Multi-stimuli responsive supramolecular polymers and their electrospun nanofibers

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Electronic Supplementary Information

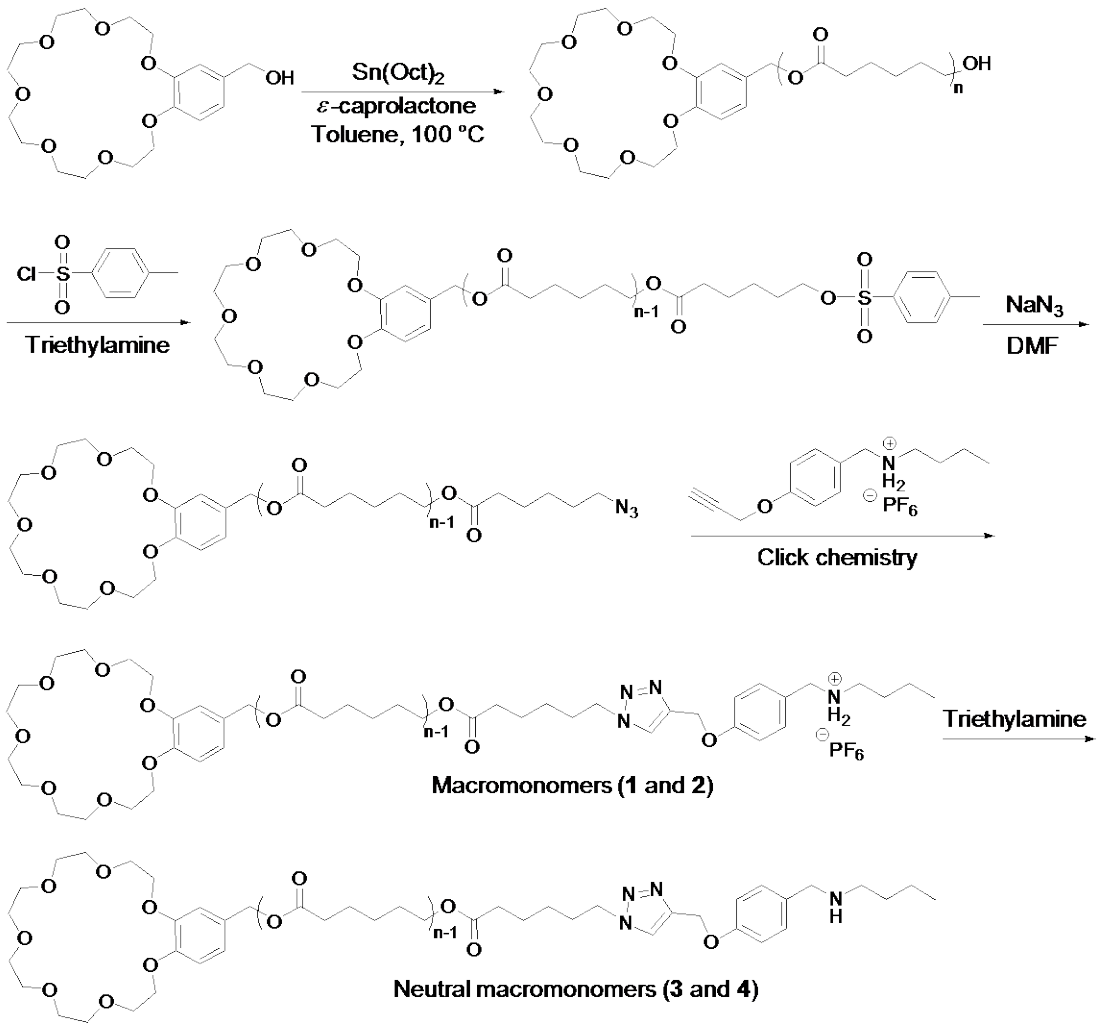
1. Materials and methods

All reagents were commercially available and used as supplied without further purification.

macromonomer **1**, macromonomer **2**, neutral macromonomer **3** ($M_{n,GPC}$ = 5.5 kDa, M_w/M_n = 1.16, n = 43; M_{NMR} = 3.9 kDa, n_{NMR} = 29, n donates the unit number of PCL) and neutral macromonomer **4** ($M_{n,GPC}$ = 7.1 kDa, M_w/M_n = 1.23, n = 57; M_{NMR} = 5.0 kDa, n_{NMR} = 39) were prepared according to the published procedures.[S3] NMR spectra were recorded with a Bruker Advance DMX 500 spectrophotometer or a Bruker Advance DMX 400 spectrophotometer using the deuterated solvents as the lock and the residual solvents or TMS as the internal reference. 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 and the samples were placed between a glass slide and a glass cover for observation. 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. Differential Scanning Calorimetry (DSC) measurements were conducted on a Perkin-Elmer DSC 8500 instrument in a dry nitrogen atmosphere. Indium and tin standards were used for calibration for low and high-temperature regions, respectively. All samples were first heated to 90 °C from 30 °C at a rate of 30 °C/min and kept at that temperature for 3 min; subsequently, they were cooled to −70 °C from 90 °C at a rate of −10 °C/min and kept at that temperature for 5 min; then they were reheated to 90 °C at a rate of 10 °C/min. The crystallization temperature (T_c) was taken as the minimum of the exothermic peak, whereas the melting temperature (T_m) was taken as the maximum of the endothermic peak. The crystallization and melting temperatures were determined from the second and third temperature cycles. Field-emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S4800 instrument (Japan) operating at an accelerating voltage of 3.0 kV.

Preparation of nanofibers by Electrospinning: The sample (**MRSP1** or **3**) was dissolved in $CHCl_3$ at the designed concentration. The electrical field was generated by a variable high voltage power supply (DW-P403-3ACDF). The applied voltage was 12 kV and the distance between the spinneret and the grounded plate was 15 cm. All solutions are fed by NE-1000 syringe pumps at 2.0 mL/h.

2. Synthetic routes to macromonomers and their neutral macromonomers



Scheme S1. Synthetic routes to macromonomers (**1** and **2**) of multi-stimuli responsive supramolecular polymers (**MRSP1** and **MRSP2**) and their corresponding neutral macromonomers (**3** and **4**) by a combination of ring-opening polymerization and click reaction.[S1–S3]

*3. ^{1}H NMR spectra of **MRSPs** and their neutral macromonomers*

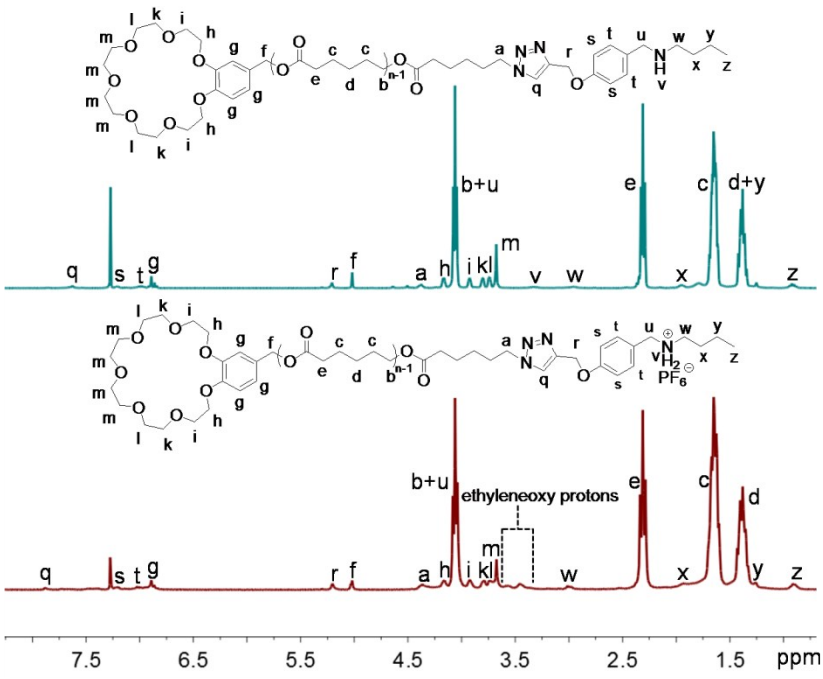


Fig. S1. Partial ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectra of macromonomer **1** (20.0 g/L, bottom) and its neutral macromonomer **3** (20.0 g/L, top).

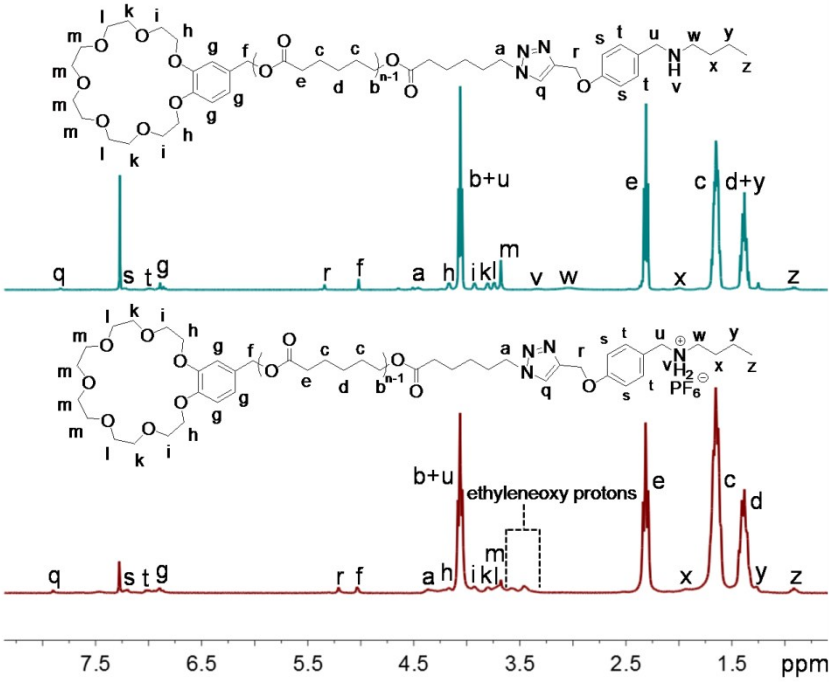


Fig. S2. Partial ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) spectra of macromonomer **2** (20.0 g/L, bottom) and its neutral macromonomer **4** (20.0 g/L, top).

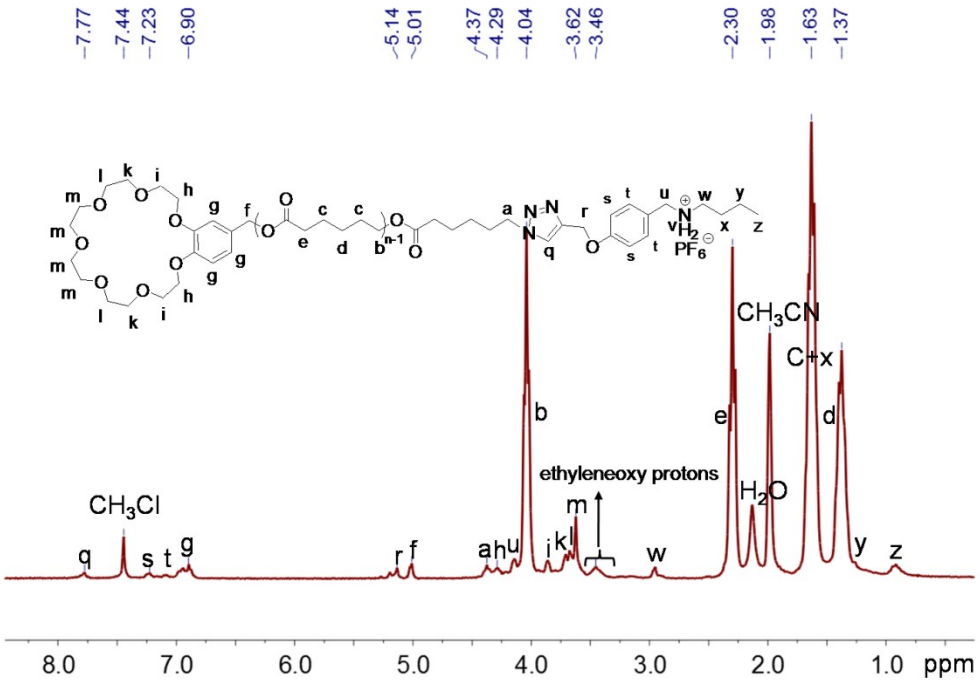


Fig. S3. Partial ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN = 2:1 (*v*/*v*), 293 K) spectrum of macromonomer **1** (20.0 g/L).

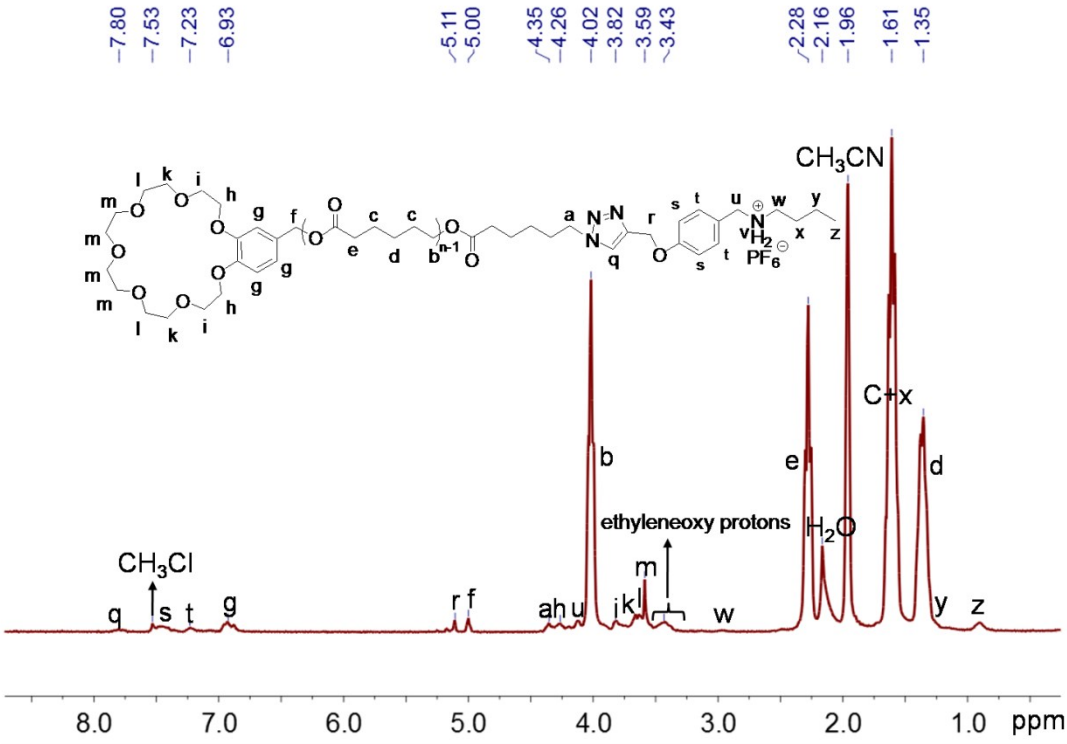


Fig. S4. Partial ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN = 2:1 (*v*/*v*), 293 K) spectrum of macromonomer **2** (20.0 g/L).

4. GPC traces of neutral macromonomers

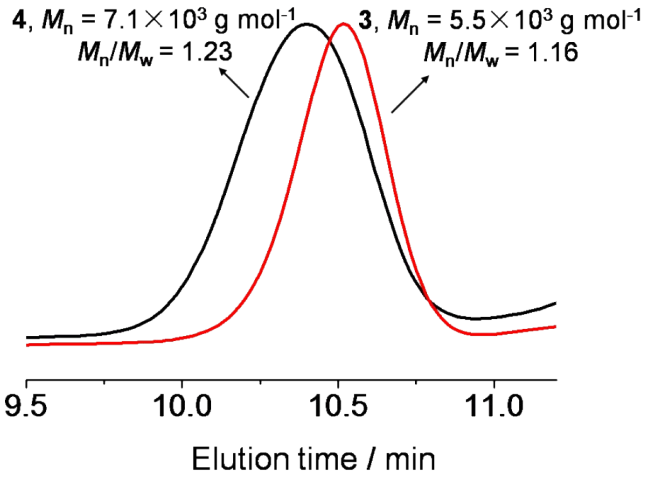


Fig. S5. GPC traces of neutral macromonomers (**3** and **4**).

*5. Concentration dependent ^{1}H NMR experiments of **MRSP2***

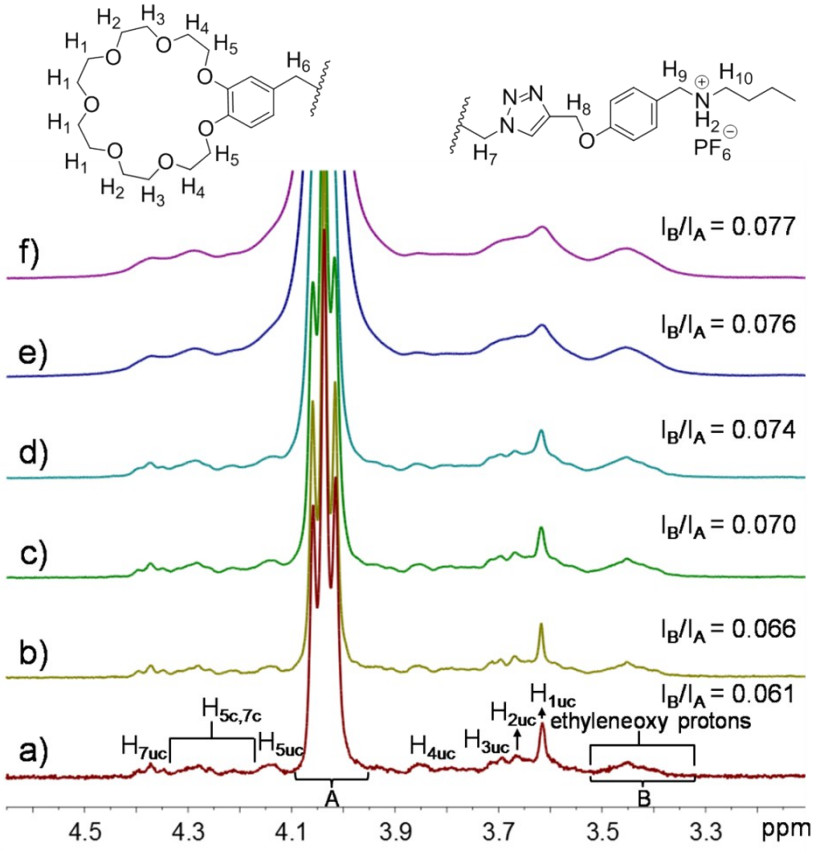


Fig. S6. Partial ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN = 2:1 (*v*/*v*), 293 K) spectra of **MRSP2** at different concentrations: a) 5.00 g/L; b) 10.0 g/L; c) 20.0 g/L; d) 40.0 g/L; e) 80.0 g/L; f) 120 g/L. Complexed and uncomplexed moieties are denoted by "c" and "uc", respectively.

*6. Cation-, pH-, and anion-responsive ^{1}H NMR experiments of **MRSP2***

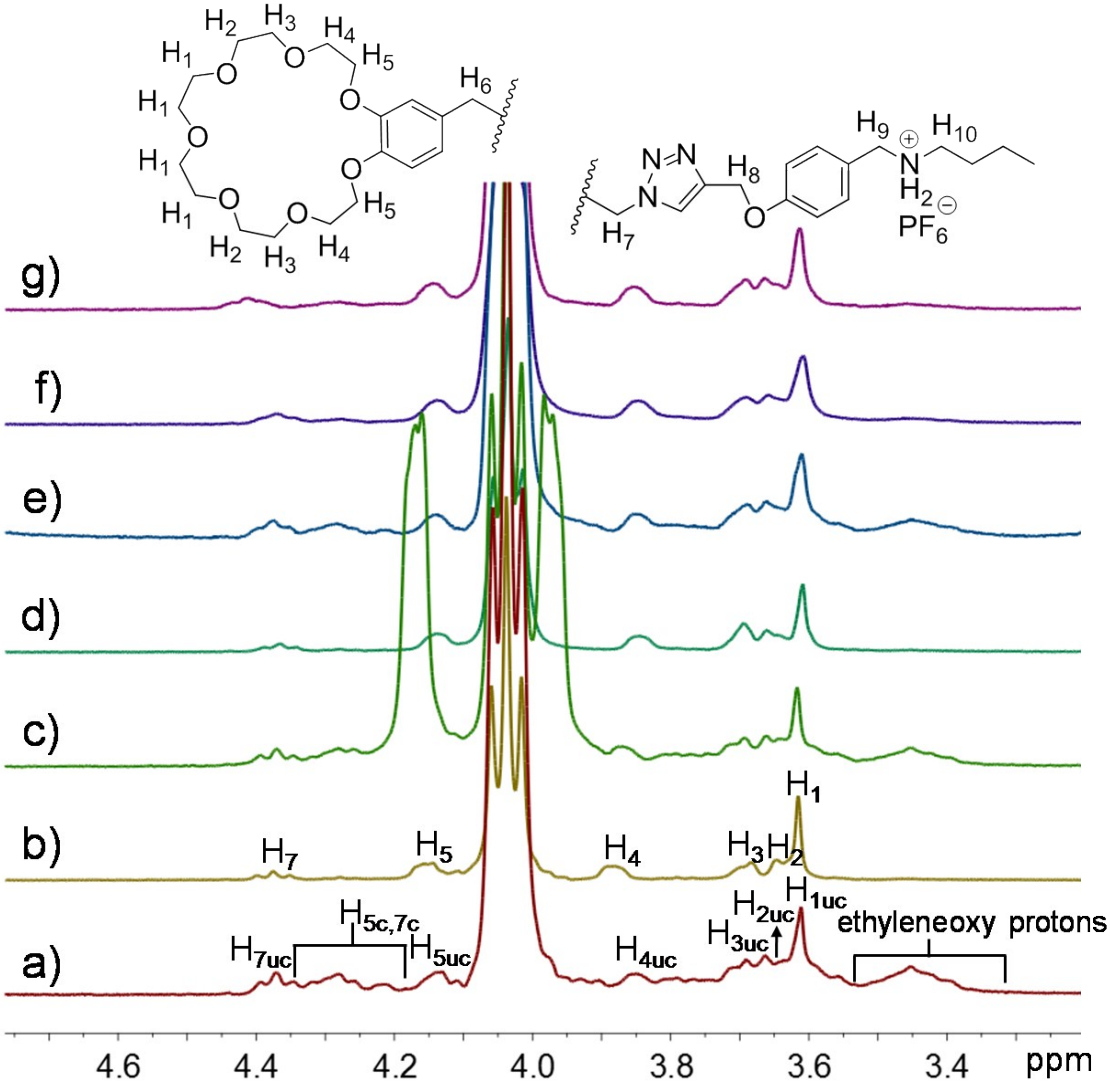


Fig. S7. Partial ^{1}H NMR (400 MHz, $CDCl_3$:CD_3CN = 2:1 (*v*/*v*), 293 K) spectra: a) **MRSP2** (20.0 g/L); b) after addition of 1.5 equiv. KPF_6 to a; c) after addition of 2.0 equiv. of DB18C6 to b; d) after addition of 1.5 equiv. of Et_3N to a; e) after addition of 2.0 equiv. of CF_3COOH to d; f) after addition of 1.5 equiv. of TBACl to a; g) after addition of 2.0 equiv. of $AgPF_6$ to f; Complexed and uncomplexed moieties are denoted by "c" and "uc", respectively.

*7. Partial variable temperature ^1H NMR spectra of **MRSP2***

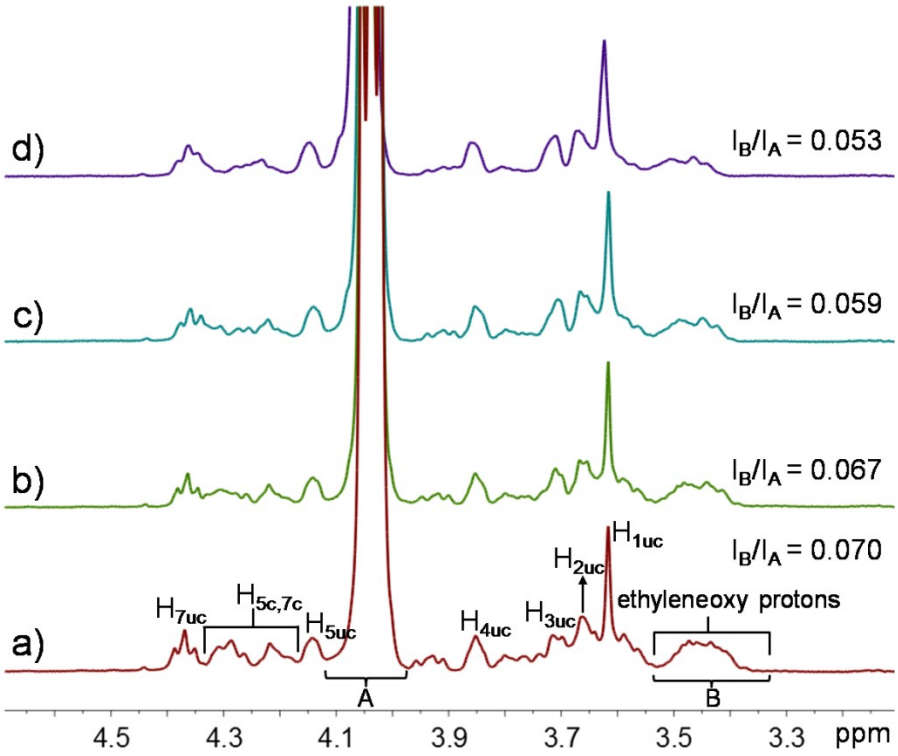


Fig. S8. Partial variable temperature ^1H NMR spectra of **MRSP2** (20.0 g/L, 500 MHz, $CDCl_3$:CD_3CN = 2:1 (*v*/*v*)): a) 293 K, b) 303 K, c) 313 K, d) 323 K. Complexed and uncomplexed moieties are denoted by "c" and "uc", respectively.

*8. DSC curves of **MRSPs** and their neutral macromonomers*

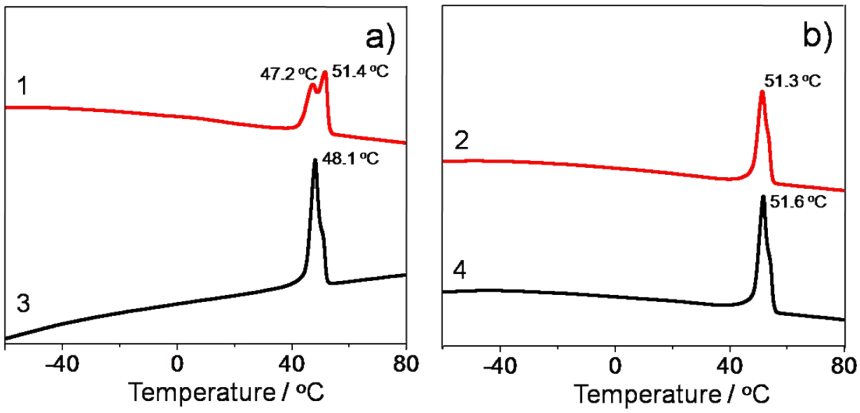


Fig. S9. DSC curves of **MRSP1** and its neutral macromonomer **3** a); **MRSP2** and its neutral macromonomer **4** b) in the heating process.

9. References

S1. Z. Ge, J. Hu, F. Huang and S. Liu, *Angew. Chem., Int. Ed.,* 2009, **48**, 1798.

S2. X. Yan, D. Xu, X. Chi, J. Chen, S. Dong, X. Ding, Y. Yu and F. Huang, *Adv. Mater.,* 2012, **24**, 362.

S3. J. Chen, X. Yan, X. Chi, X. Wu, M. Zhang, C. Han, B. Hu, Y. Yu and F. Huang, *Polym. Chem.,* 2012, **3**, 3175.