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A water-soluble supramolecular polymeric dual sensor for temperature and pH with an associated direct visible readout

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Abstract

We report a multi-stimuli responsive polymeric sensor consisting of a pseudorotaxane-like architecture fabricated from a 1,5-diaminonaphthalene end-functionalized poly(*N*-isopropyl)acrylamide (**Napht-N-PNIPAM**) and cyclobis(paraquat-*p*-phenylene) (**CBPQT^{4+},4Cl$^-$**). The coloured nature of the poly-pseudorotaxane provides a sensor for temperature and pH in water with an associated visible readout. To create this dual responsive polymeric sensor, a new chain transfer agent (**Napht-N-CTA**) incorporating a pH-responsive 1,5-diaminonaphthalene unit was synthesized and used for the polymerization of *N*-isopropylacrylamide *via* Reversible Addition-Fragmentation Chain Transfer (RAFT). The ability of **Napht-N-PNIPAM** to form a pseudorotaxane architecture with **CBPQT^{4+},4Cl$^-$** in aqueous media was studied by means of UV-Vis, NMR (^{1}H, 2D-ROESY, DOSY) and ITC experiments. Interestingly, the pseudorotaxane architecture can be reversibly dissociated upon either heating the sample above its cloud point or protonating the nitrogen atoms of the 1,5-diaminonaphthalene-based guest unit by adjusting the pH to around 1. In both cases a dramatic colour change occurs from intense blue-green to colourless.

Introduction

Stimuli-responsive polymeric materials have attracted considerable attention and have become a much studied sub-discipline in contemporary polymer chemistry [1-6]. This burgeoning field has significantly benefitted by advances in controlled (radical) polymerizations, which has led to rapid development of novel stimuli-responsive polymers with bespoke and well-defined (macro)molecular

architectures with largely predictable physicochemical properties. The growing interest in smart polymers able to respond to different stimuli including: temperature, light, pH, ionic strength, and analyte concentration has led to the development of functional polymers with a range of new applications [7-14], including smart drug delivery systems for instance [15-17]. In addition, the last decade has provided stimuli-responsive polymers capable of sensing and responding to environmental changes or the presence of analytes. Compared to their molecular-scale brethren, macromolecular based sensors offer several advantages including improved detection sensitivity, better dispersability in aqueous media, and flexibility of processing thus facilitating their integration into viable devices.

Temperature and pH play a central role in many fields of science and engineering, and as a consequence, attention has been directed towards the design of smart polymeric systems capable of monitoring these two parameters. Usually these polymeric sensor systems incorporate reporter units which take advantage of the intrinsic responsiveness of polymers to their microenvironment such as the structural changes that accompany temperature (e.g. Lower Critical Solution Temperature, LCST) or pH changes. Although numerous responsive polymer matrices incorporating either temperature or pH sensitive fluorescent probes have been reported in literature [18-24], it is noteworthy that very few dual-fluorescent sensors capable of monitoring both temperature and pH changes have been described in literature [25]. Moreover, in comparison to fluorescence based sensors, only a limited number of absorbance-based visible polymeric sensors has been reported to date. More particularly, thermo or pH responsive polymeric sensors featuring a visible readout have largely focused upon solvatochromic dyes (e.g. mercocyanine or coumarin or rhodamine type dyes, dispersed red 1, bromothymol blue) that have been physically or covalently embedded into a thermoresponsive polymer matrix [25-32].

Recently, our group has reported a straightforward supramolecular approach to elaborate a new family of thermosensors with an associated direct visible readout [33]. This host-guest concept is based on the thermo-responsiveness of coloured complexes formed from naphthalene functionalized PNIPAM as guests and cyclobis(paraquat-*p*-phenylene) (**CBPQT^{4+},4Cl$^-$**) as host, that above their cloud points undergo LCST-induced dethreading, thereby resulting in a complete disappearance of the characteristic purple colour associated with complexes of this type. This concept was notably exploited to create supramolecular-based programmable, reprogrammable thermometers that also display a thermal memory function. Here, we report on the elaboration of a new supramolecular polymeric system, consisting of a 1,5-diaminonaphthalene end functionalized PNIPAM (**Napht-N-PNIPAM**) complexed with **CBPQT^{4+},4Cl$^-$**, capable of sensing both temperature and

pH with a visual readout. In this paper, the synthesis of **Napht-N-PNIPAM** and its propensity to form a strong coloured host-guest assembly in aqueous media with **CBPQT^{4+},4Cl$^-$** is reported in detail, as well as the thermo and pH responsiveness of **Napht-N-PNIPAM.CBPQT** supramolecular complex.

Results & Discussion

A novel RAFT agent **Napht-N-CTA** was conveniently prepared from the coupling reaction of 1,5-bis[2-(2-hydroxyethoxy)ethylamino]naphthalene[34] **1** and 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methyl propionic acid (compound **2**, Scheme 1).
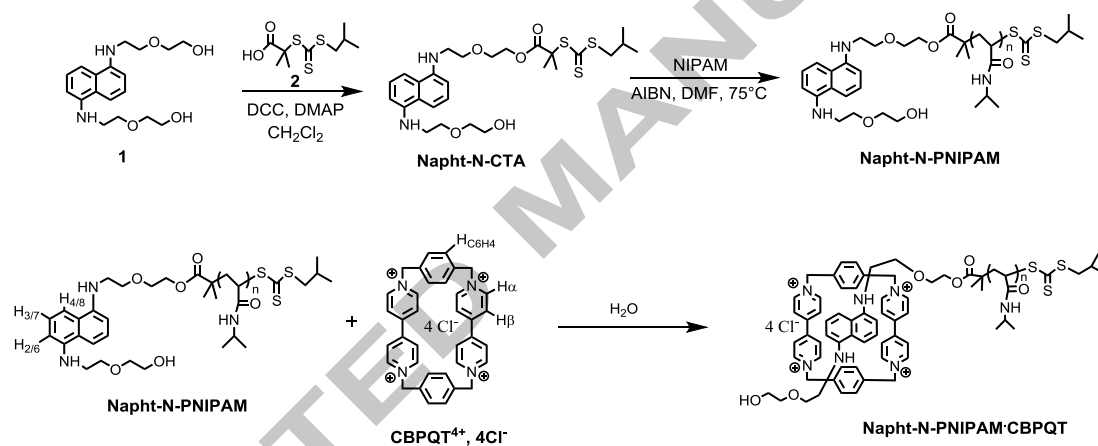
Scheme 1. Synthesis of the RAFT agent Napht-N-CTA and the polymer Napht-N-PNIPAM

The structure of the **Napht-N-CTA** was confirmed by ^{1}H NMR, ^{13}C NMR and 2D NMR (see ESI Figures S1, S2 and S3 respectively) spectroscopies. ^{1}H NMR spectrum of **Napht-N-CTA** recorded in CD$_3$CN revealed the presence of the characteristic signals of protons belonging to the naphtalene unit ($\delta_{H2/6}$ = $\delta_{H3/7}$ = 7.4 ppm and $\delta_{H4/8}$ = 6.9 ppm) and the methyl fragment of the isobutyl group (δ_{CH_3} = 0.9 ppm). Furthermore, the ^{13}C spectrum clearly displayed chemical shifts at 172.1 ppm and 222.2 ppm ascribed to the amide carbonyl group and the thiocarbonyl fragment of the RAFT agent, respectively.

The ability of the **Napht-N-CTA** to promote RAFT polymerizations was demonstrated with *N*-isopropylacrylamide (NIPAM). The polymerization of NIPAM (150 equiv.) was carried out with azobis(isobutyronitrile) (AIBN, 0.2 equiv.) as a radical source and Napht-N-CTA (1 equiv.) in DMF at 75°C for 1h. The absolute molecular weight and the dispersity index (*Đ*) of the polymer were determined by SEC (*Mn*$_{abs}$ = 14810 g/mol, *Đ* = 1.07, *dn/dc* = 0.0886 mL/g, Figure S 4). In addition, the structure of **Napht-N-PNIPAM** was confirmed by ^{1}H NMR spectroscopy in D$_2$O, which displayed the

characteristic signals of PNIPAM (δ_{N-CH} =3.95 ppm, δ_{CH3} = 1.20 ppm, Figure S 5) in addition to those belonging to the naphthalene moiety ($\delta_{H2/6}$ = $\delta_{H3/7}$ = 7.5 ppm, $\delta_{H4/8}$ = 6.9 ppm, Figure 1a).

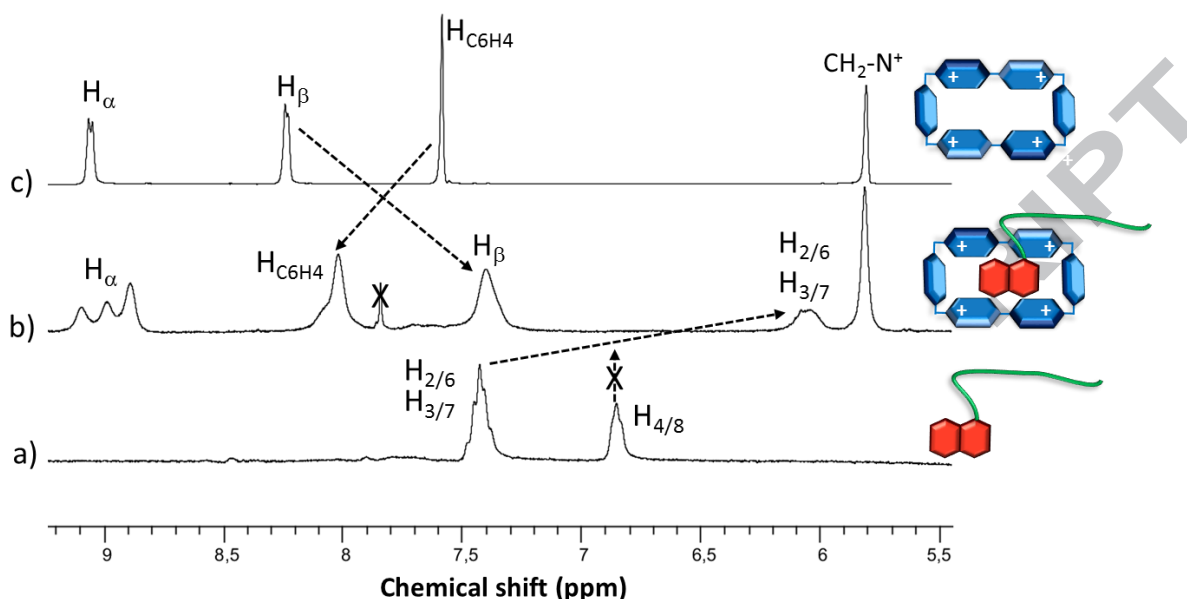**Figure 1. Partial ^{1}H NMR spectra of: a) Napht-N-PNIPAM, b) Napht-N-PNIPAM⁻CBPQT and c) CBPQT[4+],4Cl⁻. Recorded at 18°C in D₂O.**

Next, the ability of electron-rich **Napht-N-PNIPAM** to form a 1:1 complex with the electron-deficient **CBPQT[4+], 4Cl⁻** was investigated. The addition of aliquots of **CBPQT[4+], 4Cl⁻** to a solution of **Napht-N-PNIPAM** in water resulted in the immediate appearance of an intense blue-green colour, which is consistent with the formation of a donor-acceptor complex between the π-electron rich **Napht-N-PNIPAM** and the π-electron deficient **CBPQT[4+], 4Cl⁻**. This observation was confirmed by the appearance of a band centered at 697 nm in its UV-vis sprectrum (Figure 2a).
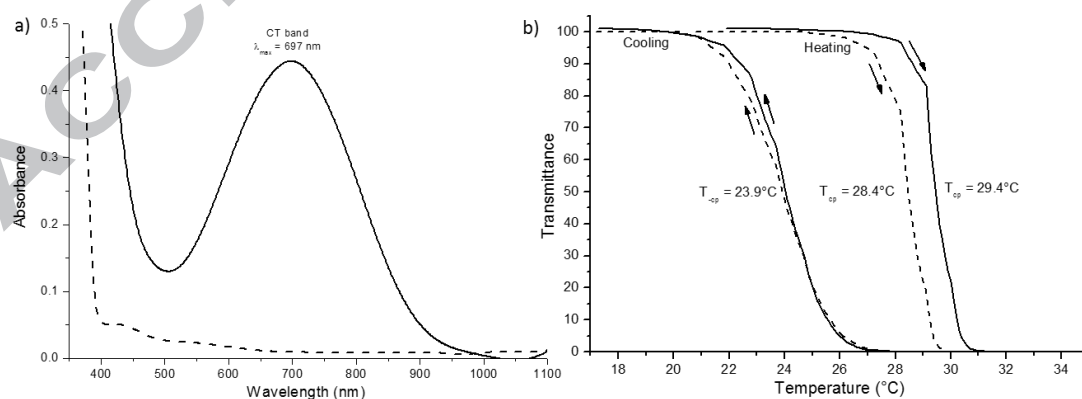

Figure 2. UV-vis spectra (a) and thermo-sensitive phase transition recorded at 950 nm (b) of Napht-N-PNIPAM (---) and Napht-N-PNIPAM in presence of 1 equivalent of CBPQT[4+] (—).

Next, we have studied the complex formation between **Napht-N-PNIPAM** and **CBPQT^{4+}, 4Cl$^-$** in aqueous media by using NMR spectroscopy (^{1}H, 2D-ROESY, DOSY, COSY). The ^{1}H NMR spectrum of a 1:1 mixture **Napht-N-PNIPAM** and **CBPQT^{4+}, 4Cl$^-$** revealed significant shifts for the H$_\beta$ ($\Delta\delta$ = -0.96 ppm), H$_{C6H4}$ ($\Delta\delta$ = +0.31 ppm) protons of **CBPQT^{4+}, 4Cl$^-$** and H$_{2/6}$, H$_{3/7}$ ($\Delta\delta$ = -1.38 ppm), H$_{4/8}$ ($\Delta\delta$ = -5.7 ppm) of **Napht-N-PNIPAM** (Figure 1b), that is in good agreement with previously reported data for complexes of this type. [34]

^{1}H NMR titration experiments were also carried out on **Napht-N-PNIPAM** upon adding aliquots of **CBPQT^{4+}, 4Cl$^-$** (Figure S 6). ^{1}H NMR spectra clearly indicated the existence of the signal for uncomplexed H$_{4/8}$ protons upon the addition of aliquots of **CBPQT^{4+}, 4Cl$^-$**, thereby suggesting a slow exchange at the NMR timescale between the uncomplexed and complexed forms. Moreover, the ^{1}H NMR titration revealed the complete disappearance of the signal of uncomplexed H$_{4/8}$ protons at 6.9 ppm when 1 equiv. of **CBPQT^{4+}, 4Cl$^-$** was added, thus indicating the formation of a 1:1 complex between **Napht-N-PNIPAM** and **CBPQT^{4+}, 4Cl$^-$**. Further proof regarding the formation of a pseudorotaxane architecture between **Napht-N-PNIPAM** and **CBPQT^{4+}, 4Cl$^-$** was also obtained from its 2D ROESY spectrum that indeed displayed a dipolar correlation between H$_{2/6}$, H$_{3/7}$ and H$_{C6H4}$ protons belonging to the guest and host partners, respectively (Figure 3a).
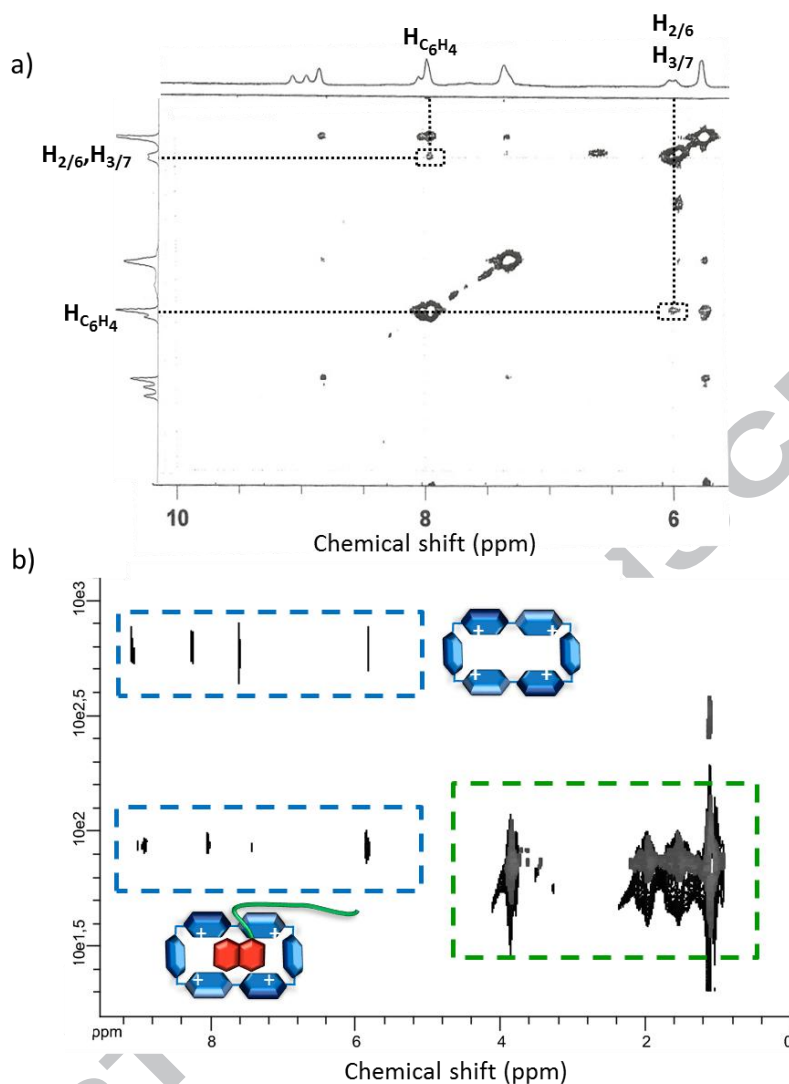
Figure 3. a) 2D-ROESY 1H-1H spectrum (D$_2$O) of Napht-N-PNIPAM·CBPQT, b) Superimposed ^{1}H NMR DOSY (D$_2$O) experiments of free CBPQT^{4+},4Cl$^-$ (upper black spectrum), Napht-N-PNIPAM (grey spectrum) and the 1:1 complex Napht-N-PNIPAM·CBPQT (bottom black spectrum)

Next, to demonstrate the robustness of the host-guest interaction between **Napht-N-PNIPAM** and **CBPQT^{4+},4Cl$^-$**, two-dimensional diffusion ordered spectroscopy (DOSY) ^{1}H NMR spectroscopy and isothermal titration microcalorimetry (ITC) experiments were undertaken. 2D-DOSY ^{1}H NMR spectroscopy experiments showed for solutions of their individual components (**CBPQT^{4+}, 4Cl$^-$** and **Napht-N-PNIPAM**) have a diffusion coefficient value of 1585 μm^2 s^{-1} and 73.3 μm^2 s^{-1}, respectively (Figure 3b). When DOSY experiments were undertaken on 1:1 **Napht-N-PNIPAM·CBPQT** solution of the complex, the protons belonging to **CBPQT^{4+}, 4Cl$^-$** moved to a lower and identical diffusion coefficient to that of **Napht-N-PNIPAM** (73.3 μm^2 s^{-1}). Moreover, no signals for the free **CBPQT^{4+}, 4Cl$^-$** were observed, thus confirming the efficiency of the coupling between **CBPQT^{4+}, 4Cl$^-$** and **Napht-N-PNIPAM**. In addition, ITC experiments indicated that addition of aliquots of **CBPQT^{4+}, 4Cl$^-$** to a dilute solution of **Napht-N-PNIPAM** in water gave rise to a large exothermic response (ΔH = -46.08 (±0.26)

kcal/mol) in good agreement with the relatively large estimated association constant of K_a = 9.2 (±0.7) x10^4 M^{-1} (Figure S 7).

Thermo-responsiveness of Napht-N-PNIPAM·CBPQT complex in water

The thermoresponsiveness of the **Napht-N-PNIPAM·CBPQT** complex was first investigated by turbidity measurements using UV-vis spectroscopy (Figure 2b). The cloud point of the polymer complexed with **CBPQT^{4+}, 4Cl$^-$** in water was determined as 29.4°C from the midpoint of the transmittance value (Figure 2b). This value was slightly higher than the cloud point estimated for **Napht-N-PNIPAM** (T_{cp} = 28.4°C, Figure 2b), thereby indicating that the hydrophilicity-hydrophobicity balance of the material can be displaced toward a more hydrophilic structure by masking the hydrophobicity of the naphthalene unit through the formation of a pseudorotaxane-like architecture with the more hydrophilic **CBPQT^{4+}, 4Cl$^-$** host [10]. More interestingly, despite the high K_a value, the phase transition of the complex (T>T_{cp}) induced a complete disappearance of the green-blue colour of the aqueous solution, suggesting a disruption of the complex upon crossing the T_{cp}. This was also evidenced by the fact that the UV-vis spectra of **Napht-N-PNIPAM** and **Napht-N-PNIPAM·CBPQT, 4Cl$^-$** were quite similar upon cooling the samples (Figure 2b). To get further insight on the cloud point-mediated host-guest disassembly, variable temperature ^{1}H NMR spectroscopy experiments were carried out. More particularly, we have investigated the changes in the ^{1}H NMR spectra of **Napht-N-PNIPAM·CBPQT** complex upon cycling the temperature between 18°C (T<T_{cp}) and 35°C (T>T_{cp}) in D$_2$O. As expected, the ^{1}H NMR spectra of **Napht-N-PNIPAM·CBPQT** upon heating from 18°C (Figure 4a) to 35°C (Figure 4b) revealed a complete disappearance of the protons belonging to the polymer due to the precipitation of the polymer at 35°C (T>T_{cp}). Moreover, the signals recorded at 35°C on Figure 44b perfectly fit to the signal of the protons of uncomplexed CBPQT^{4+} (Figure 4c), clearly suggesting that the dethreading of the complexation occurred upon heating the complex over the cloud point. In addition, when the temperature was cooled below the cloud point, the colour of the solution turned back to intense blue-green. This feature was monitored by UV-vis spectroscopy and it appeared that the maximum of absorbance of the absorption at 697 nm did not change even after 3 cycles of heating/cooling cycles, suggesting that the complexation/dethreading upon simply heating and cooling the aqueous solution is reversible (Figure S 8).
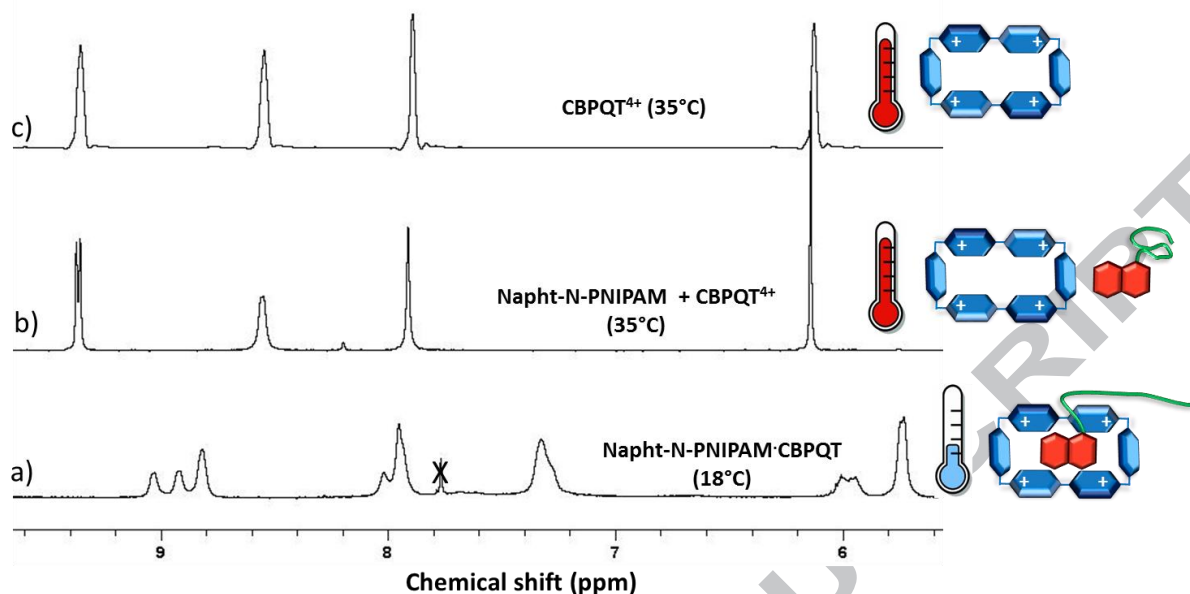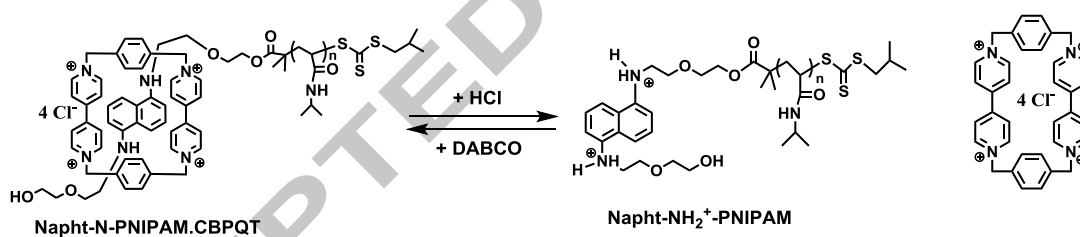
Figure 4. Partial ^{1}H NMR spectra (D$_2$O) of Napht-N-PNIPAM$^.$CBPQT at a) 18°C, b) 35°C and c) CBPQT^{4+},4Cl$^-$ at 35°C.

pH-responsiveness of Napht-N-PNIPAM$^.$CBPQT complex in water

Scheme 2. Study of the pH-responsiveness of Napht-N-PNIPAM

After demonstrating the thermo-sensitivity of **Napht-N-PNIPAM$^.$CBPQT**, its pH-responsiveness was next studied (Scheme 2). Here, the main objective was to exploit the propensity of the diaminonaphthalene unit located on PNIPAM to become protonated in acidic environments, thus affording the corresponding **Napht-NH$_2$$^+$-PNIPAM** to promote the dethreading of the pseudorotaxane architecture through Coulombic repulsion. Upon the addition of aliquots of aqueous HCl to a solution containing the **Napht-N-PNIPAM$^.$CBPQT** complex, the intense green colour (λ_{max} = 697 nm) disappeared rapidly and a colourless solution was observed as depicted in Figure 5. The UV spectrum upon adding HCl was almost identical to that of the uncomplexed polymer. Moreover, the reversibility of the procedure was demonstrated by adding aliquots of aqueous basic solution of 1,4-diazabicyclo[2.2.2]octane (DABCO, 1.5M in H$_2$O) until pH = 7 was reached. In this way, the colour of

the solution turned from colourless to intense blue-green and the obtained UV spectrum showed the characteristic band at 697 nm (Figure S 9). It is noteworthy that performing 3 complete cycles of pH = 1/pH = 7 switching provided evidence for successive decomplexation /complexation (Figure S 9).
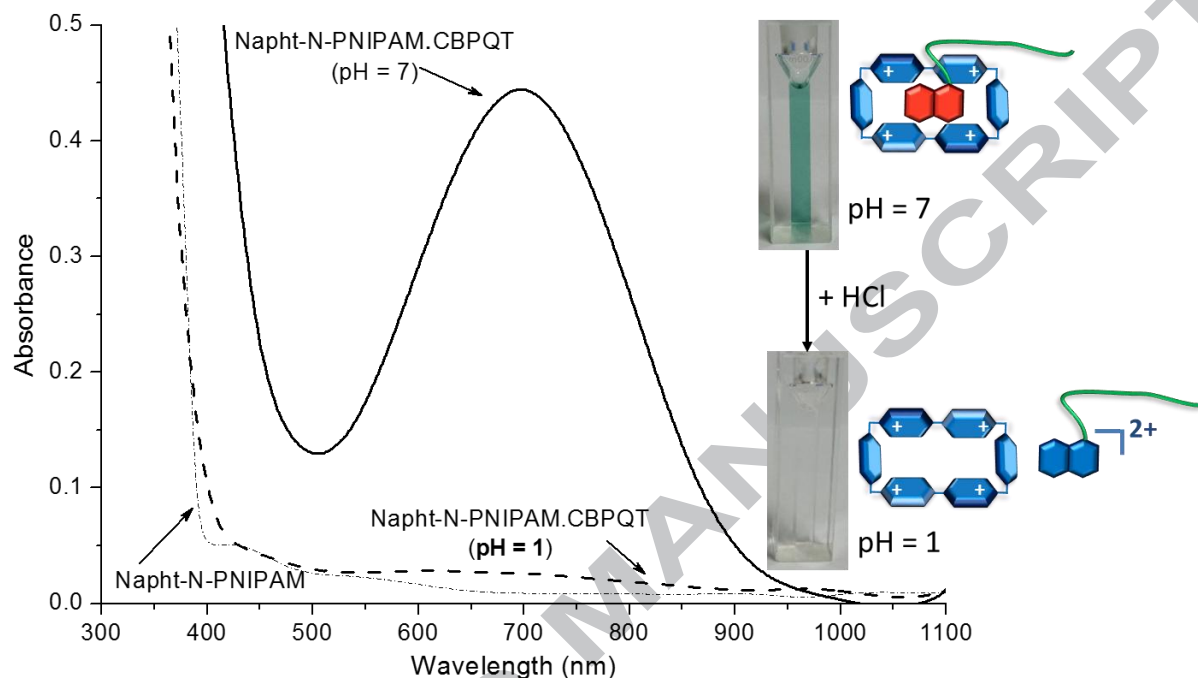

Figure 5. UV-vis spectra of uncomplexed Napht-N-PNIPAM and Napht-N-PNIPAM in presence of 1 equiv. of CBPQT^{4+}, 4Cl^{-} at pH = 1 and pH =7

In addition to UV-vis investigations, ^{1}H NMR spectroscopy experiments were performed to corroborate optical studies in acidic medium. As shown on Figure 6, when aliquots of DCl (35 wt% in D$_2$O) were added to the **Napht-N-PNIPAM·CBPQT^{4+}** complex (spectrum b), signals corresponding to the protons of uncomplexed **CBPQT^{4+}, 4Cl^{-}** were observed (*i.e.* H$_\alpha$, H$_\beta$,H$_{C6H4}$), indicating that the protonation of the naphthalene unit efficiently led to the disruption of the host/guest complex upon decreasing the pH of the solution.
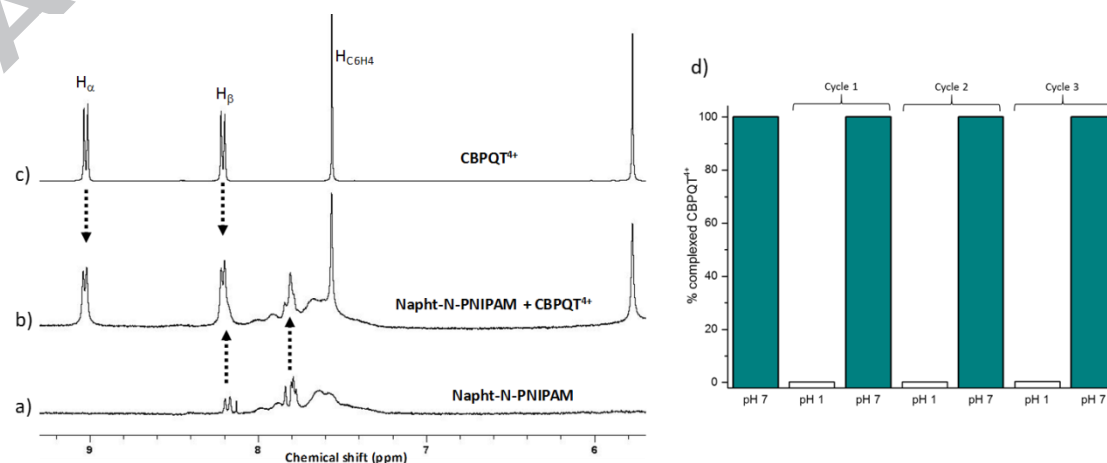
Figure 6. Partial ^{1}H NMR spectra (35%wt DCl in D$_2$O) of a) Napht-NH$_2^+$-PNIPAM, b) polymer complex in acidic medium and c) CBPQT^{4+}, 4 Cl$^-$. Chart d) represents the reversibility of pH = 7/pH = 1 switching process upon the addition of DCl (35%wt in D$_2$O) and DABCO (1.5M in D$_2$O) showing the complexation/dethreading phenomena.

The reversibility of the procedure was demonstrated by adding aliquots of an aqueous solution of DABCO (1.5M in D$_2$O) until pH = 7 was reached. As stated previously, the colour of the solution turned intense blue-green when the pH was adjusted to 7. In the ^{1}H NMR spectrum (Figure S 10), the signals of the protons of free CBPQT^{4+} disappeared while characteristic signals resulting from host-guest complexation appeared. Moreover, the reversibility of the procedure was demonstrated by performing 3 complete pH = 1/pH = 7 cycles by simply adding aliquots of solutions of DCl and DABCO, respectively. The resulting ^{1}H NMR spectra (Figure S 10) clearly demonstrate the reversibility of the experiment and the stability of the species after several cycles.

Conclusion

In this contribution, we have synthesized, using a RAFT procedure, a novel well-defined thermoresponsive polymer (Napht-N-PNIPAM) bearing a pH-sensitive 1,5-diaminonaphthalene moiety. We have demonstrated its ability to form a strong coloured Napht-N-PNIPAM·CBPQT based pseudorotaxane-like architecture in water with CBPQT^{4+}, 4Cl$^-$ by performing ^{1}H NMR spectroscopy, ITC and UV-Vis measurements. Interestingly, this complex can be conveniently disassembled either beyond its cloud point or in acidic conditions, thereby leading in both cases to the visual disappearance of the intense blue-green solution. Hence, such supramolecular assemblies can be considered as a dual sensor capable to sense both temperature and pH with a direct visible readout. Based on this supramolecular approach, we are currently designing more sophisticated multifunctional sensors capable of monitoring temperature, pH and CO$_2$. Our work in this area will be reported in due course.

Acknowledgments

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Supporting Information.

Materials. All reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. *N*-Isopropylacrylamide (NIPAM) and azobis(isobutyronitrile) (AIBN) were recrystallized from hexane and methanol, respectively. 1,5-bis[2-(2-hydroxyethoxy)ethylamino]naphthalene[1] (compound **1**), 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid[2] (compound **2**) were synthesized according the procedure described in literature.

Analytical Techniques. ^{1}H NMR and ^{13}C spectra were recorded with a Bruker Advance 300 or 400 MHz spectrometer. Polymers were analyzed by size exclusion chromatography in THF at 40 °C with a flow rate of 1 mL/min and a polymer concentration of 3 mg/mL after filtration through a 0.45 μm pore-size membrane. SEC measurements were performed on a Waters system equipped with three columns (Styragel HR1, Styragel HR3, Styragel HR4) placed in series and coupled with two Wyatt detectors: a differential refractive index (RI) detector, and a Multi Angle Light Scattering (MALS) detector (laser λ = 670 nm). The absolute number-average molar masses were calculated from combined LS and RI signals with the Astra software, using an average refractive index increment (dn/dC) of 0.0886 mL/g for Napht-N-PNIPAM. The dn/dC was measured with the RI detector by injecting polymer solutions at six different concentrations. Isothermal titration calorimetry (ITC) experiments were performed at 15 °C using a nano-ITC titration calorimeter from TA Instruments. A 250μL injection syringe was used with stirring at 400 rpm. Samples were dissolved in deionised water and the solutions were gently degassed under vacuum before use. Each titration comprised an initial 1μL pre-injection followed by 24 x 10μL injections of CBPQT^{4+},4Cl^{-} (10.18 mM) into a solution of Napht-N-PNIPAM (1.21 mM). Control experiments with identical injections of CBPQT^{4+},4Cl^{-} into water alone were used to correct titration data. UV/vis measurements were carried out on a Agilent UV-vis spectrophotometer equipped with a temperature controller. For cloud point measurements (concentration of polymer of 3mg/mL), spectra were recorded at 950 nm with a cooling/heating rate of 1°C/min and cloud point values were determined at 50% transmittance. Full UV-spectra were recorded at 20°C (concentration of polymer of 10mg/mL).

Synthesis of Napht-N-CTA. A solution of 1,5-bis[2-(2-hydroxyethoxy)ethylamino]naphthalene **1** (1.00g, 2.99mmol), 2-(1-isobutyl)sulfanylthiocarbonylsulfanyl-2-methylpropionic acid **2** (0.893g, 3.59mmol), DCC (0.74g, 3.59mmol) and DMAP (40mg, 0.33mmol) in dry DCM (80 mL) was stirred for 1 h at 0°C under nitrogen then at room temperature for 24h. After removal of the solid by filtration,

the solvent was evaporated to afford a crude product which was subjected to column chromatography (SiO$_2$: petroleum spirit / ethyl acetate 3:2). The fractions containing the product were combined and the eluent was removed in vacuum, affording the product CTA agent as brownish oil. Yield: 36 %
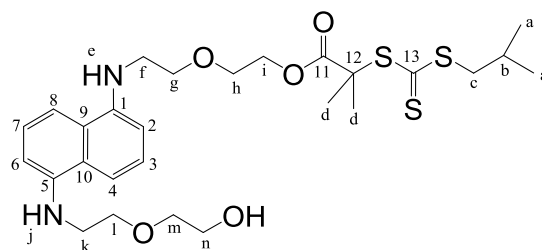
^{1}H NMR (300 MHz, CD$_3$CN), δ (ppm from TMS): 0.95 (d, J = 6.56 Hz, 6H, H$_a$), 1.69 (s, 6H, H$_d$), 1.91 (m, J = 6.57 Hz, 1H, H$_b$), 3.19 (d, J = 6.74 Hz, 2H, H$_c$), 3.44 (m, 4H, H$_{f,k}$), 3.60 (m, 2H, H$_m$), 3.66 (m, 2H, H$_n$), 3.72 (m, 2H, H$_h$), 3.81 (m, 4H, H$_{l,g}$), 4.26 (m, 2H, H$_i$), 5.00 (br, 2H, H$_{e,j}$), 6.65 (t, 2H, H$_{4/8}$), 7.26 (d, 2H, H$_{2/6}$), 7.31 (t, 2H, H$_{3/7}$).
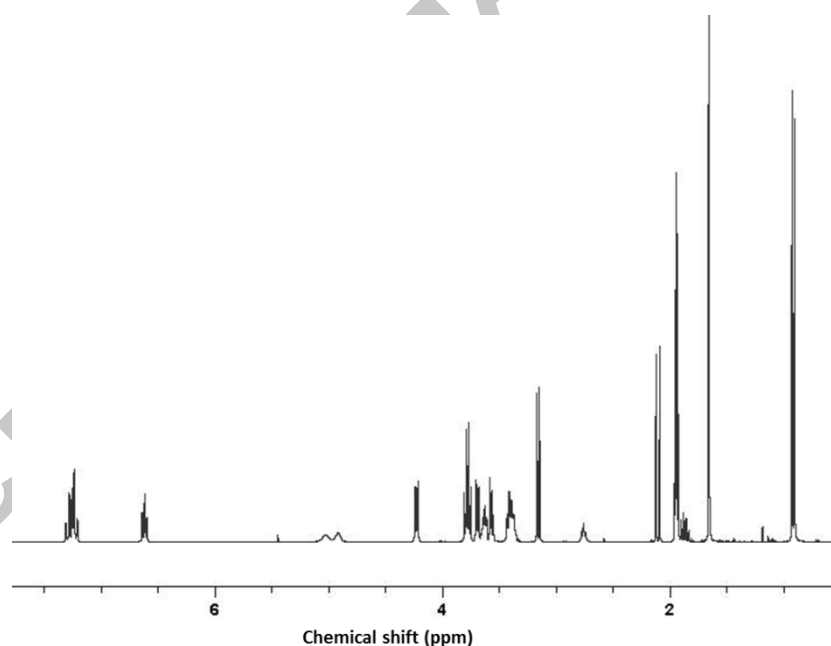
Figure S 1. ^{1}H NMR (CD$_3$CN) spectrum of Napht-N-CTA

^{13}C NMR (75 MHz, CD$_3$CN), δ: 20.7 (C$_a$), 24.4 (C$_d$), 27.5 (C$_b$), 43.2 (C$_{k/f}$), 44.5 (C$_c$), 55.7 (C$_{12}$), 60.7 (C$_i$), 64.8 (C$_h$), 68.2 (C$_n$), 68.7 (C$_{g/l}$), 71.9 (C$_m$), 103.9 (C$_{2/6}$), 108.8 (C$_{4/8}$), 123.8 (C$_{9,10}$), 125 (C$_{3/7}$), 143.9 (C$_{1/5}$), 172.1 (C$_{11}$), 222.2 (C$_{13}$).
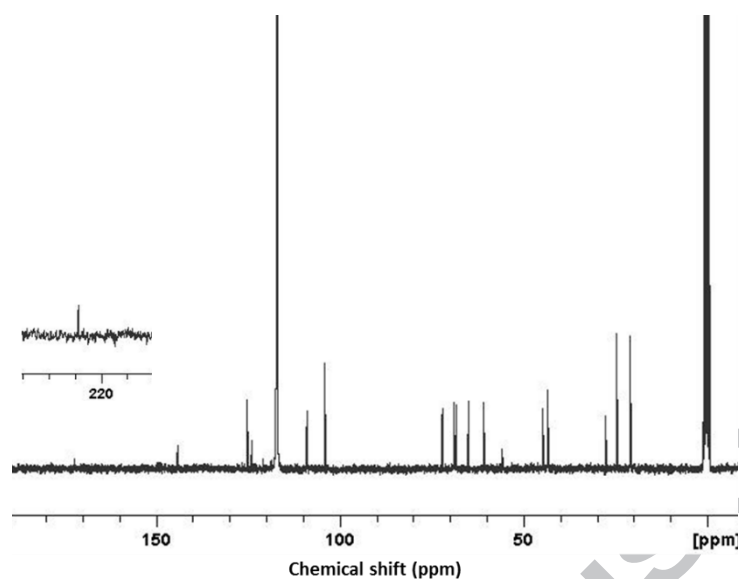
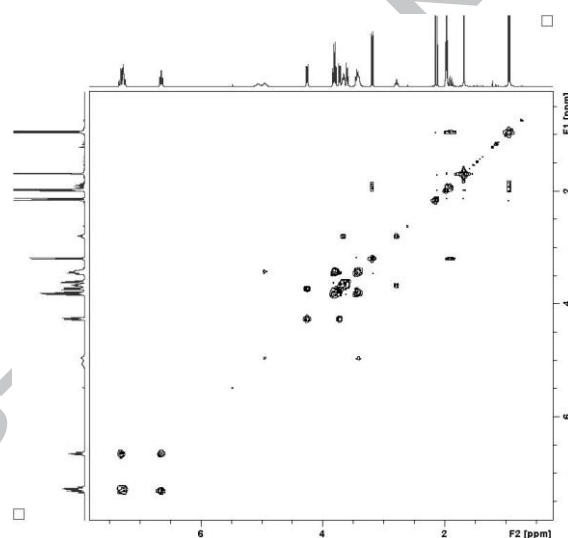**Figure S 2.** ^{13}C NMR (CD$_3$CN) spectrum of Napht-N-CTA

Figure S 3. COSY(^{1}H-^{1}H) NMR spectrum of Napht-N-CTA (CD$_3$CN)

Synthesis of Napht-N-PNIPAM using RAFT polymerization. In a Schlenk tube were added *N*-isopropylacrylamide (2.25g, 19.81mmol), AIBN (4.4mg, 0.026mmol) and Napht-N-CTA (75mg, 0.132mmol) in DMF (5mL). The mixture was deoxygenated by nitrogen bubbling for 1h. The mixture was then heated to 75°C. After 1 hour, the final polymer Napht-N-PNIPAM was recovered by precipitation in diethyl ether. After filtration, the product was dried under vacuum until constant weight. NMR conversion = 70 %, Mn$_{abs}$ = 14810 g/mol, Đ = 1.07 (dn/dc = 0.0886 mL/g in THF).
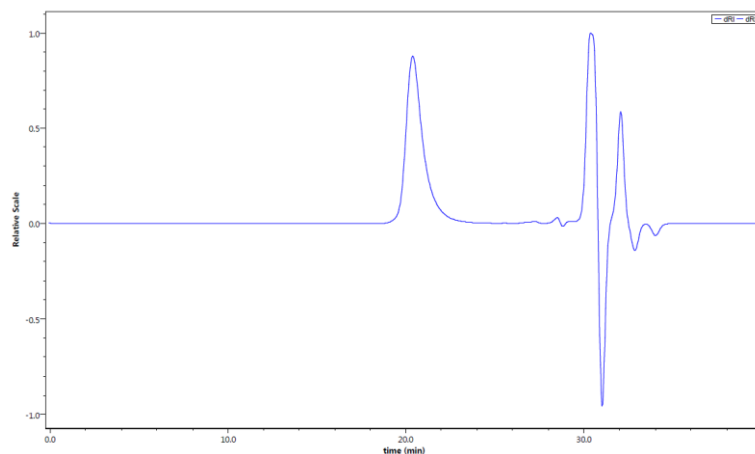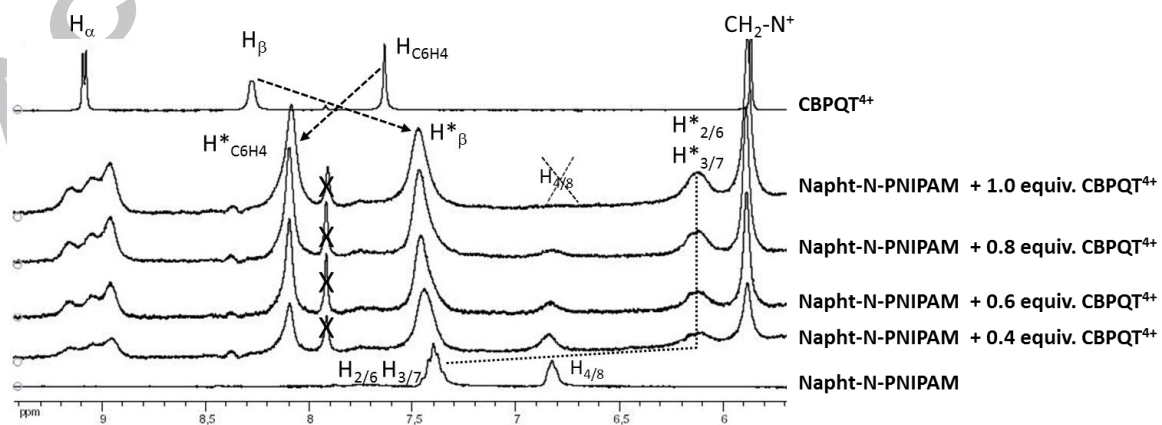
Figure S 4. GPC trace (THF) of Napht-N-PNIPAM
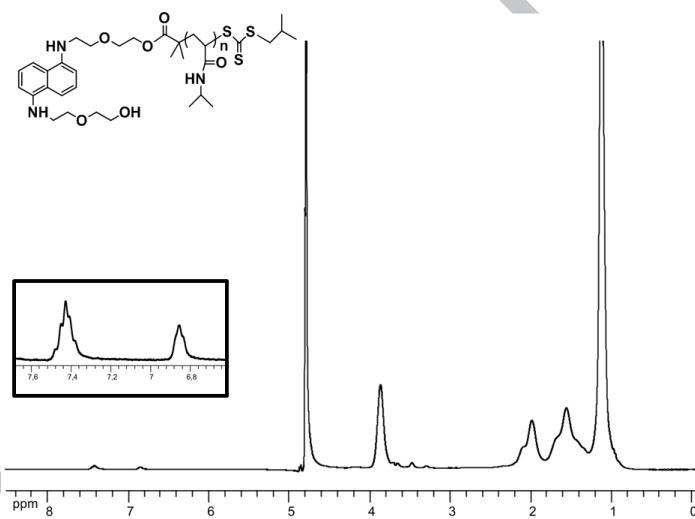
Figure S 5. ^{1}H NMR (D$_2$O) spectrum of Napht-N-NIPAM

Figure S 6. ^{1}H NMR (D$_2$O) titration of Napht-N-PNIPAM upon the addition of aliquots of CBPQT^{4+},4Cl$^-$ in D$_2$O. Protons marked with * correspond to protons complexed in the host/guest supramolecular assembly (The symbol X at 7.9 ppm corresponds to remaining DMF in the analyzed samples)
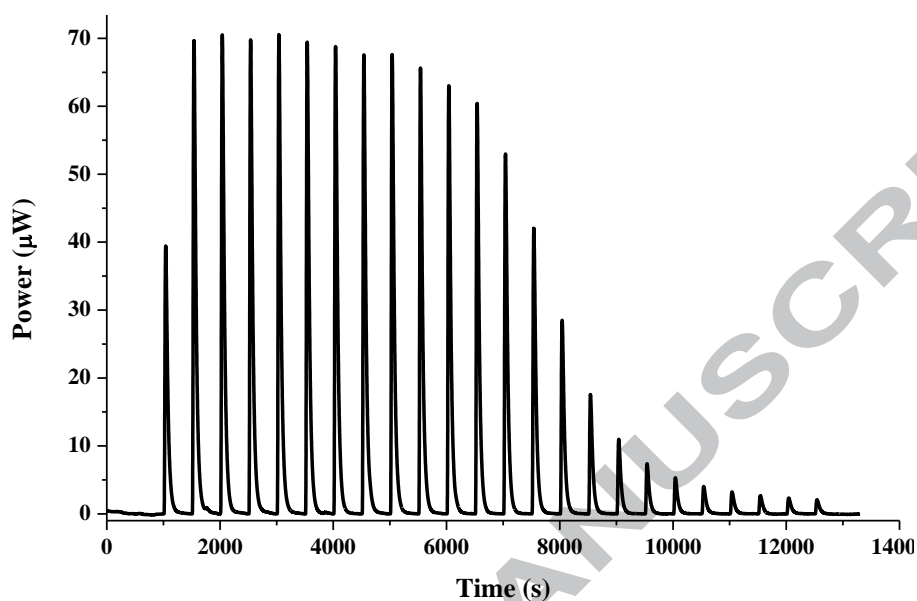

Figure S 7. Isothermal titration calorimetry data for the addition of aliquots of CBPQT^{4+} (10.18mM) to Napht-N-PNIPAM (1.21 mM). Recorded in H$_2$O at 15°C.
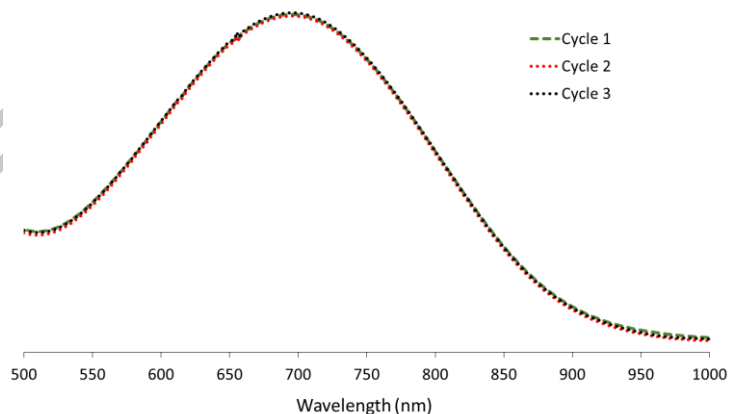

Figure S 8. UV-vis spectra at 20°C of Napht-N-PNIPAM·CBPQT after 3 cycles of heating (over the cloud point) and cooling (cycle 1: green curve, cycle 2: red curve and cycle 3: black curve).

A solution of Napht-N-PNIPAM·CBPQT in water was heated over the cloud point and then cooled down to 20°C. Then, a UV-vis spectrum was recorded demonstrating the presence of the charge transfer band. Three cycles were carried out to prove the reversibility of the complexation/dethreading process.

pH = 1 / pH = 7 switching of an aqueous solution of Napht-N-PNIPAM˙CBPQT monitored by UV-vis spectroscopy.
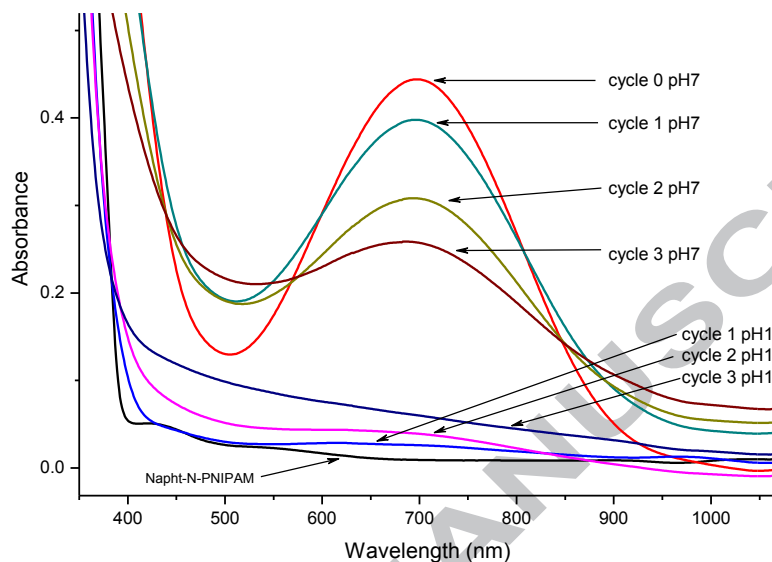

Figure S 9. UV-vis spectra of Napht-N-PNIPAM˙CBPQT at pH = 1 and 7

To a solution of Napht-N-PNIPAM˙CBPQT in water at pH = 7 (cycle 0, pH7, Figure S 9) were added aliquots of HCl (1M) to obtain pH = 1 (cycle 1, pH1, Figure S 9). It leads to protonation of naphthalene unit located at the end chain of PNIPAM and then to the disruption of the host-guest complex (no absorption band at 697 nm). The process is reversible when aliquots of DABCO (1.5M) are added to the mixture in order to obtain pH = 7 (cycle 1, pH7, Figure S 9) since the band at 697 nm appears. Repeating the procedure of HCl/DABCO additions led to similar results, i.e. disappearance and reappearance of the absorption band (3 cycles in total) without any signs of decomposition (NMR data not shown). The observed decrease of the absorbance upon addition of aliquots is due to the dilution phenomenon in the UV cell.

pH = 1 / pH = 7 switching of an aqueous solution of Napht-N-PNIPAM monitored by ^{1}H NMR.
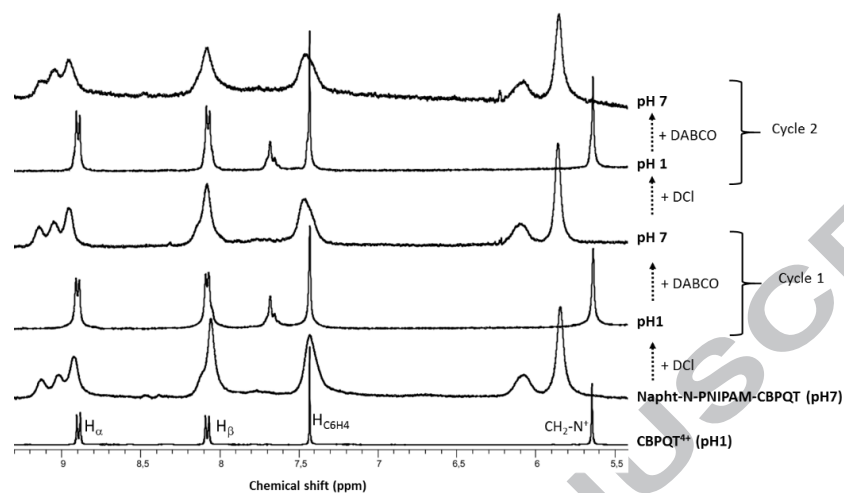

Figure S 10. ^{1}H NMR spectra of Napht-N-PNIPAM upon the addition of solution of DCl and DABCO (for more clearness, only 2 complete pH = 1/pH = 7 cycles is shown)
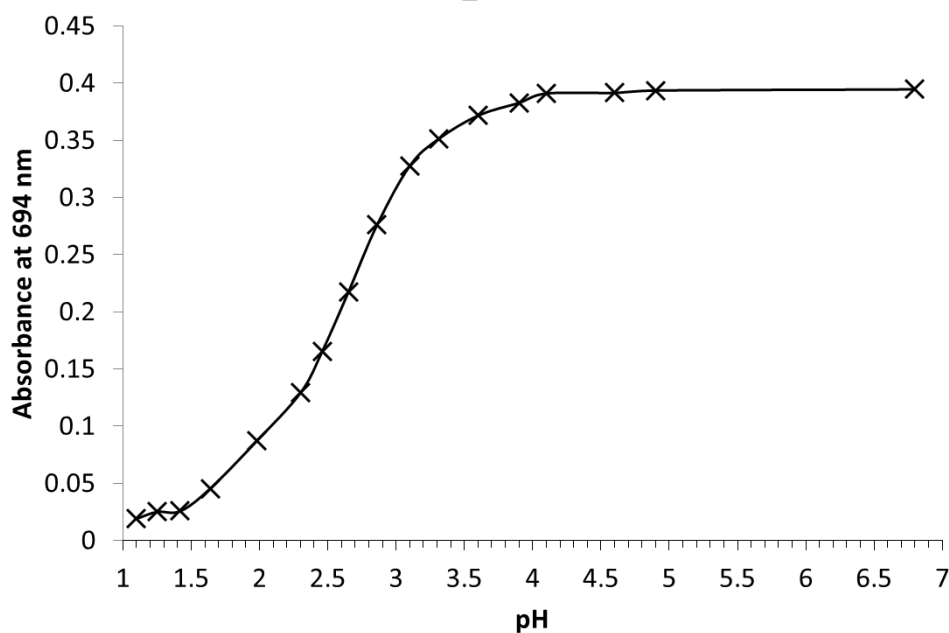

Figure S 11. Titration of Napht-N-PNIPAM.CBPQT (initial pH = 6.8) upon the addition of aliquots of HCl followed by UV-Vis spectroscopy (complex concentration = 13.3 mg/mL H_2O)

References

[1] Sue C-H, Basu S, Fahrenbach AC, Shveyd AK, Dey SK, Botros YY, et al. Enabling tetracationic cyclophane production by trading templates. Chem Sci. 2010;1(1):119-125.
[2] Qiu X-P, Tanaka F, Winnik FM. Temperature-Induced Phase Transition of Well-Defined Cyclic Poly(N-isopropylacrylamide)s in Aqueous Solution. Macromolecules. 2007;40(20):7069-7071.

Graphical Abstract
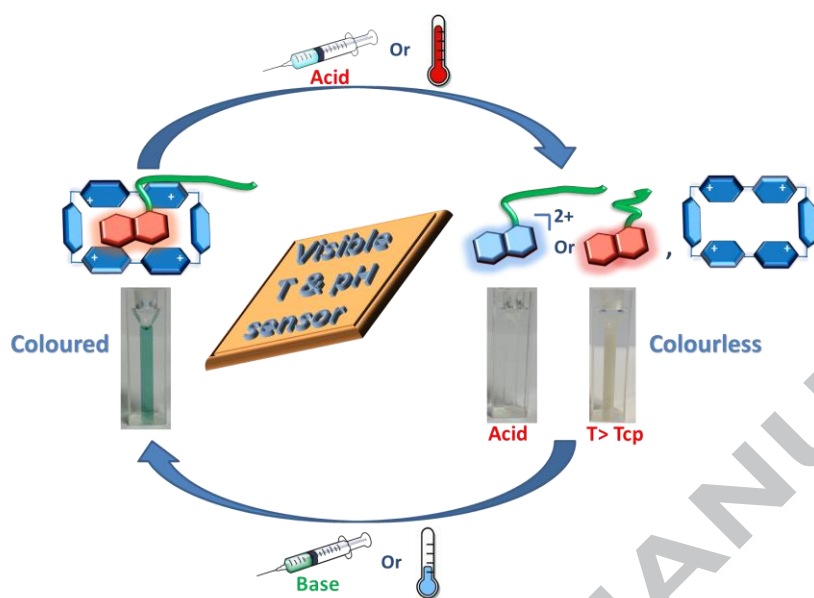
Highlights :

- Synthesis of a multi-stimuli responsive diaminonaphthalene functionalized PNIPAM
- Elaboration of a water-soluble host-guest supramolecular polymeric dual sensor
- The pseudorotaxane polymer architecture can be reversibly dissociated on demand