Electronic Supplementary Information (ESI)

Synthesis of thermoresponsive phenyl- and naphthyl-terminated poly(NIPAM) derivatives using RAFT and their complexation with cyclobis(paraquat-*p*-phenylene) derivatives in water

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Instrumentation.

^{1}H NMR spectra were recorded at 25°C, with a Bruker Avance 300 spectrometer. Size exclusion chromatography (SEC) measurements were performed on a Waters 515 GPC system with a Waters 1410 refractive index detector. Two columns (Styragel HR3, Styragel HR4) placed in series were employed for the chromatography. The system was calibrated against linear polystyrene (PS) standards ranging molecular weight from 580 to 377 400 Da. Experiments were performed at 40°C in THF eluent with a flow rate 1.0 mL/min. UV/vis measurements were carried out on a Varian Cary 50 Scan UV-vis spectrophotometer equipped with a Cary temperature controller. For LCST (Lower Critical Solution Temperature) measurements, spectra were recorded at 700 nm and LCST values were determined at 50% transmittance. GC measurements were performed on a Varian CP 3800 GC used with Alltech column (length = 30 m, diameter = 0.32 mm).

All electrochemical experiments were performed using an Autolab PGSTAT 30 workstation. The experiments were carried out in 0.5M NaCl aqueous solution. A three-electrode configuration was used with a platinum disk (2 mm diameter) as working electrode, an Ag/AgCl reference electrode, and a platinum wire as the counter electrode. The solution was purged with nitrogen prior to recording the electrochemical data and all measurements were recorded at 298 K under a nitrogen atmosphere.

Isothermal titration calorimetry (ITC) experiments were performed at 25 °C using a MicroCal VP-ITC titration microcalorimeter (MicroCal, Northampton, MA) with a sample cell volume of 1.4 mL, following standard procedures. A 250µL injection syringe was used with stirring at 310 rpm. Samples were dissolved in deionised water and the solutions were degassed gently under vacuum before use. Each titration comprised an initial 1µl pre-injection followed by 25 x 10µl injections of guest P1(0.043 mM), P2(0.043 mM), P3(0.055 mM) into host solution CBPQT-Cl (0.85 mM). Control experiments with identical injections of P1, P2 or P3 into water alone were used to correct titration data.

Materials.

All reagents were purchased from Aldrich Chemical Company and were used as received unless otherwise stated. 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid[1] and cyclobis(paraquat-*p*-phenylene) tetrakis(hexafluorophosphate) ($CBPQT^{4+}$,4 PF_6^-)[2] were

synthesized according to literature procedures. Azobis(isobutyronitrile) (AIBN) and *N*-isopropylacrylamide (NIPAM) was recrystallized from ethanol and hexane, respectively.

1-[2-(2-Hydroxyethoxy)ethoxy]-5-[2-(2-methoxyethoxy)ethoxy]naphthalene was synthesized according the procedure described in literature,[3] both 1,5-bis[2-[2-[2-methoxyethoxy]ethoxy] ethoxy]naphthalene and 1,5-bis[2-[2-methoxyethoxy]ethoxy]phenylene were synthesized according a modified procedure of the literature[3] from the corresponding alcohols.[4, 5]

Synthesis of CTA1.[1]

A solution of the 1,5-bis[2-[2-methoxyethoxy]ethoxy]naphthalene (1.92 g, 5.486 mmol), EDCI (1.57 g, 8.23 mmol), DMAP (1.00 g, 8.23 mmol) and 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid[1] (1.43 g, 6.03 mmol) in dry DCM (100 mL) was stirred for 12h at 0°C under nitrogen. The organic solution was subsequently washed with HCl (0.1M, 100 mL), $NaHCO_3$ (0.1M, 100 mL), brine (100 mL) and dried over Na_2SO_4. The solvent was evaporated to afford a crude product which was subjected to column chromatography (SiO_2: diethyl ether / petroleum spirit, 3:17). The fractions containing the product were combined and the eluent was removed in vacuum, affording CTA1 as yellow oil. Yield: 65 %

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.89 (d, J = 6.9Hz,6H), 1.61 (s, 6H), 1.85 (m, 1H), 3.09 (d, J = 6.9Hz, 2H), 3.34 (s, 3H), 3.53 (m, 2H), 3.70-3.79 (m, 4H), 3.87-3.96 (m, 4H), 4.19 (m, 4H), 4.24 (m, 2H), 6.76 (d, J = 8.1Hz, 2H), 7.27 (t, J = 8.1Hz, 2H), 7.79 (d, J = 8.1Hz, 2H).

^{13}C NMR ($CDCl_3$): δ (ppm) = 21.9 ($CH(\mathbf{C}H_3)_2$), 25.2 ($C(\mathbf{C}H_3)_2$), 27.8 ($\mathbf{C}H(CH_3)_2$), 45.0 ($\mathbf{C}H_2$-S), 56.0 ($O\mathbf{C}H_3$), 59.2 ($\mathbf{C}(CH_3)_2$), 65.2, 68.0, 69.1, 69.7, 70.8, 71.9 ($\mathbf{C}H_2$-O), 105.7, 114.6, 125.1, 126.6, 154.2 (**C**=C), 172.7 (**C**=O), 221.5 (**C**=S).

Synthesis of CTA2 and CTA3.

Both chain transfer agents were obtained from a similar synthesis of CTA1. For CTA2 (yield of 68%) and *CTA3* (yield of 64%), 1,5-bis[2-[2-[2-methoxyethoxy]ethoxy] ethoxy]naphthalene and 1,5-bis[2-[2-methoxyethoxy]ethoxy]phenylene respectively was used instead of 1,5-bis[2-[2-methoxyethoxy]ethoxy]naphthalene.[3]

CTA2. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.90 (d, J=7.1Hz, 6H), 1.61 (s, 6H), 1.87 (m, 1H), 3.10 (d, J = 7.1Hz, 2H), 3.30 (s, 3H), 3.47 (s, 2H), 3.60 (s, 4H), 3.64 (s, 4H), 3.68-3.77 (m, 4H), 3.93 (m, 4H), 4.19 (m, 4H), 4.23 (m, 2H), 6.77 (d, J = 7.8Hz, 2H), 7.27 (t, J = 8.0Hz, 2H), 7.78 (d, J = 8.4Hz, 2H).

^{13}C NMR ($CDCl_3$): δ = 22.0 ($CH(\mathbf{C}H_3)_2$), 25.3 ($C(\mathbf{C}H_3)_2$), 27.9 ($\mathbf{C}H(CH_3)_2$), 45.2 ($\mathbf{C}H_2$-S), 56.0 ($O\mathbf{C}H_3$), 59.0 ($\mathbf{C}(CH_3)_2$), 65.1, 67.9, 68.9, 69.8, 70.6, 70.7, 71.0, 72.0 ($\mathbf{C}H_2$-O), 105.6, 114.6, 125.1, 126.7, 154.3 (**C**=C), 173.0 (**C**=O), 221.8 (**C**=S).

CTA3. ^{1}H NMR ($CDCl_3$): δ (ppm) = 0.92 (d, J = 6.7Hz, 6H), 1.62 (s, 6H), 1.88 (m, 1H), 3.10 (d, J = 6.9Hz, 2H), 3.32 (s, 3H), 3.60 (s, 2H), 3.71-3.79 (m, 4H), 3.79-3.88 (m, 4H), 4.03-4.14 (m, 4H), 4.30 (m, 2H), 6.78 (s, 4H).

^{13}C NMR ($CDCl_3$): δ = 22.0 ($CH(\mathbf{C}H_3)_2$), 25.3 ($C(\mathbf{C}H_3)_2$), 27.9 ($\mathbf{C}H(CH_3)_2$), 45.2 ($\mathbf{C}H_2$-S), 54.6 ($O\mathbf{C}H_3$), 59.1 ($\mathbf{C}(CH_3)_2$), 65.1, 68.0, 68.9, 69.8, 70.7, 71.9 ($\mathbf{C}H_2$-O), 115.5, 153.1 (**C**=C), 170.7 (**C**=O), 220.7 (**C**=S).

Typical procedure for counterion exchange from CBPQT^{4+},4 PF_6^- into CBPQT^{4+},4 Cl^-.

To a saturated solution of CBPQT^{4+},4 PF_6^- (300 mg,) in nitromethane (3 mL) was added, in excess, a saturated solution of tetraethylammonium chloride in nitromethane[6]. The precipitate was then isolated by filtration, washed successively with nitromethane and diethyl ether. The solid CBPQT^{4+},4 Cl^- was then dried under vacuum overnight. Yield = 100%.

The same procedure was followed for the synthesis of CBPQT^{4+},4 Br^- and CBPQT^{4+},4 I^- except tetraethylammonium bromide and tetraethylammonium iodide, respectively, were used instead of tetraethylammonium chloride.

CBPQT^{4+},4 I^-. ^{1}H NMR (D_2O): δ (ppm) = 5.83 (s, 8H), 7.59 (s, 8H), 8.27-8.29 (m, 8H), 9.06-9.07 (m, 8H).

CBPQT^{4+},4 Br^-. ^{1}H NMR (D_2O): δ (ppm) = 5.83 (s, 8H), 7.60 (s, 8H), 8.25-8.27 (m, 8H), 9.07-9.09 (m, 8H).

General RAFT polymerization procedure.

A solution of chain transfer agent (CTA1, CTA2 or CTA3, 1 equiv.), AIBN (0.1 or 0.25 equiv.) and a freshly recrystallized NIPAM (100 equiv.) in DMF (5mL) was deoxygenated by bubbling nitrogen for 30 min at room temperature. The reaction flask was placed in a preheated oil bath to the desired temperature (70°C or 80°C). At the end of the polymerization, the solution was cooled to room temperature. The polymer was isolated by precipitation in diethyl ether followed by two successive precipitations from THF into diethyl ether.

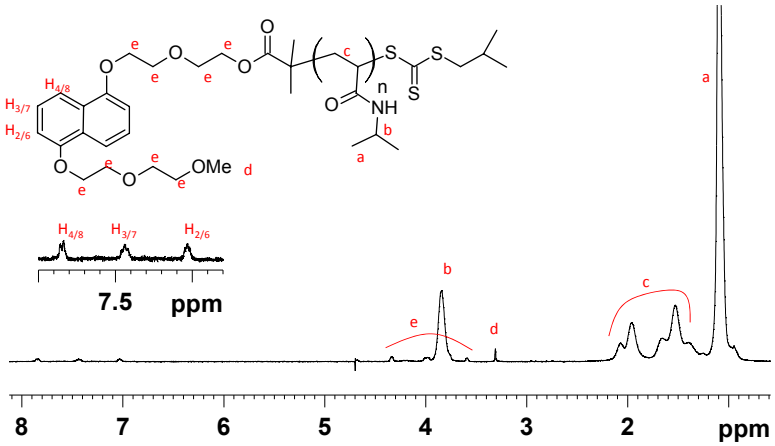

Fig.S1. ^{1}H NMR (D_2O) spectrum of CTA1-PNIPAM.

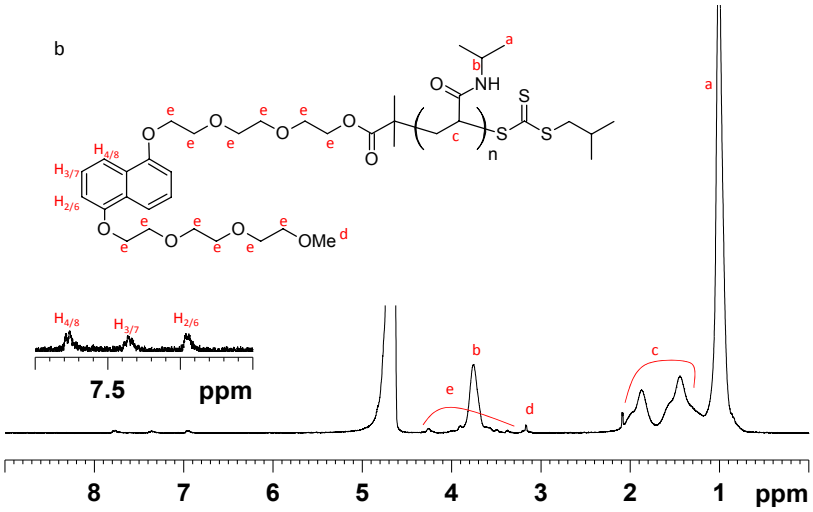

Fig.S2. ^{1}H NMR (D_2O) spectrum of CTA2-PNIPAM.

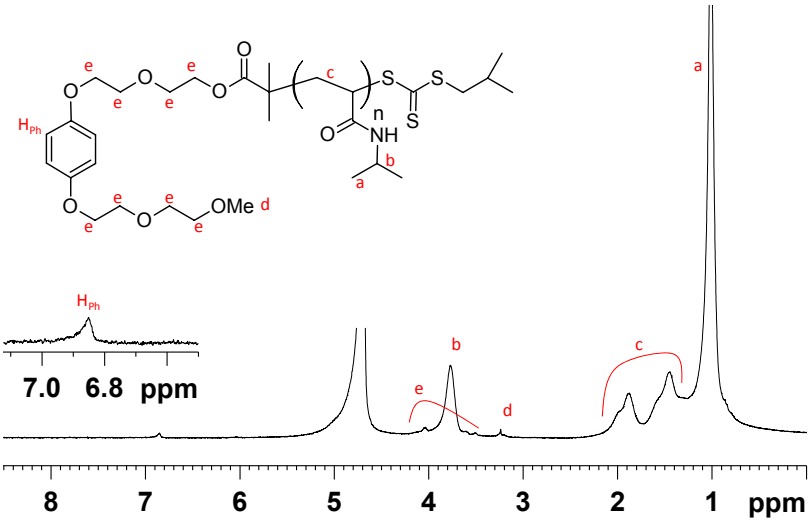

Fig.S3. ^{1}H NMR (D_2O) spectrum of CTA3-PNIPAM.

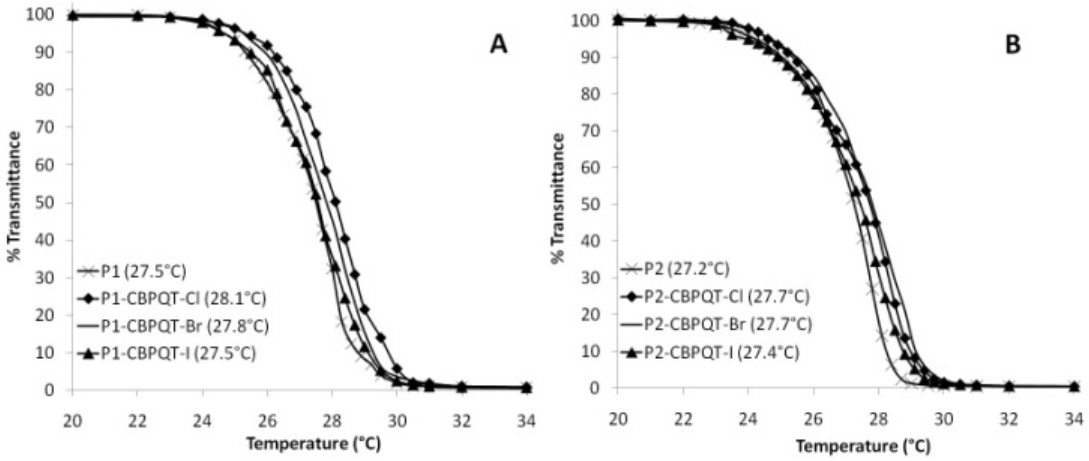

Fig.S4. Influence of the counterion on phase transitions of complexed polymer systems between $CBPQT^{4+}$,$4X^-$ and P1 (graphic A) or P2 (graphic B), data recorded by UV/vis spectroscopy at 700 nm, 2 g/L.Values in brackets correspond to the cloud point, as determined at 50% transmittance.

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