanol again. The above dissolution-precipitation cycle was repeated three times. After drying in a vacuum oven overnight at room temperature, polymer **4** was obtained as a white solid (12.8 g, 85%, $M_{n,GPC}$ = 5.05 kDa, M_w/M_n = 1.12, n = 41). The DP was determined to be 27 by ^{1}H NMR analysis in $CDCl_3$ (Figure S4a).

*2.3 Synthesis of polymer **5***

To a previously flamed 500 mL one-neck round-bottom flask, **4** (9.00 g, 1.78 mmol), triethylamine (2.48 mL, 17.8 mmol), trimethylamine hydrochloride (24 mg, 0.25 mmol), and dry CH_2Cl_2 (250 mL) were added. After cooling to 0 °C, *p*-toluenesulfonyl chloride (3.39 g, 17.8 mmol) in dry CH_2Cl_2 (80 mL) was added dropwise over 1 h at 0 °C. The reaction mixture was kept stirring overnight at room temperature. After removal of insoluble salts by filtration, the solvent was removed on a rotary evaporator. The residue was dissolved in THF and passed through a neutral alumina column to remove residual salts. After concentration and repeated precipitation into an excess of cold methanol, **5** was obtained as a white solid (8.74 g, 94%; $M_{n,GPC}$ = 5.2 kDa, M_w/M_n = 1.07).

*2.4 Synthesis of polymer **6***

To a 250 mL round-bottom flask, **5** (6.40 g, 1.23 mmol), DMF (100 mL), and NaN_3 (0.80 g, 12 mmol) were added. The reaction mixture was allowed to stir at 50 °C for 24 h. After removal of most of the solvent at reduced pressure, the remaining portion was diluted with THF, and then precipitated into an excess of cold methanol. The sediment was re-dissolved in THF and passed through a neutral alumina column to remove residual sodium salts, and precipitated into an excess of cold methanol. The obtained product, **6**, was dried in a vacuum oven, yielding a white solid (5.37 g, 86%, $M_{n,GPC}$ = 5.1 kDa, M_w/M_n = 1.11).

2.5 Synthesis of macromonomer ***1***[S3]

A mixture of **6** (3.60 g, 0.706 mmol), **7** (0.334 g, 0.918 mmol), $CuSO_4$•$5H_2O$ (35.3 mg, 0.141 mmol) and sodium ascorbate (0.112 mg, 0.564 mmol) in DMF (100 mL) was stirred at 50 ºC for 24 h under nitrogen gas. The mixture was diluted with THF (80 mL) and passed through a basic alumina column. After removal of most of the solvent under reduced pressure, the residue was purified by precipitation (three times) into excess cold diethyl ether. After drying in a vacuum oven overnight at room temperature, macromonomer **1** was obtained as a pale yellow solid (3.01 g, 78%).

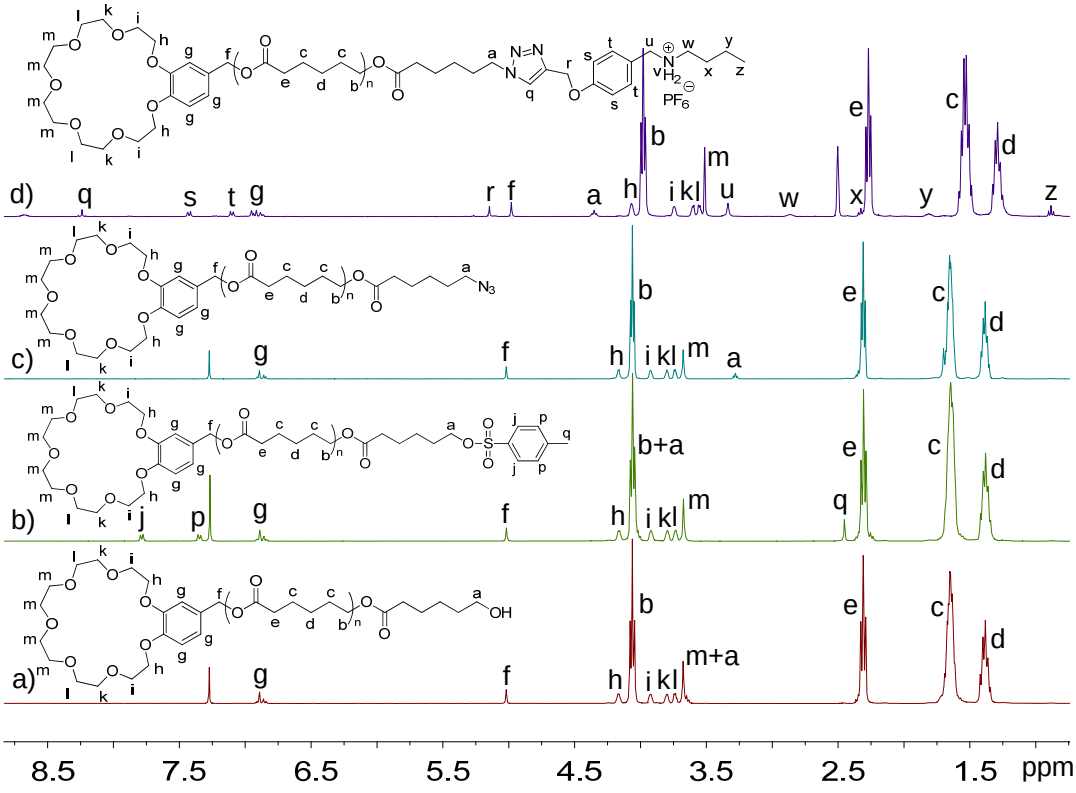

Figure S4. ^{1}H NMR spectrum (400 MHz, 20 °C) of (a) **4**, (b) **5**, and (c) **6** in $CDCl_3$ and (d) **1** in DMSO-d_6.

3. Synthesis of neutral macromonomer ***8***

A mixture of **1** (1.50 g, 0.275 mmol) and triethylamine (0.19 mL, 1.4 mmol) in THF (50 mL) was stirred at 50 ºC for 2 h. After removal of the solvent and triethylamine under reduced pressure, the residue was dissolved in THF and purified by precipitation (three times) into excess cold methanol. After drying in a vacuum oven overnight at room temperature, neutral macromonomer **8** was obtained as a white solid (1.32 g, 90%, $M_{n,GPC}$ = 5.3 kDa, M_w/M_n = 1.12).

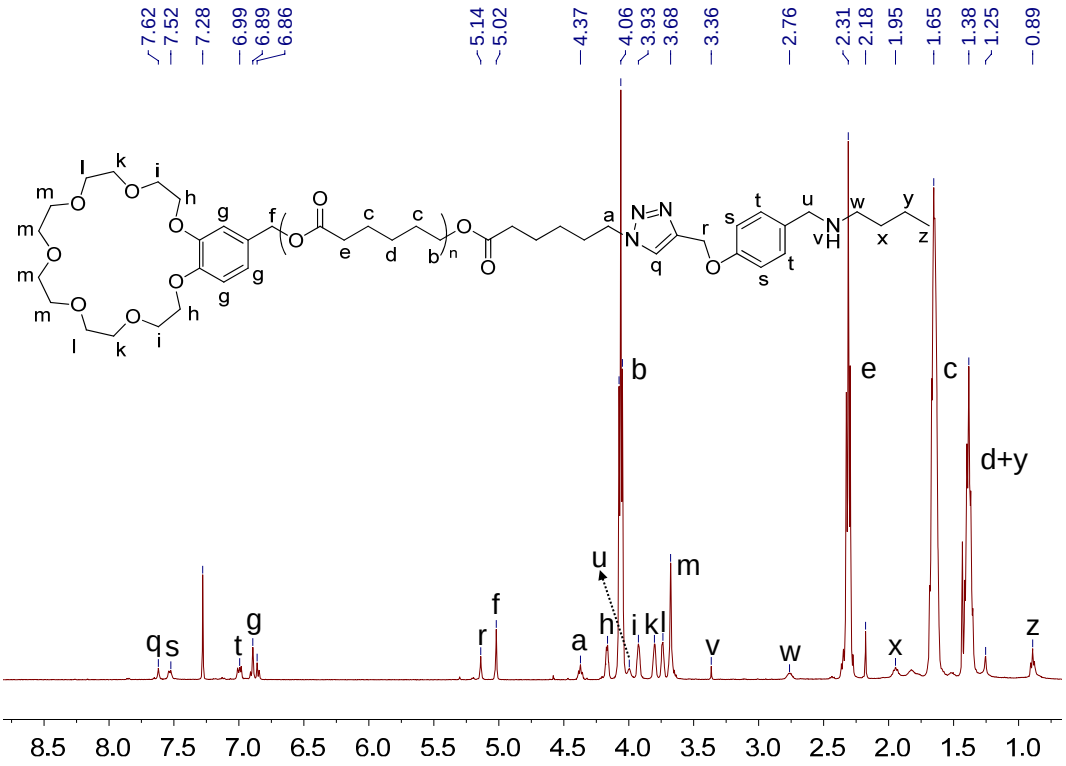

Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 20 °C) of **8**.

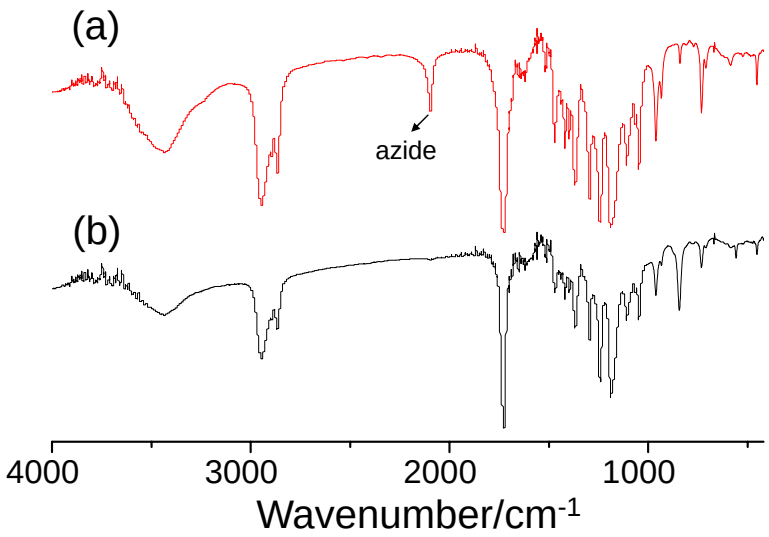

Figure S6. FT-IR spectra of (a) **6** and (b) **7**.

4. pH- and cation-responsive experiments of macromonomer ***1***

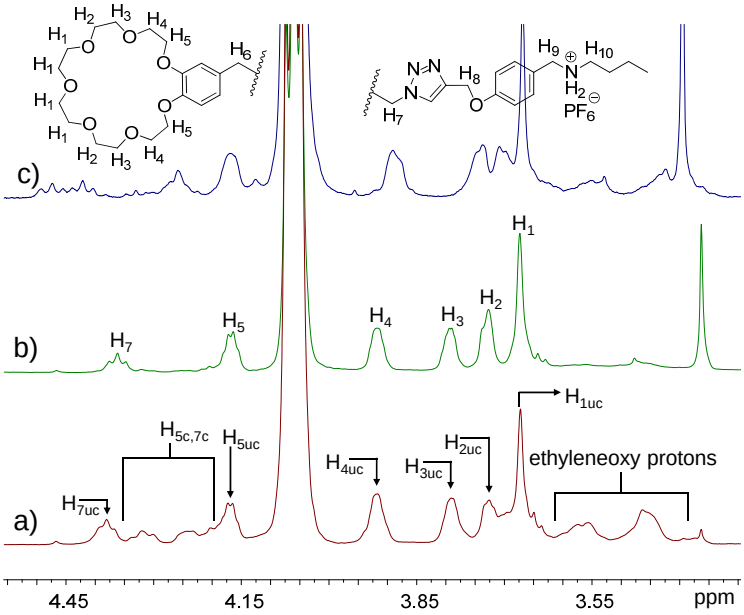

Figure S7. Partial ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) spectra: a) macromonomer **1** (25 g/L); b) after addition of 1.5 equiv. of Et_3N to a; c) after addition of 2.0 equiv. of TFA to b. Complexed and uncomplexed moieties are denoted by "c" and "uc", respectively.

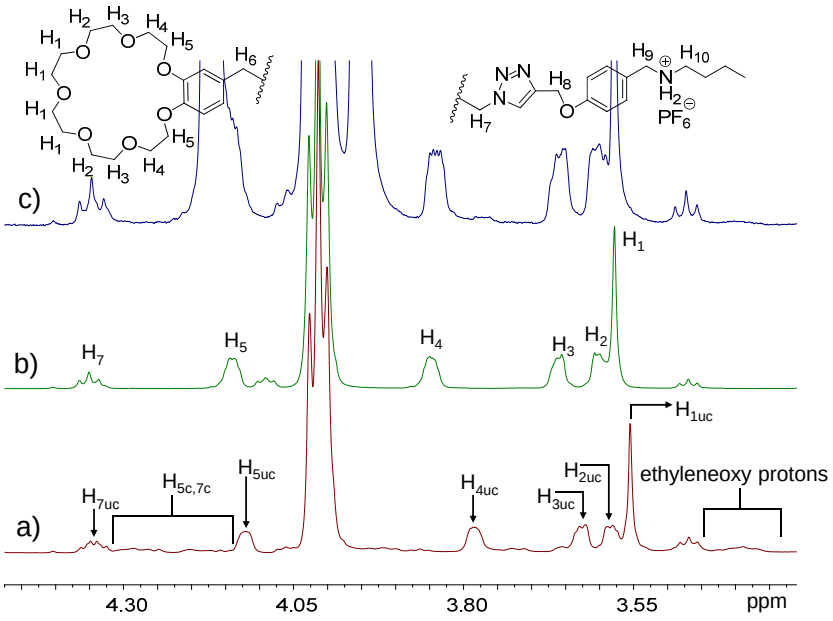

Figure S8. Partial ^{1}H NMR (400 MHz, CD_3CN, 20 °C) spectra: a) macromonomer **1** (25 g/L); b) after addition of 1.5 equiv. KPF_6 to a; c) after addition of 2.0 equiv. of DB18C6 to b. Complexed and uncomplexed moieties are denoted by “c” and “uc”, respectively.

*5. Partial variable temperature ^{1}H NMR spectra of macromonomer **1***

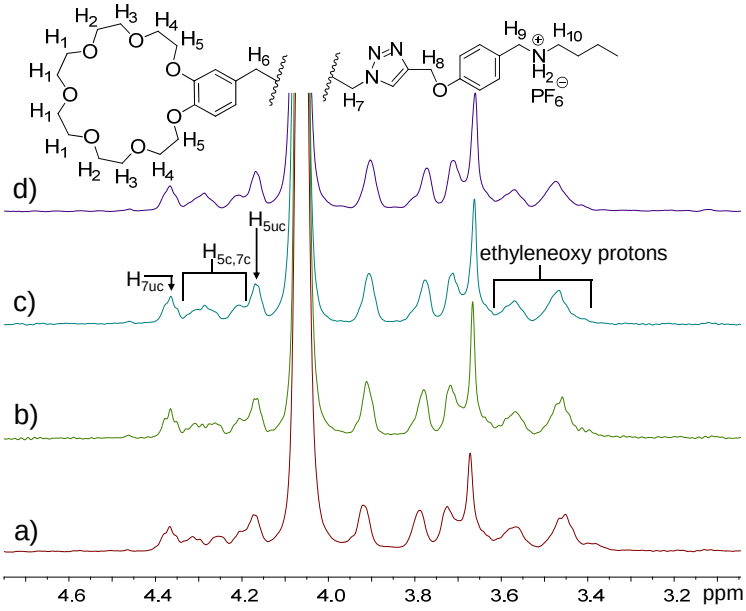

Figure S9. Partial variable temperature ^{1}H NMR spectra of macromonomer **1** (100 g/L, 500 MHz, $CDCl_3$): a) 298 K, b) 308 K, c) 318 K, d) 328 K. Complexed and uncomplexed moieties are denoted by "c" and "uc", respectively.

*6. DSC analysis of macromonomer **1** and neutral macromonomer **8***

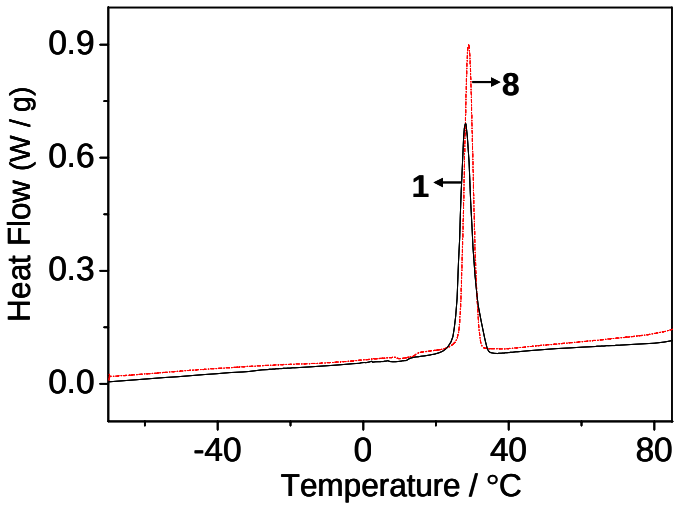

Figure S10a. DSC curves of macromonomer **1** and neutral macromonomer **8** in the cooling process.

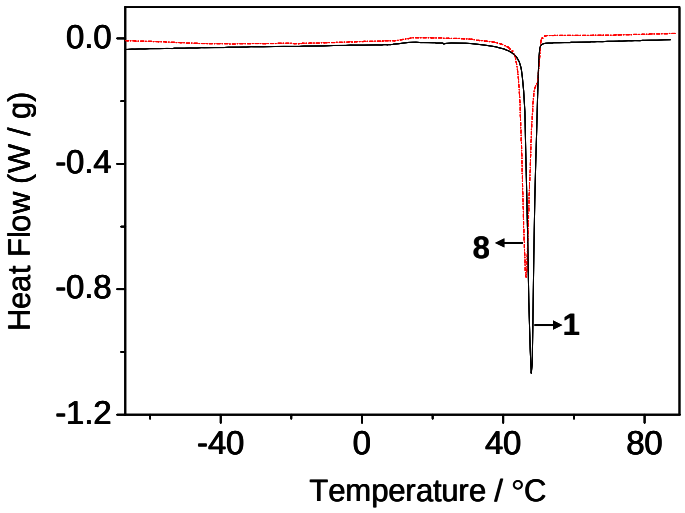

Figure S10b. DSC curves of macromonomer **1** and neutral macromonomer **8** in the heating process.

7. The evidence that the resonances associated with complexation increase with increasing concentration

Table 1. The analysis of concentration dependent ^{1}H NMR spectra (Fig. 1a–f) of macromonomer **1**.

C^{a} / g L^{-1}	A^{b}	B^{c}	B / A^{d}
12.5	100	7.50	0.075
25.0	100	7.86	0.079
50.0	100	8.04	0.080
100	100	8.21	0.082
175	100	8.70	0.087
250	100	9.10	0.091

[a] The concentration of macromonomer **1**; [b] The integration of main chain peaks of PCL (δ = 3.97–4.14 ppm); [c] The integration of a complexed peak (δ = 3.30–3.52 ppm); [d] The integration ratio of the complexed peak (δ = 3.30–3.52 ppm) to the main chain peaks of PCL (δ = 3.97–4.14 ppm).

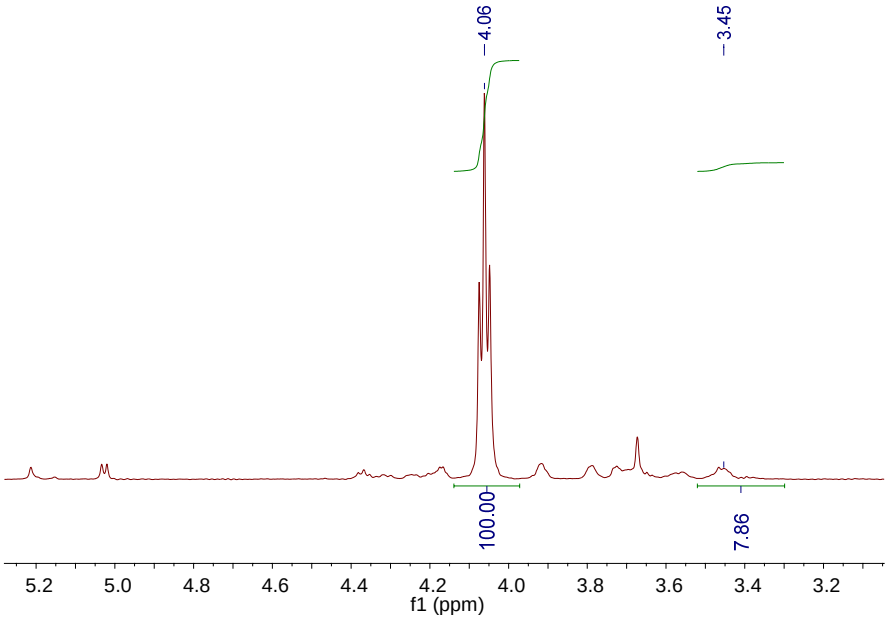

Figure S11a. Partial ^{1}H NMR (400 MHZ, $CDCl_3$, 293 K) spectrum of **1** at 25.0 g/L.

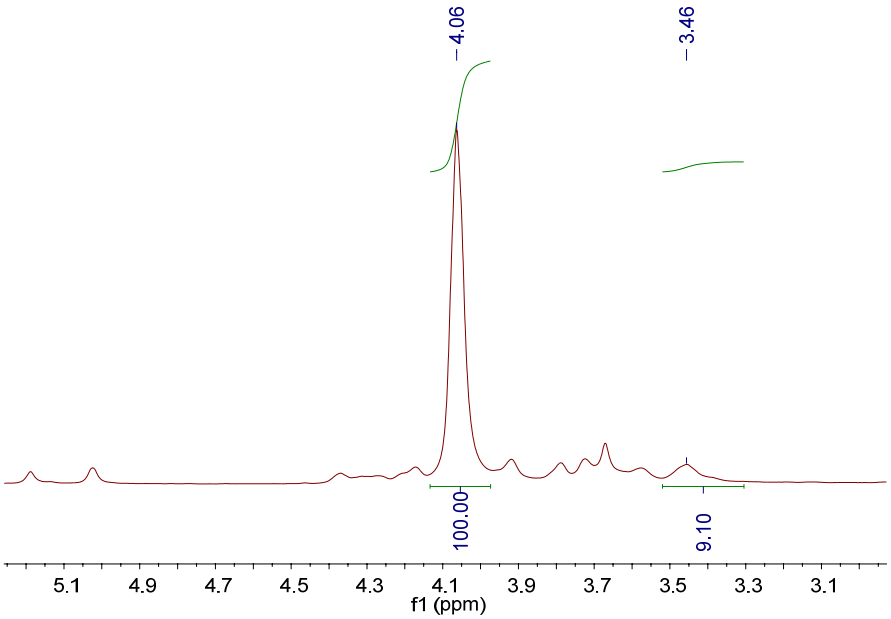

Figure S11b. Partial ^{1}H NMR (400 MHZ, $CDCl_3$, 293 K) spectrum of **1** at 250 g/L.

REFERENCES

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S2. X. Yan, M. Zhou, J. Chen, X. Chi, S. Dong, M. Zhang, X. Ding, Y. Yu, S. Shao and F. Huang, *Chem. Commun.*, 2011, **47**, 7086.

S3. Z. Ge, J. Hu, F. Huang and S. Liu, *Angew. Chem., Int. Ed.*, 2009, **48**, 1798.