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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**<sup>4+</sup>, **4Cl**<sup>-</sup>). 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**<sup>4+</sup>, **4Cl**<sup>-</sup> in aqueous media was studied by means of UV-Vis, NMR (<sup>1</sup>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.

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## 1. 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 physico-chemical 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 dispersibility 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

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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, coumarin, rhodamine, 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 thermoresponsiveness of coloured complexes formed from naphthalene functionalized PNIPAM as guests and cyclobis(paraquat-*p*-phenylene) (**CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup>) as host. These systems 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**<sup>4+</sup>, **4Cl**<sup>−</sup>, 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**<sup>4+</sup>, **4Cl**<sup>−</sup> is reported in detail, as well as the thermo and pH responsiveness of **Napht-N-PNIPAM-CBPQT** supramolecular complex.

## 2. 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).

The structure of the **Napht-N-CTA** was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and 2D NMR (see ESI Figs. S1–S3 respectively) spectroscopies. <sup>1</sup>H NMR spectrum of **Napht-N-CTA** recorded in CD<sub>3</sub>CN revealed the presence of the characteristic signals of protons belonging to the naphthalene unit ( $\delta_{\text{H}_{2/6}} = \delta_{\text{H}_{3/7}} = 7.4$  ppm and  $\delta_{\text{H}_{4/8}} = 6.9$  ppm) and the methyl fragment of the isobutyl group ( $\delta_{\text{CH}_3} = 0.9$  ppm). Furthermore, the <sup>13</sup>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.

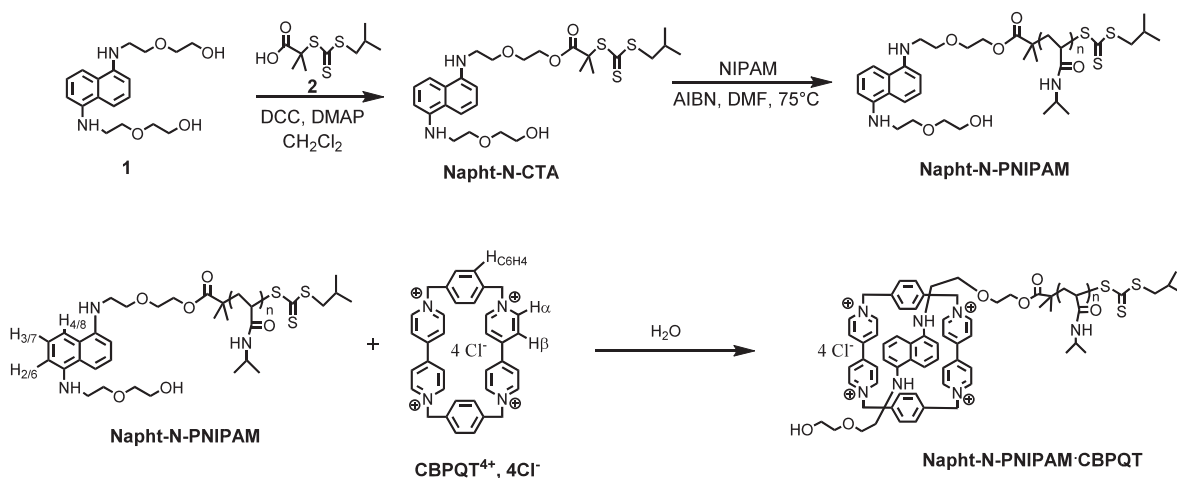
The ability of the **Napht-N-CTA** to promote RAFT polymerizations was demonstrated with *N*-isopropylacrylamide (NIPAM). The polymerization of NIPAM (150 equiv.) was carried out with azobis(isobutyronitrile) (AIBN, 0.2 equiv.) as a radical source and **Napht-N-CTA** (1 equiv.) in DMF at 75 °C for 1 h. The absolute molecular weight and the dispersity index (*D*) of the polymer were determined by SEC ( $M_{\text{n,abs}} = 14,810$  g/mol,  $\bar{D} = 1.07$ ,  $dn/dc = 0.0886$  mL/g, Fig. S4). In addition, the structure of **Napht-N-PNIPAM** was confirmed by <sup>1</sup>H NMR spectroscopy in D<sub>2</sub>O, which displayed the characteristic signals of PNIPAM ( $\delta_{\text{N-CH}} = 3.95$  ppm,  $\delta_{\text{CH}_3} = 1.20$  ppm, Fig. S5) in addition to those belonging to the naphthalene moiety ( $\delta_{\text{H}_{2/6}} = \delta_{\text{H}_{3/7}} = 7.5$  ppm,  $\delta_{\text{H}_{4/8}} = 6.9$  ppm, Fig. 1a).

Next, the ability of electron-rich **Napht-N-PNIPAM** to form a 1:1 complex with the electron-deficient **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> was investigated. The addition of aliquots of **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> 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  $\pi$ -electron rich **Napht-N-PNIPAM** and the  $\pi$ -electron deficient **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup>. This observation was confirmed by the appearance of a band centered at 697 nm in its UV-vis spectrum (Fig. 2a).

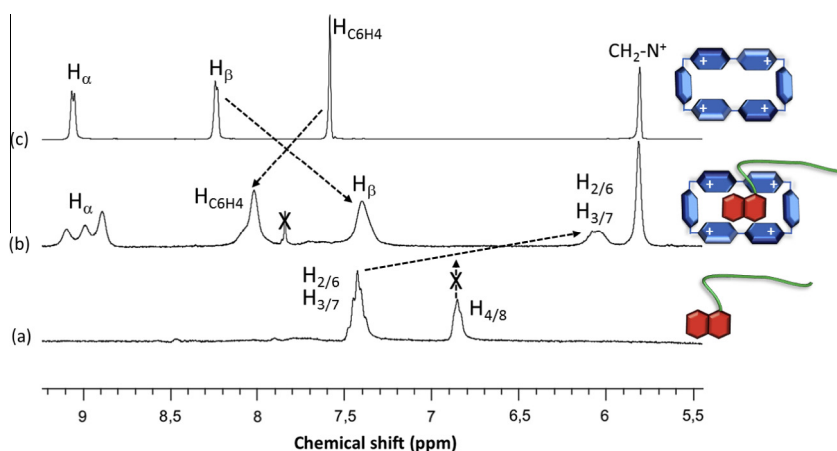
Next, we have studied the complex formation between **Napht-N-PNIPAM** and **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> in aqueous media by using NMR spectroscopy (<sup>1</sup>H, 2D-ROESY, DOSY, COSY). The <sup>1</sup>H NMR spectrum of a 1:1 mixture **Napht-N-PNIPAM** and **CBPQT**<sup>4+</sup>, **4Cl**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

<sup>1</sup>H NMR titration experiments were also carried out on **Napht-N-PNIPAM** upon adding aliquots of **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> (Fig. S6). <sup>1</sup>H NMR spectra clearly indicated the existence of the signal for uncomplexed H<sub>4/8</sub> protons upon the addition of aliquots of **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup>, thereby suggesting a slow exchange at the NMR timescale between the uncomplexed (Fig. 1c) and complexed forms. Moreover, the <sup>1</sup>H NMR titration revealed the complete disappearance of the signal of uncomplexed H<sub>4/8</sub> protons at 6.9 ppm when 1 equiv. of **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> was added, thus indicating the formation of a 1:1 complex between **Napht-N-PNIPAM** and **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup>. Further proof regarding the formation of a pseudorotaxane architecture between **Napht-N-PNIPAM** and **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> was also obtained from its 2D ROESY spectrum that indeed displayed a dipolar correlation between H<sub>2/6</sub>, H<sub>3/7</sub> and H<sub>C6H4</sub> protons belonging to the guest and host partners, respectively (Fig. 3a).

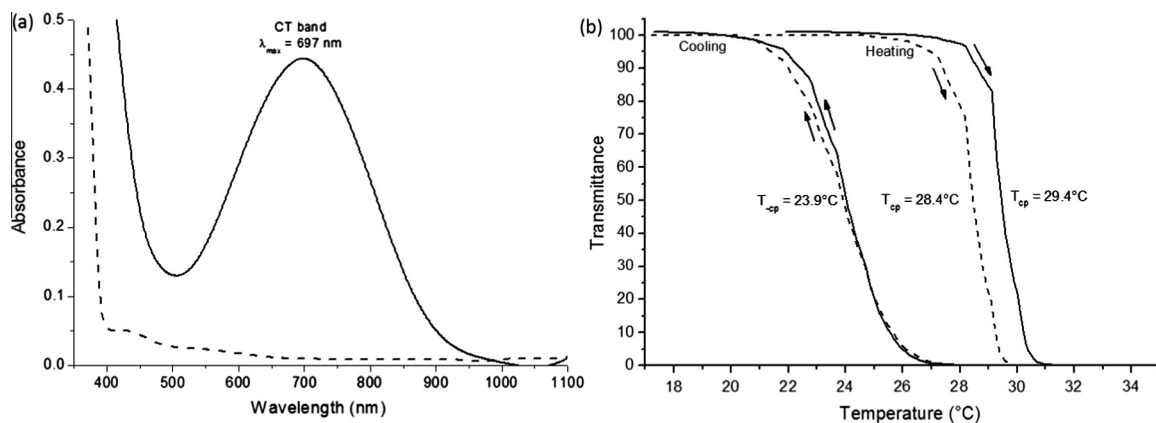
Next, to demonstrate the robustness of the host-guest interaction between **Napht-N-PNIPAM** and **CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup>, two-dimensional diffusion ordered spectroscopy (DOSY) <sup>1</sup>H NMR spectroscopy and isothermal titration microcalorimetry (ITC) experiments were undertaken. 2D-DOSY <sup>1</sup>H NMR spectroscopy experiments showed for solutions of their individual components (**CBPQT**<sup>4+</sup>, **4Cl**<sup>−</sup> and **Napht-N-PNIPAM**) have a diffusion coefficient value of 1585  $\mu\text{m}^2 \text{s}^{-1}$  and 73.3  $\mu\text{m}^2 \text{s}^{-1}$ , respectively (Fig. 3b).



**Scheme 1.** Synthesis of the RAFT agent **Napht-N-CTA** and the polymer **Napht-N-PNIPAM**.



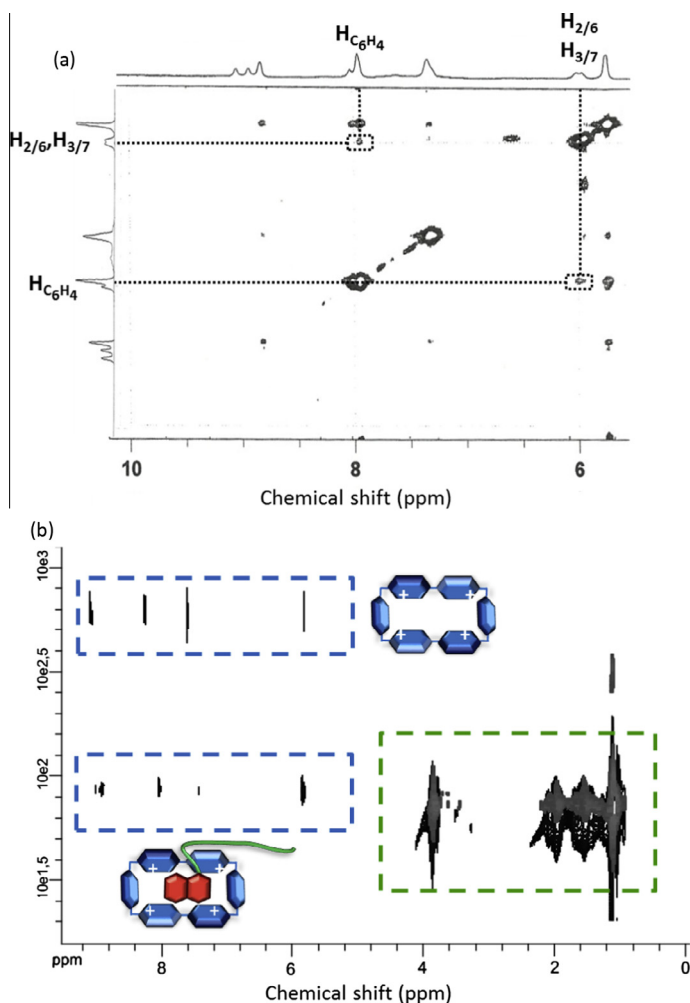
**Fig. 1.** Partial  $^1\text{H}$  NMR spectra of: (a) **Napht-N-PNIPAM**, (b) **Napht-N-PNIPAM-CBPQT** and (c) **CBPQT $^{4+}$ , 4Cl $^-$** . Recorded at 18 °C in  $\text{D}_2\text{O}$ .



**Fig. 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 $^{4+}$**  (-).

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** ( $73.3 \mu\text{m}^2 \text{s}^{-1}$ ). Moreover, no signals for the free **CBPQT $^{4+}$ , 4Cl $^-$**  were observed, thus confirming the efficiency of the



**Fig. 3.** (a) 2D-ROESY  $^1\text{H}$ - $^1\text{H}$  spectrum ( $\text{D}_2\text{O}$ ) of **Napht-N-PNIPAM-CBPQT**, (b) Superimposed  $^1\text{H}$  NMR DOSY ( $\text{D}_2\text{O}$ ) 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).

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 ( $\Delta H = -46.08 (\pm 0.26)$  kcal/mol) in good agreement with the relatively large estimated association constant of  $K_a = 9.2 (\pm 0.7) \times 10^4 \text{ M}^{-1}$  (Fig. S7).

### 2.1. Thermo-responsiveness of **Napht-N-PNIPAM-CBPQT** complex in water

The thermo-responsiveness of the **Napht-N-PNIPAM-CBPQT** complex was first investigated by turbidity measurements using UV-vis spectroscopy (Fig. 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 (Fig. 2b). This value was slightly higher than the cloud point estimated for **Napht-N-PNIPAM** ( $T_{cp} = 28.4$  °C, Fig. 2b), thereby indicating that the hydrophilicity-hydrophobicity balance of the material can be displaced towards 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 (Fig. 2b). To get further insight on the cloud point-mediated host-guest disassembly, variable temperature  $^1\text{H}$  NMR spectroscopy experiments were carried out. More particularly, we have investigated the changes in the  $^1\text{H}$  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  $\text{D}_2\text{O}$ . As expected, the  $^1\text{H}$  NMR spectra of **Napht-N-PNIPAM-CBPQT** upon heating from 18 °C (Fig. 4a) to 35 °C (Fig. 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,

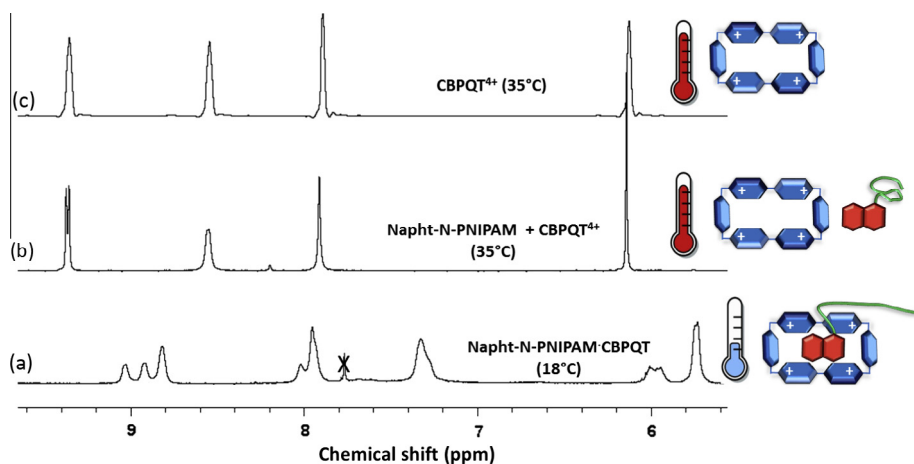


Fig. 4. Partial  $^1\text{H}$  NMR spectra ( $\text{D}_2\text{O}$ ) of **Napht-N-PNIPAM-CBPQT** at (a) 18 °C, (b) 35 °C and (c) **CBPQT $^{4+}$** , **4Cl $^-$**  at 35 °C.

the signals recorded at 35 °C shown in Fig. 4b perfectly fit to the signal of the protons of uncomplexed **CBPQT $^{4+}$**  (Fig. 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, suggesting that the complexation/dethreading upon simply heating and cooling the aqueous solution is reversible (Fig. S8).

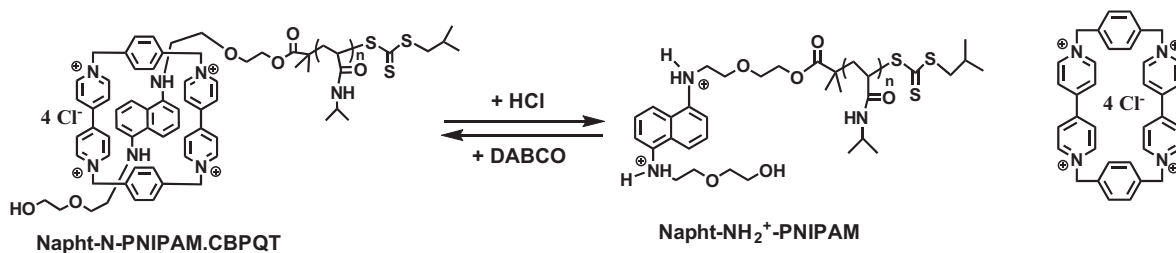
## 2.2. pH-responsiveness of **Napht-N-PNIPAM-CBPQT** complex in water

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 diamionaphthalene 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 ( $\lambda_{\text{max}} = 697$  nm) disappeared rapidly and a colourless solution was observed as shown in Fig. 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, 1.5 M in  $\text{H}_2\text{O}$ ) 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 (Fig. S9). It is noteworthy that performing 3 complete cycles of pH = 1/pH = 7 switching provided evidence for successive decomplexation/complexation (Fig. S9).

In addition to UV-vis investigations,  $^1\text{H}$  NMR spectroscopy experiments were performed to corroborate optical studies in acidic medium. As shown in Fig. 6, when aliquots of DCl (35 wt% in  $\text{D}_2\text{O}$ ) 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.*  $\text{H}_\alpha$ ,  $\text{H}_\beta$ ,  $\text{H}_{\text{C6H4}}$ ), 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.

The reversibility of the procedure was demonstrated by adding aliquots of an aqueous solution of DABCO (1.5 M in  $\text{D}_2\text{O}$ ) 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  $^1\text{H}$  NMR spectrum (Fig. S10), 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



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

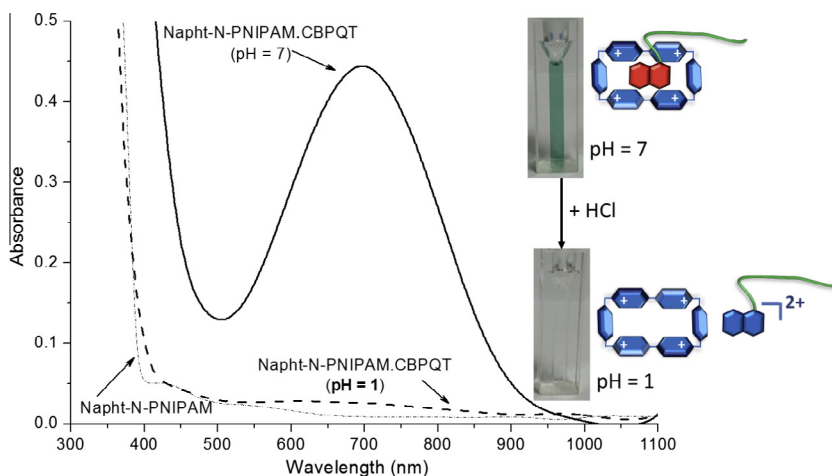


Fig. 5. UV–vis spectra of uncomplexed **Napht-N-PNIPAM** and **Napht-N-PNIPAM** in presence of 1 equiv. of **CBPQT<sup>4+</sup>**, **4Cl<sup>-</sup>** at pH = 1 and pH = 7.

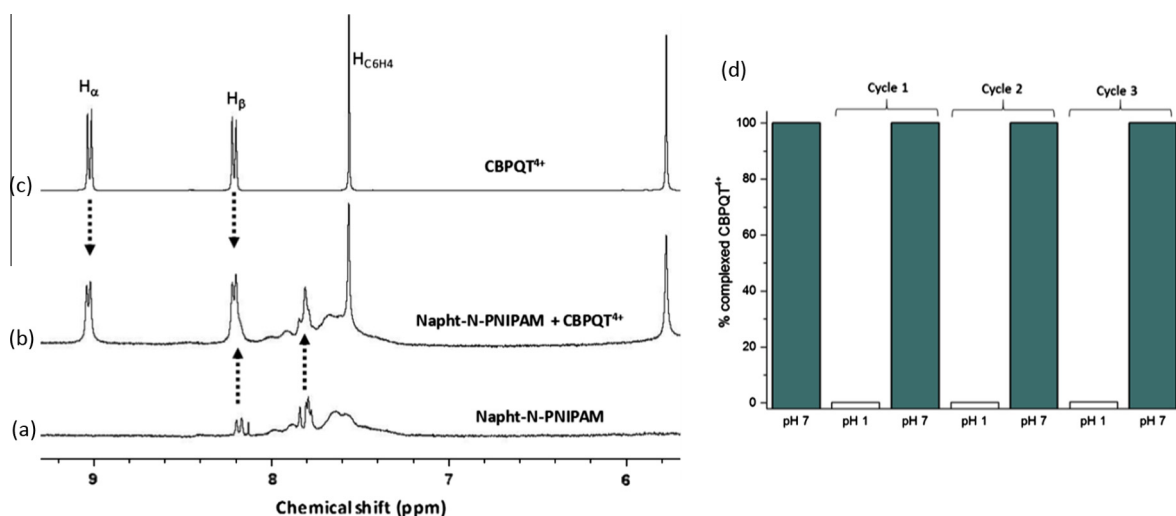


Fig. 6. Partial  $^1\text{H}$  NMR spectra (35 wt% DCl in  $\text{D}_2\text{O}$ ) of (a) **Napht-NH<sub>2</sub>-PNIPAM**, (b) polymer complex in acidic medium and (c) **CBPQT<sup>4+</sup>**, **4Cl<sup>-</sup>**. Chart (d) represents the reversibility of pH = 7/pH = 1 switching process upon the addition of DCl (35 wt% in  $\text{D}_2\text{O}$ ) and DABCO (1.5 M in  $\text{D}_2\text{O}$ ) showing the complexation/dethreading phenomena.

complete pH = 1/pH = 7 cycles by simply adding aliquots of solutions of DCl and DABCO, respectively (Fig. 6d). The resulting  $^1\text{H}$  NMR spectra (Fig. S10) clearly demonstrate the reversibility of the experiment and the stability of the species after several cycles.

### 3. 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<sup>4+</sup>**, **4Cl<sup>-</sup>** by performing  $^1\text{H}$  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 of sensing 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  $\text{CO}_2$ . Our work in this area will be reported in due course.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.eurpolymj.2015.02.033>.

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