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RESEARCH ARTICLE

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Thermoresponsive catechol end-functionalized polymers/CBPQT^{4+}, 4Cl^{-} supramolecular assembly

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Abstract

In the past decade, the adhesive properties of catechol derivatives have inspired researchers for the design of various macromolecular architectures featuring fascinating properties and finding applications in energy storage, coatings, adhesives and biomaterials. In this work, the complexation of catechol end-functionalized polymers prepared by RAFT polymerization was investigated in aqueous media with the electron-deficient tetracationic cyclophane cyclobis(paraquat-*p*-phenylene) (CBPQT^{4+}) by using UV–Vis and ^{1}H NMR experiments. The formation of pseudorotaxanes between the catechol end-functionalized polymers and the CBPQT^{4+},4Cl^{-} leads to the formation of colored guest-specific complexes displaying tunable complexation properties. In particular, we demonstrated that the thermo-responsiveness i.e. the lower critical solution temperature (LCST) of the catechol end-functionalized poly(NIPAM) could be used as a simple and convenient tool to disrupt the complexation with CBPQT^{4+}; 4Cl^{-} resulting in the disappearance of the characteristic color of the Catechol/BB complex while releasing the cyclophane in the aqueous solution. Furthermore, these supramolecular host/guest assemblies could be disrupted, on demand, by the addition of a competitive Naphthalene derivative leading to the appearance of the characteristic purple color of Naphthalene/CBPQT^{4+} complexes. These results pave the way for the design of a new generation of stimuli responsive materials with control properties.

KEYWORDS

catechol end-functionalized polymers, CBPQT^{4+}, host-guest complexation, thermo-responsive polymers

1 | INTRODUCTION

Nature is a fascinating source of inspiration for stimulating research in materials science. Indeed, recent progress in the adhesion mechanism of marine mussels[1] has led to the emergence of a new generation of materials mimicking the properties of these natural systems and finding various applications in coatings,[2] adhesives[3] and biomaterials.[4] In

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these materials, the catechol moiety, according to its ability to strongly binds onto organic and inorganic substrates, was used as versatile building block for the design of a large range of macromolecular architectures featuring fascinating properties and functions.[5] Among these architectures, macromolecules able to respond to an external stimulus such as temperature, pH, ionic strength, light, biologic environment and others have attracted considerable attention in the perspective to develop adaptative materials with various functions finding applications in smart coatings,[6] sensors and actuators,[7] drug delivery[8] and tissue engineering.[9] In particular, thermoresponsive polymers due to changes in their solubility above the lower critical solution temperature (LCST) were utilized to develop thermally modulated systems such as self-oscillating membrane,[10] self- healing hydrogel[11] and thermoresponsive hydrogels.[12]

To synthesize such materials integrating the catechol unit, the main efficient strategy consists in the utilization of controlled radical polymerizations initiated or mediated by catechol-functionalized initiators or chain transfer agents (CTA). Typically, the reversible addition–fragmentation chain transfer (RAFT) polymerization has shown promising results to obtain well-defined catechol polymers with various architectures. In this way, our group reported the synthesis of well-defined catechol end-functionalized polymers via the RAFT polymerization process and we investigated their grafting onto titanium surface[13] as well as the formation of multi-stimuli responsive diblock copolymers integrating a reversible junction.[14]

As the ability to manipulate such macromolecules still remains challenging to broad the scope of applications, we next investigated the possibility to functionalize such polymers by reversible host/guest supramolecular interactions to produce stimuli sensitive macromolecular architectures. Indeed, an interesting aspect of combining the macromolecular and the supramolecular chemistry relies on the possibility to delicately and reversibly regulate the formation of host/guest interactions by exploiting the reversibility of such assembly or the intrinsic properties of the polymer backbone in order to design multi-stimuli responsive materials.

In this context, the electron-deficient cyclophane cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$)[15,16] has emerged as an important building block for the creation of functional supramolecular systems with tunable complexation properties. The pseudorotaxanes constructed from $CBPQT^{4+}$ have attracted interest due to the formation of colored guest-specific complexes with electron rich guest in both aqueous and organic media. One interesting aspect of this supramolecular system is based on their tunable complexation properties. Indeed, the colored guest-specific complexes can be disrupted, on demand, through the application of different stimuli such as temperature,[17] the application of an electrochemical potential[18] or the introduction of a competitive guest molecule.[19] In this way, this electron-deficient cyclophane cyclobis(paraquat-*p*-phenylene) was introduced into thermo-responsive polymers backbone or hydrogel to construct various smart materials including thermo-responsive micelles,[20] hydrogels,[21] diblock copolymers[22] and functionalized polymers with memory function.[23]

In this article, we report on the ability of catechol terminated-polymer, prepared by the RAFT polymerization, to act as a guest for the construction of supramolecular assemblies with the tetracationic cyclophane $CBPQT^{4+}$; $4Cl^-$ in water. In particular, we demonstrated that the thermo-responsiveness of the catechol end-functionalized Poly(*N*-isopropylacrylamide) (PNIPAM) could be exploited to disrupt, on demand and in a reversible manner, the DopaPNIPAM/$CBPQT^{4+}$; $4Cl^-$ supramolecular host/guest complexes while releasing the cyclophane in the aqueous solution.

2 | RESULTS AND DISCUSSION

Catechol end-functionalized homopolymers labeled DopaPDMAc **1a** and DopaPNIPAM **1b** were first prepared by control radical polymerization via the Reversible Addition-Fragmentation chain Transfer (RAFT) process from CTA 1 featuring a catechol moiety[11] as depicted in Scheme 1. ^{1}H NMR spectroscopy and Size Exclusion Chromatography (SEC) were used to characterize the structure of these catechol end-functionalized polymers and assess to their molecular weight and dispersity (see details in Data S1–S4).

We next investigated the ability of catechol end-functionalized polymers to form supramolecular host/guest complexes with cyclobis-(paraquat-*p*-phenylene) ($CBPQT^{4+}$; $4Cl^-$).

Interestingly, the addition of an aliquot of $CBPQT^{4+}$; $4Cl^-$ to aqueous solutions containing DopaPDMAc **1a** or DopaPNIPAM **1b** leads to the appearance of an orange-yellow color (Scheme 2) suggesting the formation of pseudorotaxane architectures between catechol and $CBPQT^{4+}$; $4Cl^-$ sub-units. This observation was confirmed by UV–Vis measurements. Indeed, upon addition of $CBPQT^{4+}$; $4Cl^-$ into the catechol end-functionalized polymer solutions, a charge-transfer (CT) band centered around 460 nm was identified in UV–Vis spectra (Figure 1) and attributed to a charge transfer between the electron-deficient tetracationic cyclophane and the electron rich catechol unit.

The stoichiometry of the host/guest complex was next assessed through ^{1}H NMR Job plots investigations[24]

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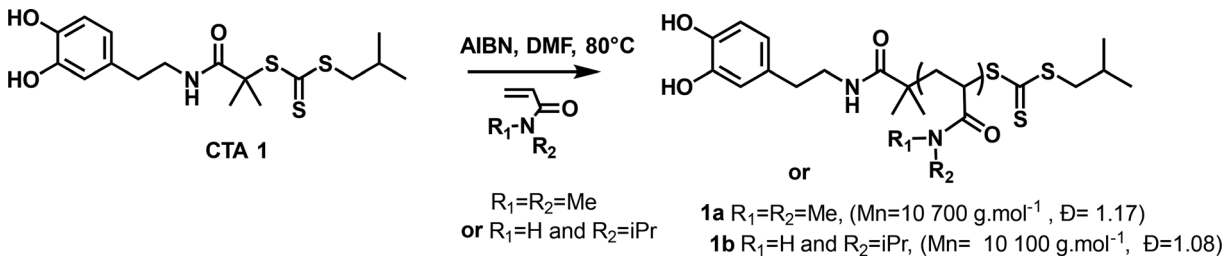
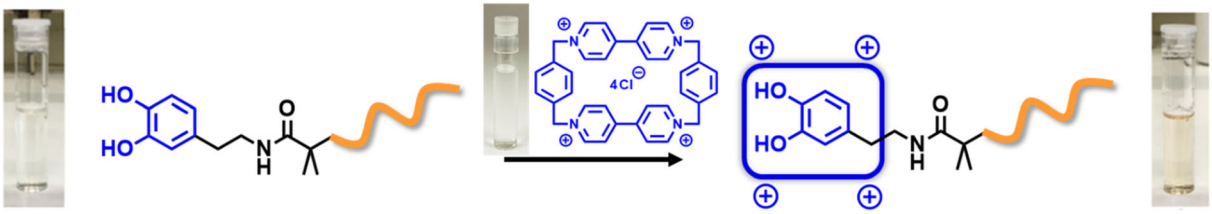


SCHEME 1 Synthesis of catechol end-functionalized polymers from the catechol functionalized CTA 1 by RAFT polymerization



SCHEME 2 Schematic illustration of the formation of colored supramolecular assembly between catechol end-functionalized polymers and $CBPQT^{4+}$,$4Cl^{-}$

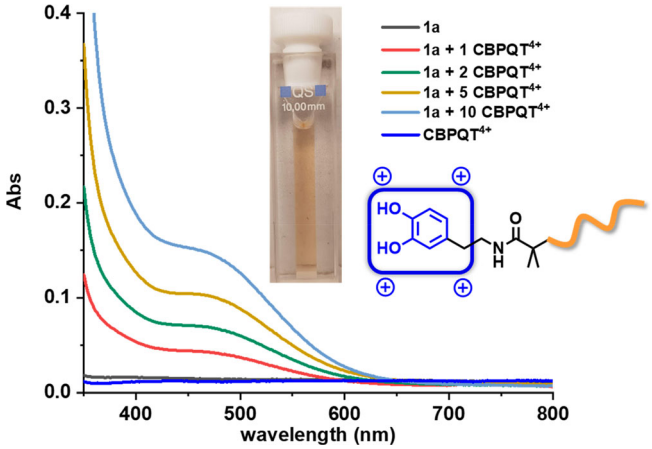


FIGURE 1 UV–Vis spectra recorded upon the addition of $CBPQT^{4+}$ $4Cl^{-}$ into an **1a** aqueous solution at 1 mM

(Figure 2) from host and guest which provide further evidence for the successful formation of the supramolecular host–guest complexation. For this purpose, the chemical shift of Hβ proton for $CBPQT^{4+}$ (host) and —C<u>H</u>$_2$—Ar for **1a** (guest) were plot as a function of mole fraction of the reactant (**1a** and $CBPQT^{4+}$ respectively). As depicted in Figure 2, the maximum of the parabolic curve is reached for $X = 0.5$ in both cases indicating a stoichiometric ratio of 1:1 between the two subunits. From UV–Vis titrations and assuming a stoichiometry of 1 to 1, association constants (Ka) of 3.7 10^{-2} M^{-1} ± 40 for **1a**/$CBPQT^{4+}$;$4Cl^{-}$ and 7.1 10^{-2} M^{-1} ± 40 for **1b**/$CBPQT^{4+}$;$4Cl^{-}$ were calculated by employing a non-linear fitting method (see details in Data S5).

These results are in accordance with a previous Ka value reported by Kaifer and al[25] for the dopamine/$CBPQT^{4+}$ host/guest complex (1070 M^{-1} ± 120). It can be noticed from UV–Vis calculations that the nature of the polymer chains has limited impact on the catechol molecular recognition properties with $CBPQT^{4+}$. Afterwards, ^{1}H NMR titrations were undertaken to further investigate the complexation between the $CBPQT^{4+}$; $4Cl^{-}$ and catechol end-functionalized polymers **1a** and **1b**.

We can first observe in Figures 3 and 4 that both host and guest subunits are in fast exchange on the NMR timescale. The addition of $CBPQT^{4+}$; $4Cl^{-}$ in DopaPDMAc **1a** (see Data S6) and DopaPNIPAM **1b** solutions (Figures 3 and 4) resulted in significant shifts of both $CBPQT^{4+}$ and catechol proton resonances. In particular, the comparison of the ^{1}H NMR spectra of free $CBPQT^{4+}$ and its corresponding complexes with DopaPDMAc and DopaPNIPAM showed chemical shift changes for the H_β and *p*-phenylene protons of the cyclophane. The latter are shifted upfield and downfield respectively (Figure 3) upon the addition of 0.5 eq of $CBPQT^{4+}$ suggesting that the catechol ring interacts with the cavity of the macrocycle. In addition, aromatic protons from catechol moiety of **1b** shift upfield from 6.8 to 4.9 ppm while the two methylene groups of catechol shift from 3.39 to 3.28 ppm (—C<u>H</u>$_2$—NH_2) and from 2.72 to 2.29 (—C<u>H</u>$_2$—Ph) respectively (Figure 4). This dramatic shift in the proton resonances in ^{1}H NMR spectra for both units indicates the formation of a host/guest inclusion complex between $CBPQT^{4+}$; $4Cl^{-}$ and catechol end-functionalized polymers.

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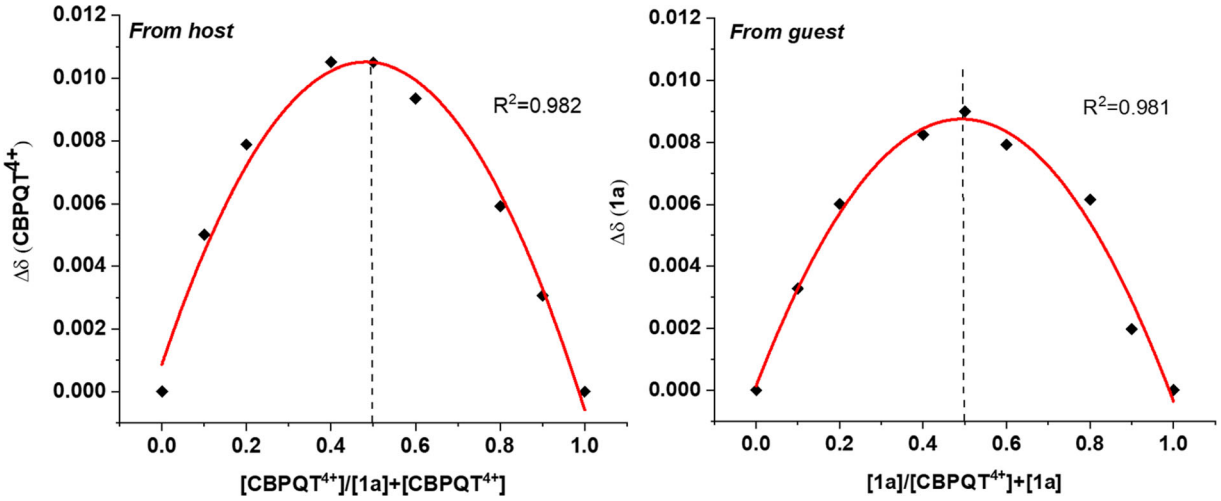

FIGURE 2 Job plots recorded by ^{1}H NMR for a 1:1 1a/CBPQT^{4+},4Cl$^-$ complex (at 298°K in D_2O)

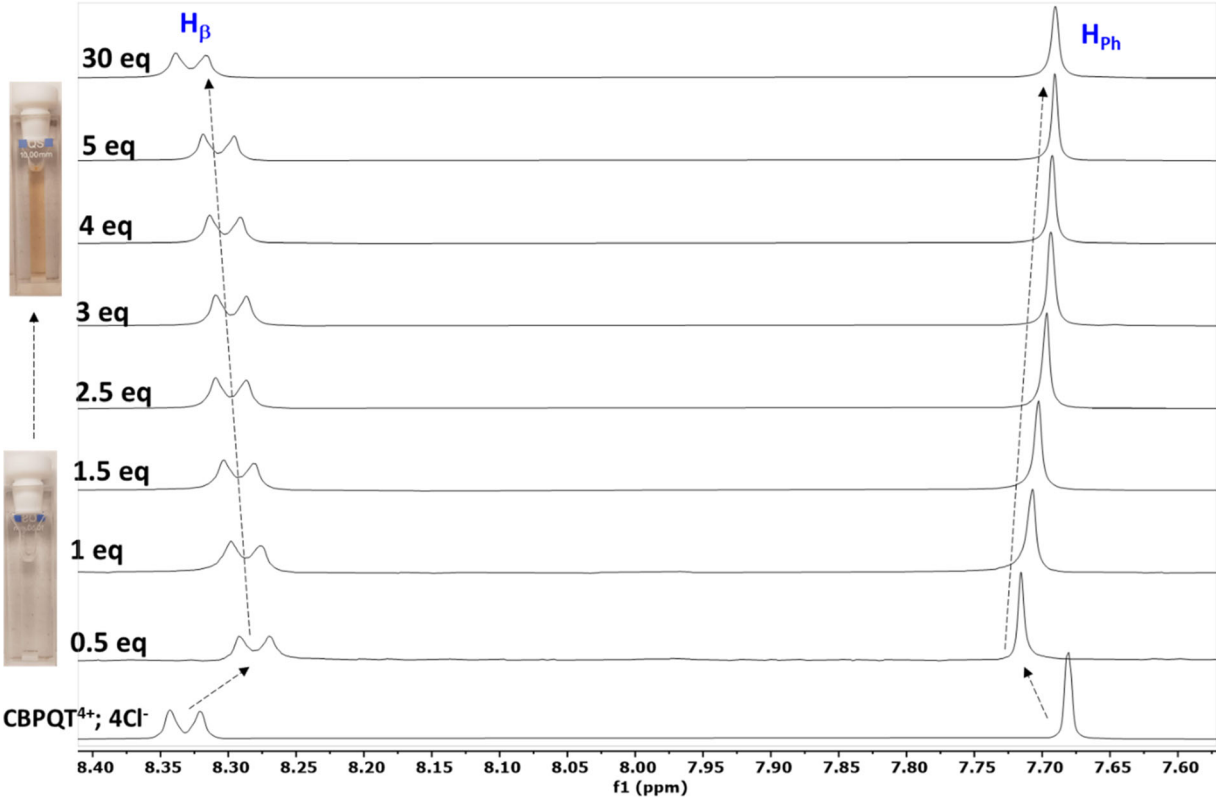

FIGURE 3 ^{1}H NMR shifts of H_β and H_{Ph} protons of CBPQT^{4+}; 4Cl$^-$ upon addition of the cyclophane in a D_2O solution containing **1b** (recorded at 20 °C)

After the addition of an excess of CBPQT^{4+} (>1 eq), the resonances of the H_β and *p*-phenylene protons of the cyclophane then shifted again downfield and upfield respectively and recover the resonance of the unmodified cyclophane when 30 eq of CBPQT^{4+} was added in the solution in accordance with the increase of free cyclophane ratio in solution (Figures 3 and 4). Moreover, association constants of 1.6 10^3 M^{-1} ± 60 for **1a**/ CBPQT^{4+}; 4Cl$^-$ and 2.6 10^2 ± 40 M^{-1} for **1b**/ CBPQT^{4+};4Cl$^-$ were calculated from ^{1}H NMR titrations by using a non-linear ^{1}H NMR fit (H_{ph} were considered for calculations, see details in Data S7) and are in good agreement with the previous Ka values calculated from UV–Vis titrations.

A control experiment was next realized by ^{1}H NMR to get further informations about the complexation

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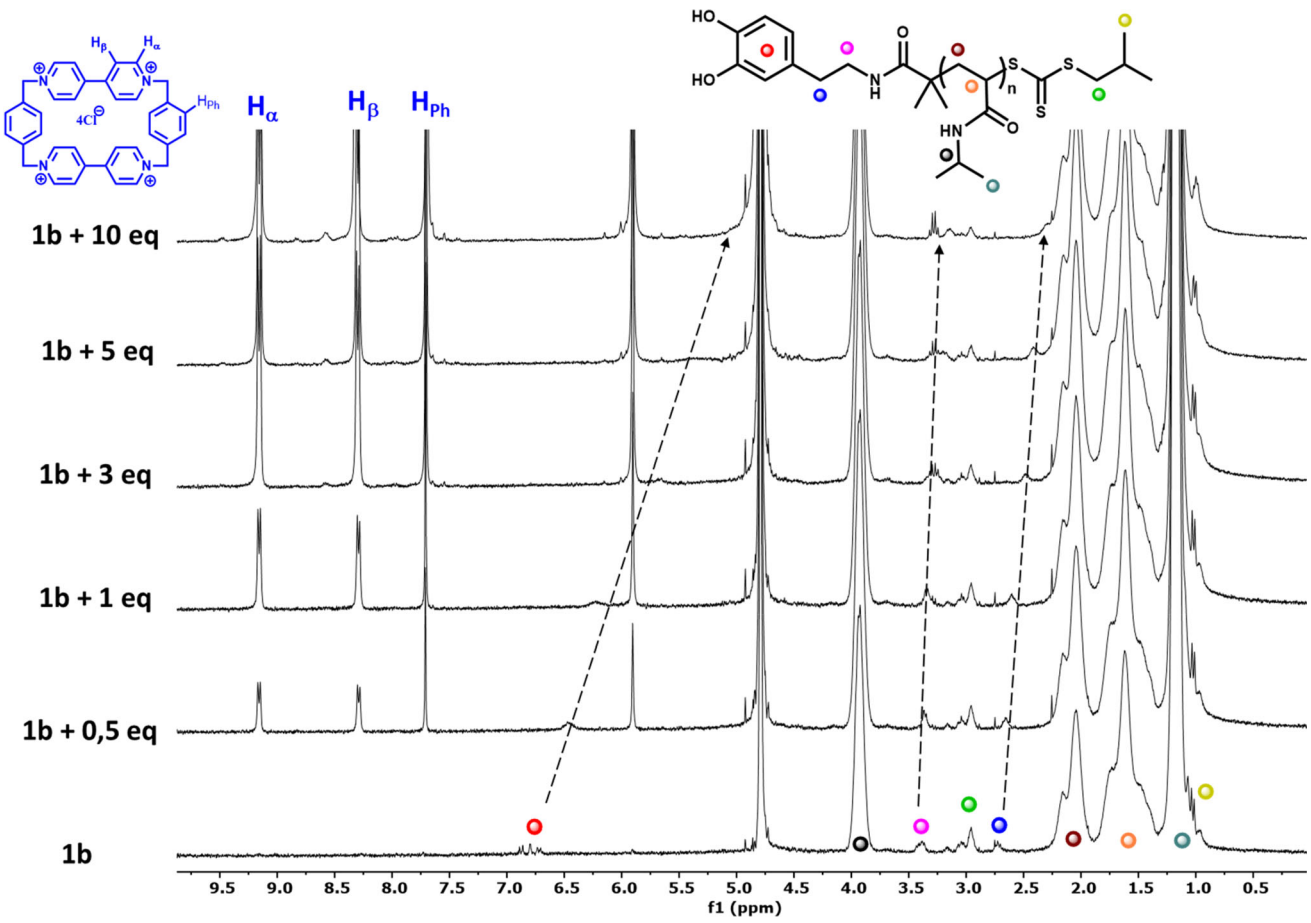

FIGURE 4 ^{1}H NMR spectra of **1b** upon the addition of aliquots of CBPQT^{4+};4Cl^{-} (recorded in D_2O at 298 K)

TABLE 1 Association constants (Ka) and diffusion coefficients of the supramolecular assemblies

Entry	Association constant NMR [M^{-1}]	Association constant UV [M^{-1}]	Diffusion coefficient[a] [10^{-11} cm^2 s^{-1}]
1b	-	-	5.88
CBPQT^{4+}; 4Cl^{-}	-	-	42.8
1a/CBPQT^{4+}; 4Cl^{-}	1.6 10^3 ± 60	3.7 10^2 ± 40	NA
1b/CBPQT^{4+}; 4Cl^{-}	2.6 10^2 ± 40	7.1 10^2 ± 40	4.54 (**1b**)
1b/CBPQT^{4+}; 4Cl^{-}	2.6 10^2 ± 40	7.1 10^2 ± 40	20.8 (CBPQT^{4+}; 4Cl^{-})

[a]DOSY NMR measured at 400 MHz.

between CBPQT^{4+}; 4Cl^{-} and catechol-end functionalized polymers. For this purpose, ^{1}H NMR spectra of **1a** were recorded in D_2O upon addition of aliquots of 1,1′-dibenzyl-4,4′-bipyridium (**DBBP**) simulating the half cavity of the CBPQT^{4+} cyclophane (see Data S8). No shift was observed in both **1a** and DBBP ^{1}H NMR spectra thus demonstrating the key role played by the cyclic cavity of the cyclophane in the complexation with the catechol moiety and further confirming the inclusion of the catechol moiety into the cyclophane cavity.

The formation of the supramolecular host/guest complexation between catechol end-functionalized polymers and CBPQT^{4+}; 4Cl^{-} was further demonstrated by two-dimensional diffusion-ordered ^{1}H NMR spectroscopy (DOSY) experiments (see Data S9). We can observe in Figure S9 that both host and guest subunits are in fast exchange on the DOSY timescale as previously observed for ^{1}H NMR. Nevertheless, the diffusion coefficients (Table 1) measured for **1b** and CBPQT^{4+}; 4Cl^{-} in the **1b**/CBPQT^{4+}; 4Cl^{-} supramolecular complex are significantly lower (50% and 23% lower for CBPQT^{4+},4Cl^{-} and **1b**, respectively) compared to their initial value (uncomplexed). These results are in accordance with the increase in molar mass upon complexation leading to lower

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diffusion for both host and guest units thus suggesting the formation of the supramolecular assemblies.

Therefore, ^{1}H NMR and UV–Vis investigations demonstrated the formation of colored pseudorotaxane-like architectures between CBPQT^{4+}; 4Cl$^-$ and catechol end-polymers in aqueous media.

Recently, we demonstrated that the thermo-responsiveness of polyNIPAM could be used as a simple and efficient tool to modulate the recognition properties of the cyclophane cyclobis(paraquat-*p*-phenylene) host toward thermo-responsive polymer exhibiting electron rich moieties such as dialkoxynaphthalene or tetrathiafulvalene in water.[26] Indeed, upon heating, the thermo-responsive polymer collapse in its globular form by dehydration thus diminishing the driving force for host guest complexation and releasing the CBPQT^{4+},4Cl$^-$ host units in the aqueous solution. In this work, we investigated the possibility to exploit this approach to regulate the formation of host/guest interactions between the thermoresponsive catechol end-functionalized polymer (DopaPNIPAM, **1b**) and the cyclophane. For this purpose, the cloud point temperature (Tcp) of **1b** was first determinate by turbidimetry experiments. As observed in Figure 5, the DopaPNIPAM **1b** exhibit a Tcp of 30 °C as measured by UV–Vis spectroscopy at 750 nm (cloud point determined at 50% transmittance).

This value is slightly lower than most poly(NIPAM)s described in literature[27] (T_{cp} = 32 °C) and can be attributed to the hydrophobic nature of the catechol[28] lowering the cloud point of the catechol end-functionalized

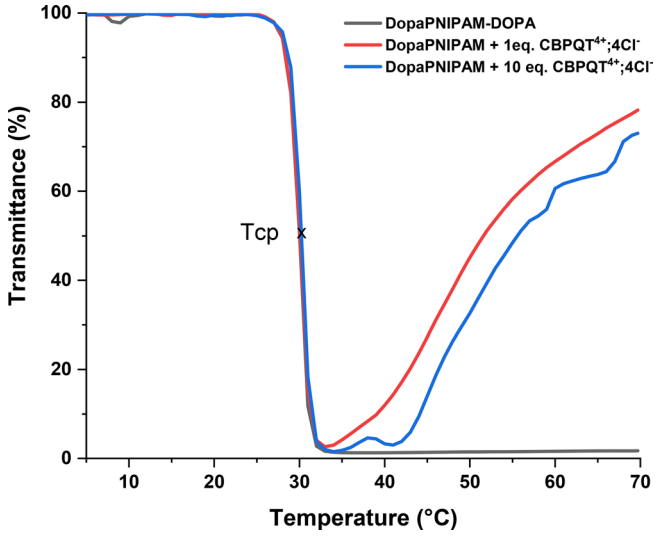

FIGURE 5 Thermo-sensitive phase transitions of **1b** and **1b**/CBPQ^{4+}/4Cl$^-$ (2.10^{-4} M in water). Recorded at 750 nm. Heating rate: 1 °C/min

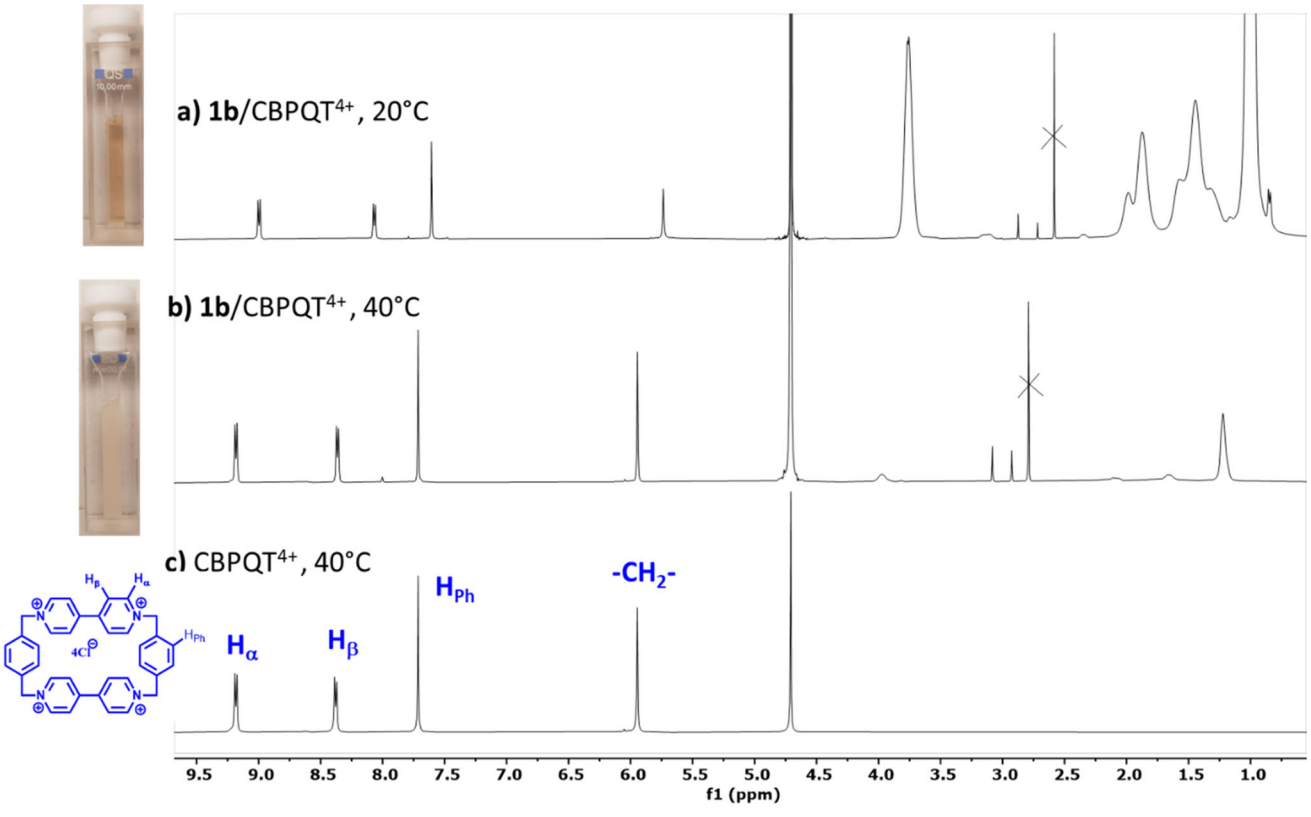

FIGURE 6 ^{1}H NMR spectra of 1b/CBPQT^{4+} complex recorded in D_2O at 25 and 40 °C

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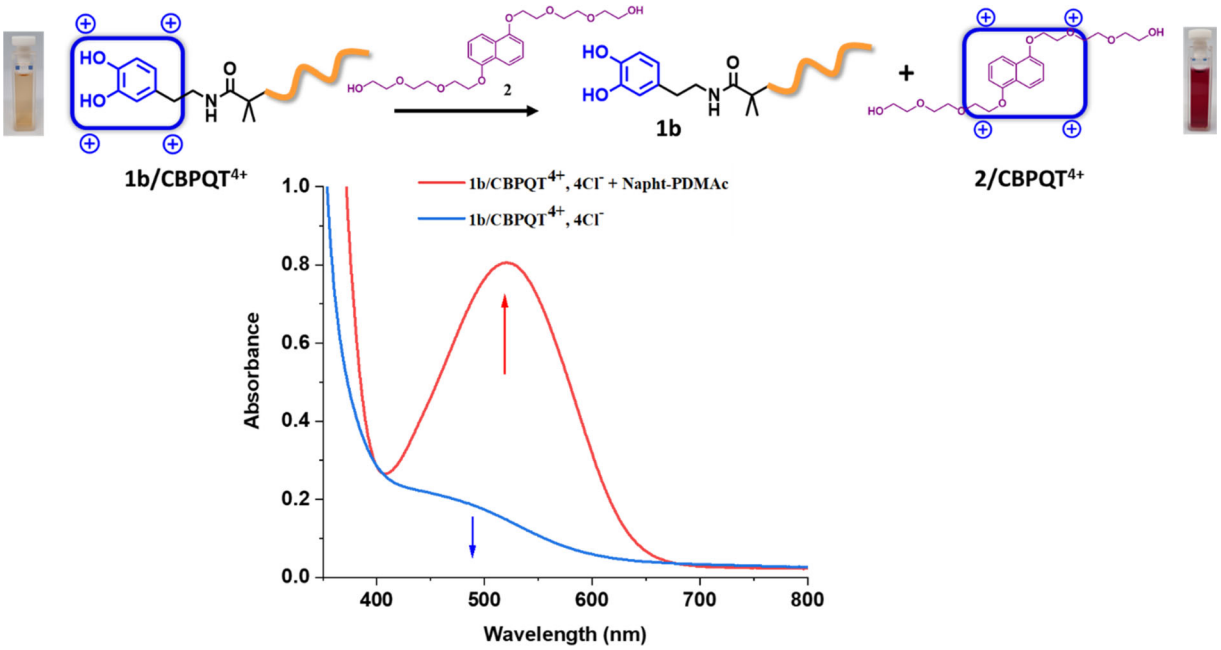

FIGURE 7 UV–Vis spectra of 1b/CBPQT^{4+},4Cl^{-} complex before (blue) and after injection of naphthalene 2 (red), [**1b**/CBPQT^{4+}] = 1 mM in water

PNIPAM **1b**. Upon the addition of CBPQT^{4+},4Cl^{-} in the solution, the Tcp of the **1b**/CBPQT^{4+},4Cl^{-} supramolecular architecture do not change. Nevertheless, an abrupt increase of the transmittance was observed after the cloud point suggesting the formation of large aggregates which precipitate at the bottom of the cuvette with the presence of CBPQT^{4+},4Cl^{-} thus lightening the solution. As described in the Figure 6 (left), when the colored Dopa-PNIPAM/CBPQT^{4+},4Cl^{-} solution reaches a temperature significantly higher than the cloud point, the solution underwent an abrupt change in turbidity leading to the complete disappearance of the orange/yellow color suggesting the detreating of the complex with the precipitation of polymer while the CBPQT^{4+} is released in water. It is noteworthy that heating the Dopa-PDMAc/CBPQT^{4+},4Cl^{-} at 40 °C in the same conditions does not lead to the disappearance of the orange color thus demonstrating the role played by the thermoresponsive polymer (Data S10) in the decomplexation. To obtain further evidence of this phenomenon, the effect of temperature on the **1b**/CBPQT^{4+},4Cl^{-} complex was investigated by ^{1}H NMR spectroscopy in D_2O (Figure 6). At 20 °C, the signal of DopaPNIPAM and CBPQT^{4+},4Cl^{-} from the complex was clearly observed in the ^{1}H NMR spectrum while the signal of the polymer disappeared when the temperature reaches the cloud point.

At 40 °C, the ^{1}H NMR spectrum displays the characteristic chemical shifts of the non-complexed CBPQT^{4+} unit at 40 °C and very small amount of the **1b** polymer (~3% of the initial amount) is observed indicating the detreating of the host–guest supramolecular complex and the release of the cyclophane in water. It is noteworthy that the integration of the signals from CBPQT^{4+},4Cl^{-} compared to those of the solvent are almost identical in both cases (see Data S11) further demonstrating the detreating of the supramolecular assembly and the release of CBPQT^{4+},4Cl^{-} in water.

Finally, we investigated the possibility to disassemble the supramolecular catechol end-functionalized polymer/CBPQ^{4+}complex, on demand, by employing a competitive guest exhibiting a more binding affinity toward the cyclophane. For this purpose, the water-soluble Naphthalene derivative **2**[29] (Figure 7, ka ~1.10^{6} M^{-1}) was added in an aqueous solution containing the **1b**/CBPQT^{4+} complex. The orange solution turned immediately purple, presumably resulting from the complexation between **2** and the CBPQT^{4+},4Cl^{-}. This result was confirmed by UV–Vis measurements. Indeed, the Figure 7 revealed a red shift in the charge transfer band from 460 to 520 nm. This CT is characteristic of the Naphthalene/ CBPQT^{4+} complexes[28] and demonstrates that the **1b**/CBPQT^{4+} complex could be disrupted, on demand, upon the addition of the more strongly binding Naphthalene derivative to the mixture.

3 | CONCLUSION

In conclusion, the formation of visible readout supramolecular host/guest complexes between catechol end-functionalized polymers and the tetracationic cyclophane

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cyclobis(paraquat-*p*-phenylene) ($CBPQT^{4+}$; $4Cl^-$) was demonstrated in aqueous media by UV–Vis and ^1H RMN experiments. The thermo-responsiveness of the catechol end-functionalized poly(NIPAM) derivative was investigated and exploited to disrupt the supramolecular assembly and to release the $CBPQT^{4+}$ in solution. Furthermore, these host/guest complexes could be disassembled, on demand, by the addition of a competitive Naphthalene derivative in solution. As catechols are commonly used as versatile building block for the design of numerous macromolecular architectures featuring various properties, the ability to control the host guest interactions between catechol and $CBPQT^{4+}$ pave the way for the design of a new generation of stimuli responsive materials with control properties.

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DATA AVAILABILITY STATEMENT

Data are available to readers upon request.

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