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Covalent hydrogels with dual temperature and time memory function based on supramolecular host-guest complexation

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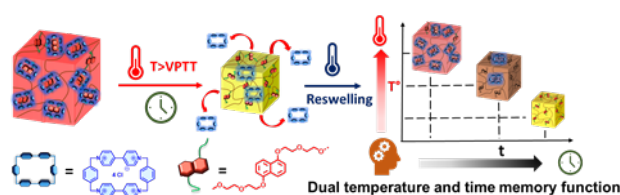
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ABSTRACT: Temperature is amongst the most important measured physical parameters. Despite that numerous polymeric temperature sensors have been reported, none of these systems can record the time that the object was heated to a certain temperature. Here, we report a supramolecular approach for developing a smart polymeric hydrogel capable of measuring the temperature and the duration of the heat exposure. This double memory principle is based on dual kinetic control of the dissociation of cyclobis(paraquat-*p*-phenylene) tetrachloride (**CBPQT⁴⁺**,**4Cl⁻**)-naphthalene host-guest complexes within a thermoresponsive naphthalene

functionalized poly(*N*-isopropylacrylamide) hydrogel. Heating-induced collapse of this LCST polymer hydrogel induces host-guest complex dissociation, followed by the diffusion-controlled release of the free **CBPQT⁴⁺,4Cl⁻** host into the medium surrounding the hydrogel. This partial host release is governed by the heat exposure time and the heating temperature that controls the extent of dehydration of the hydrogel and, thus, the diffusion rate of the **CBPQT⁴⁺,4Cl⁻**. Hence, the amount of host released is an indicator for both the heating temperature and the heating time of the hydrogel and can be recorded by determining the reswelling capability of the hydrogel in water. As such, measuring the reswelling capability provides information on how long the hydrogel system was exposed to a certain temperature.

TOC



INTRODUCTION

Memory refers to any information processing system that can encode, store, retain, and reconstitute information, for which the brain is an unsurpassed example. Over the past decade, the demand for polymeric materials that have the ability to record and store their physical and/or physicochemical state, i.e., have a memory function, has increased enormously.¹⁻⁵ In essence, such polymeric systems featuring a memory function require hysteresis in a specific property when subjected to stimuli-dependent perturbations, thereby allowing to store information in a metastable, kinetically trapped state.⁶⁻⁸

Temperature is undoubtedly the most fundamental thermodynamic parameter that is not only important in our everyday life but also in science and biology as it plays an important role in the intrinsic characteristics and the functioning of a plethora of biological, physical and

chemical systems and processes.^{9–11} As a result, temperature measurements cover a broad scope of needs and have countless applications. Temperature is not a directly measurable quantity, and thus its measurement requires the use of sensors that can detect temperature by a change in their physical or physicochemical characteristics.^{12–14} In this context, thermoresponsive polymers that can undergo temperature-induced phase transitions have appeared as promising candidates for the elaboration of smart polymeric thermometers.^{15–18} For instance, thermoresponsive polymers exhibiting a lower critical solution temperature (LCST) in solution were exploited to translate a change in their physical and/or physicochemical states into an optical output signal (e.g., fluorescence, phosphorescence, transmittance, color, etc.), thereby allowing real-time monitoring of the environmental temperature through spectroscopic or visible read-out.^{19–28} However, due to the reversibility or quasi-reversibility of the heat-induced phase transition that leads to a return to their equilibrium state after the heat treatment, only few of these polymeric thermometers have the ability to remember their thermal history. Materials capable of remembering previous thermal conditions are rather rare and have been reported based on liquid-crystalline polymeric systems,^{14,18,27,29–31} shape-memory materials,³² and more recently hydrogels^{6–8} and host-guest based supramolecular polymeric assemblies^{33,34}. A distinctive and common feature of these systems is that they exhibit a strong hysteretic temperature-triggered phase transition that allows them to exist in multiple meta-stable states in the hysteresis window. These systems can thus serve as temperature memory devices with short to long-term memory depending on the stability of kinetically trapped meta-stable states. Even though these systems can remember the thermal history, they cannot memorize the duration of the heat treatment, i.e., time, which is another essential parameter to be monitored. However, we are unaware of polymer materials that can monitor and memorize both the temperature and time of heating.

Herein, we demonstrate that a polymer hydrogel with supramolecular host-guest complexes can record both the temperature and the duration of exposure to a certain temperature. The temperature is monitored through heating-induced decomplexation of the host-guest complex, while the time is monitored through the diffusion-controlled release of the uncomplexed host into the surrounding medium. More specifically, this supramolecular thermoresponsive polymeric memory device was designed based on a poly(*N*-isopropylacrylamide) (PNIPAm) hydrogel functionalized with 3 mol% of electron rich dialkoxynaphthalene guest units (**Napht-co-PNIPAmGel**) that were complexed through host-guest interactions with the tetracationic cyclobis(paraquat-p-phenylene) (**CBPQT⁴⁺,4Cl⁻**) host (Figure 1). Upon heating-induced collapse of the PNIPAM-based LCST polymer hydrogel, the host-guest complexes dissociate followed by diffusion-controlled release of the free **CBPQT⁴⁺,4Cl⁻** host into the medium surrounding the hydrogel. This partial release of **CBPQT⁴⁺,4Cl⁻** was hypothesized to be governed by both the heat exposure time and the heating temperature as the latter controls the extent of dehydration of the hydrogel and, thus, the diffusion rate of the **CBPQT⁴⁺,4Cl⁻**. Hence, the amount of released **CBPQT⁴⁺,4Cl⁻** could be used as an indicator for both the heating temperature and the heating time of the hydrogel and can be recorded by determining the reswelling capability of the hydrogel in water. As such, measuring the reswelling capability provides information on how long the hydrogel system was exposed to a certain temperature. (Figure 1a).

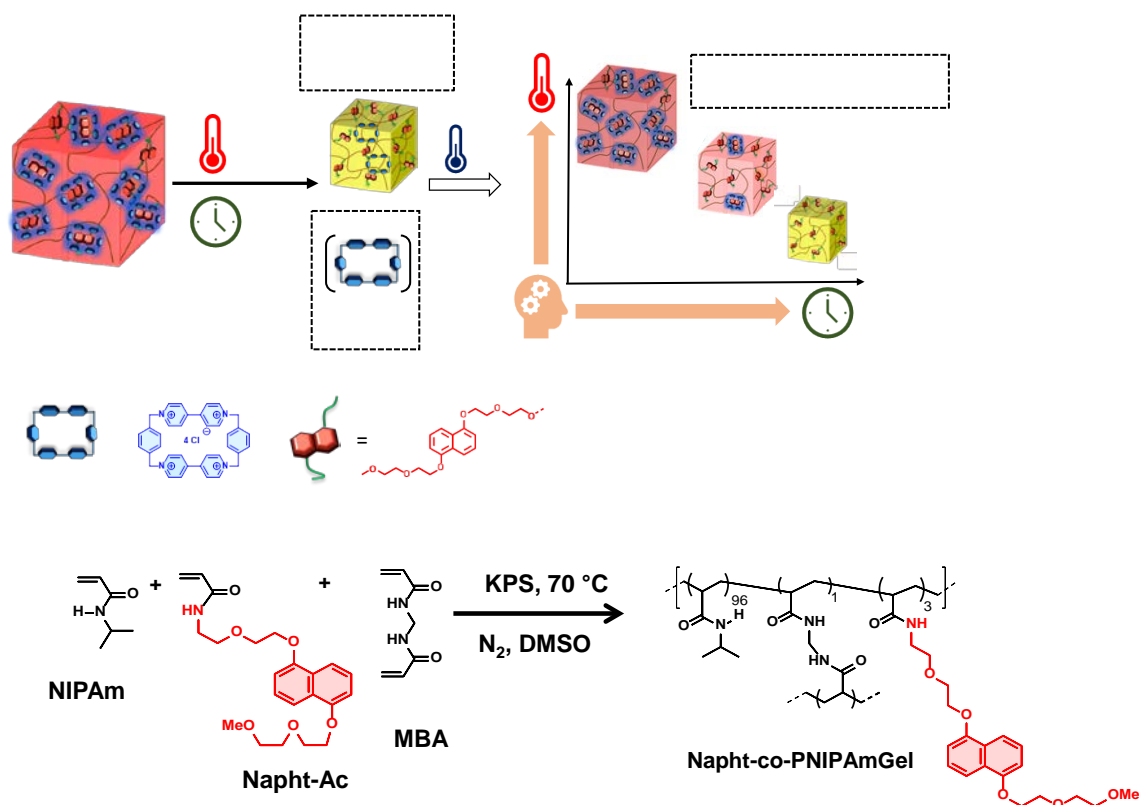


Figure 1. a) Illustration of the temperature and time memory sensing principle based on **Napht-co-PNIPAmGel** complexed with **CBPQT⁴⁺,4Cl⁻**, b) Synthesis of **Napht-co-PNIPAmGel**.

RESULTS AND DISCUSSION

The polymeric memory device **Napht-co-PNIPAmGel** containing 3 mol% of naphthalene units was prepared via free radical copolymerization (FRP) of a naphthalene acrylamide monomer (**Napht-Ac**) and *N*-isopropylacrylamide (NIPAm) in the presence of *N,N'*-methylene-bisacrylamide (MBA) as initiator and potassium persulfate (KPS) as initiator (Figure 1b). Owing to the low aqueous solubility of **Napht-Ac**, an organogel was first synthesized in dimethyl sulfoxide (DMSO), which was subsequently washed with acetone, dried and afterwards swollen in excess water to give the resulting **Napht-co-PNIPAmGel** hydrogel. After confirming that the content of naphthalene units was close to 3 mol% using high-resolution magic angle spinning (HR-MAS) NMR spectroscopy (see Supplementary

Information, Figure S1), the ability of **Napht-co-PNIPAmGel** to form host-guest complexes with **CBPQT⁴⁺,4Cl⁻** was investigated (Figure 2a). Note that equivalents are given in relation to the available naphthalene units, whereby 1 equivalent corresponds to equimolar amounts of naphthalene and **CBPQT⁴⁺,4Cl⁻**. Without **CBPQT⁴⁺,4Cl⁻**, no signals corresponding to the naphthalene units were visible in the HR-MAS ¹H NMR spectrum due to their hydrophobic nature leading to poor solvation in D₂O. However, upon the addition of aliquots of **CBPQT⁴⁺,4Cl⁻**, the formation of the charge-transfer complexes was confirmed by the appearance of the characteristic, broad **CBPQT⁴⁺,4Cl⁻** and naphthalene signals in the HR-MAS ¹H NMR spectrum, which showed the typical cross-over shift of the H_β and H_{Ph} resonances of the **CBPQT⁴⁺,4Cl⁻** when complexed with naphthalene units.³⁵ The intensity of these signals further increased with the added amount of **CBPQT⁴⁺,4Cl⁻**, at least up to the addition of one equivalent, thereby indicating that most of the naphthalene units inside the hydrogel were complexed.

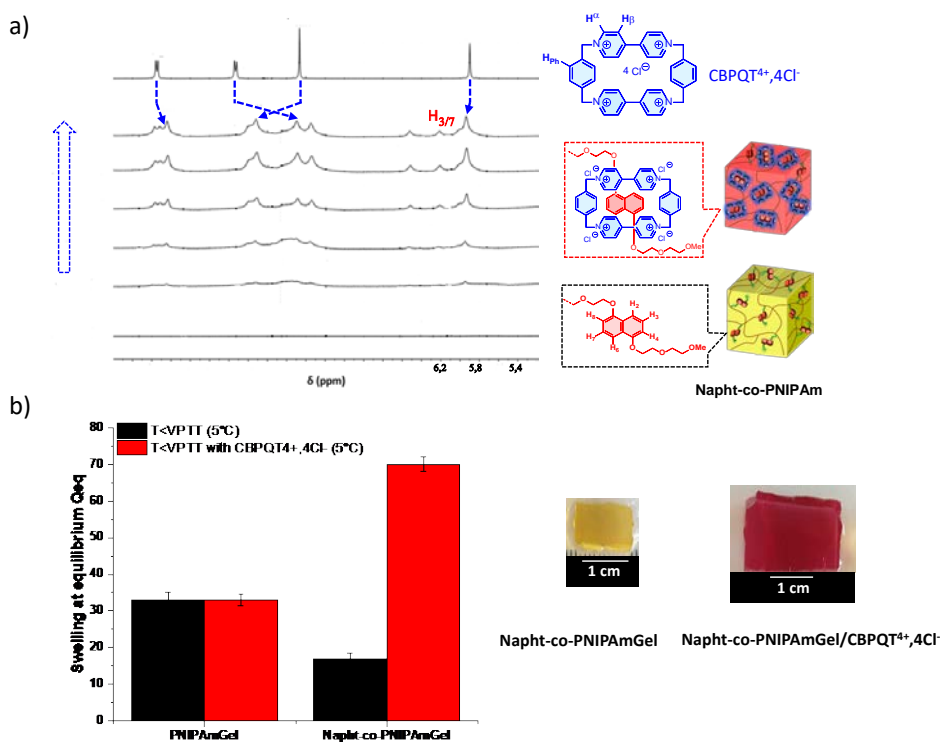


Figure 2. a) Partial HR-MAS ^1H NMR spectra of **CBPQT $^{4+}$,4Cl $^-$** and **Napht-co-PNIPAmGel** upon adding 0.2, 0.5, 0.7, 1 and 1.5 equivalents of **CBPQT $^{4+}$,4Cl $^-$** ; recorded in D_2O at 25°C . b) Swelling at equilibrium of **PNIPAmGel** and **Napht-co-PNIPAmGel** after 24h immersion at 5°C in milliQ water (black columns) and milliQ water containing 1 equivalent of **CBPQT $^{4+}$,4Cl $^-$** (red columns). Photographs of **Napht-co-PNIPAmGel** and **Napht-co-PNIPAmGel.CBPQT $^{4+}$,4Cl $^-$** at equilibrium swelling.

In the next step, the equilibrium swelling degree (Q_{eq}) of the uncomplexed and complexed hydrogels was determined in milliQ water at 5°C , which is well below the LCST phase transition temperature, after an equilibrium swelling time of 24 hours (Figure 2b) As a reference, a **PNIPAmGel** was prepared without naphthalene groups. As expected, the hydrophobic character of the naphthalene groups led to a much lower swelling degree ($Q_{\text{eq}}=17$) for the **Napht-co-PNIPAmGel** compared to the **PNIPAmGel** ($Q_{\text{eq}}=33$). The unfunctionalized **PNIPAmGel** hydrogel showed no change in its swelling capability when immersed in an aqueous solution containing **CBPQT $^{4+}$,4Cl $^-$** . In contrast, immersion of the **Napht-co-PNIPAmGel** in a solution containing **CBPQT $^{4+}$,4Cl $^-$** led to immediate purple coloration, indicative of host-guest complexation, as well as significant swelling of the hydrogel due to the incorporation of the charged **CBPQT $^{4+}$,4Cl $^-$** hosts that masks the hydrophobic naphthalene units.³⁶

PNIPAm based hydrogels are well-known to exhibit LCST-type thermoresponsive behavior inducing a volume phase transition temperature (VPTT) upon heating, which is characterized by dehydration-induced shrinking of the 3D polymer network upon heating above the VPTT. The VPTT of both **PNIPAmGel** and **Napht-co-PNIPAmGel** hydrogels were determined in the absence and in the presence of **CBPQT $^{4+}$,4Cl $^-$** via differential scanning calorimetry (DSC) (see Supplementary Information, Figure S2). The **PNIPAmGel** showed a similar VPTT of 32°C without and with **CBPQT $^{4+}$,4Cl $^-$** host molecules, indicating that the host does not

significantly influence the thermoresponsive behavior. Compared to **PNIPMAmGel**, the **Napht-co-PNIPAmGel** displayed a lower VPTT in its uncomplexed state (VPTT = 27°C) and a higher VPTT in its complexed (VPTT = 36°C) state, respectively. This trend was thus in good accordance with the evolution of equilibrium swelling properties aforementioned, showing the decrease in hydrophilicity upon incorporation of naphthalene and an increase in hydrophilicity upon complexation of **Napht-co-PNIPAmGel** with **CBPQT⁴⁺,4Cl⁻**.

We next studied the impact of the heating-induced phase transition of the complexed **Napht-co-PNIPAmGel** on the complexation state of the hydrogel by variable-temperature (VT) ¹H NMR spectroscopy (Figure 3). Figure 3a depicts the overlay of the ¹H NMR spectra of crushed **Napht-co-PNIPAmGel** pieces recorded in D₂O at different temperatures. As expected, the signals belonging to the PNIPAm polymer chains (0 – 4 ppm) significantly decreased with increasing temperature due to the dehydration induced collapse of the hydrogel leading to a decrease in chain mobility. Simultaneously, the sharp signals related to free **CBPQT⁴⁺,4Cl⁻** (5.5 – 10 ppm) appeared upon raising the temperature clearly indicating the disruption of the host-guest complexes and the release of the **CBPQT⁴⁺,4Cl⁻** host in the solution. Note that VT-¹H NMR investigations conducted on a reference, non-thermoresponsive, hydrogel consisting of poly(*N,N*-dimethylacrylamide) functionalized with 3 mol% of Napht units (**Napht-co-PDMAcGel**) complexed with **CBPQT⁴⁺,4Cl⁻** (see Supplementary Information, Figure S3) only revealed the broad signals arising from complexed **Napht.CBPQT⁴⁺,4Cl⁻** subunits, and the absence of those of free **CBPQT⁴⁺,4Cl⁻**, at 40°C (T > VPPT of **Napht-co-PNIPAmGel.CBPQT⁴⁺,4Cl⁻**), demonstrating the importance of the VPTT of **Napht-co-PNIPAmGel** to induce the dethreading of the **Napht.CBPQT⁴⁺,4Cl⁻** host-guest complexes. This LCST phase-transition induced dethreading of the **Napht.CBPQT⁴⁺,4Cl⁻** host-guest complexes has already been described for other naphthalene functionalized PNIPAm chains in solution and originates from the creation of a more hydrophobic environment in the

neighbourhood of the naphthalene units upon the collapse of the PNIPAM leading to the expulsion of the hydrophilic tetracationic **CBPQT⁴⁺,4Cl⁻** host from the collapsed polymer phase into the aqueous phase.^{24,33}

When studying the thermoresponsive behavior of the **CBPQT⁴⁺,4Cl⁻** complexed **Napht-co-PNIPAmGel** hydrogel, some interesting macroscopic features were observed. Upon heating the complexed hydrogel to 50°C ($T > VPTT$), the hydrogel rapidly (~30 s, see video in see Supplementary Information) shrunk and lost its characteristic purple colour indicating the dissociation of the **Napht.CBPQT⁴⁺,4Cl⁻** complexes above the VPTT (Figure 3b). Subsequent cooling of the hydrogel below the VPTT (5 °C) in fresh deionized water led to reappearance of the purple colour in a few seconds (see video Supplementary Information), thereby indicating that at least some of the free, uncomplexed **CBPQT⁴⁺,4Cl⁻** host units were trapped inside the dehydrated polymer matrix during the volume phase transition. The partial entrapment of free host molecules in the network was further confirmed upon its reswelling in fresh water, leading to a lower Q_{eq} of 50 compared to the initial fully complexed network ($Q_{eq} = 70$) (Figure 4). This relatively large temperature-triggered hysteresis in the swelling capability of **Napht-co-PNIPAmGel.CBPQT⁴⁺** can be ascribed to the partial release of the **CBPQT⁴⁺,4Cl⁻** units from the hydrogel material into the surrounding medium during the volume phase transition of the polymer matrix, leading to incomplete recomplexation during reswelling in fresh water resulting in a lower Q_{eq} compared to the initial fully complexed system.

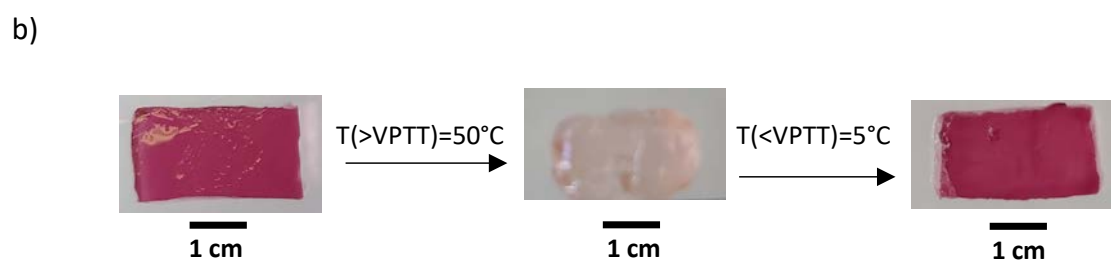
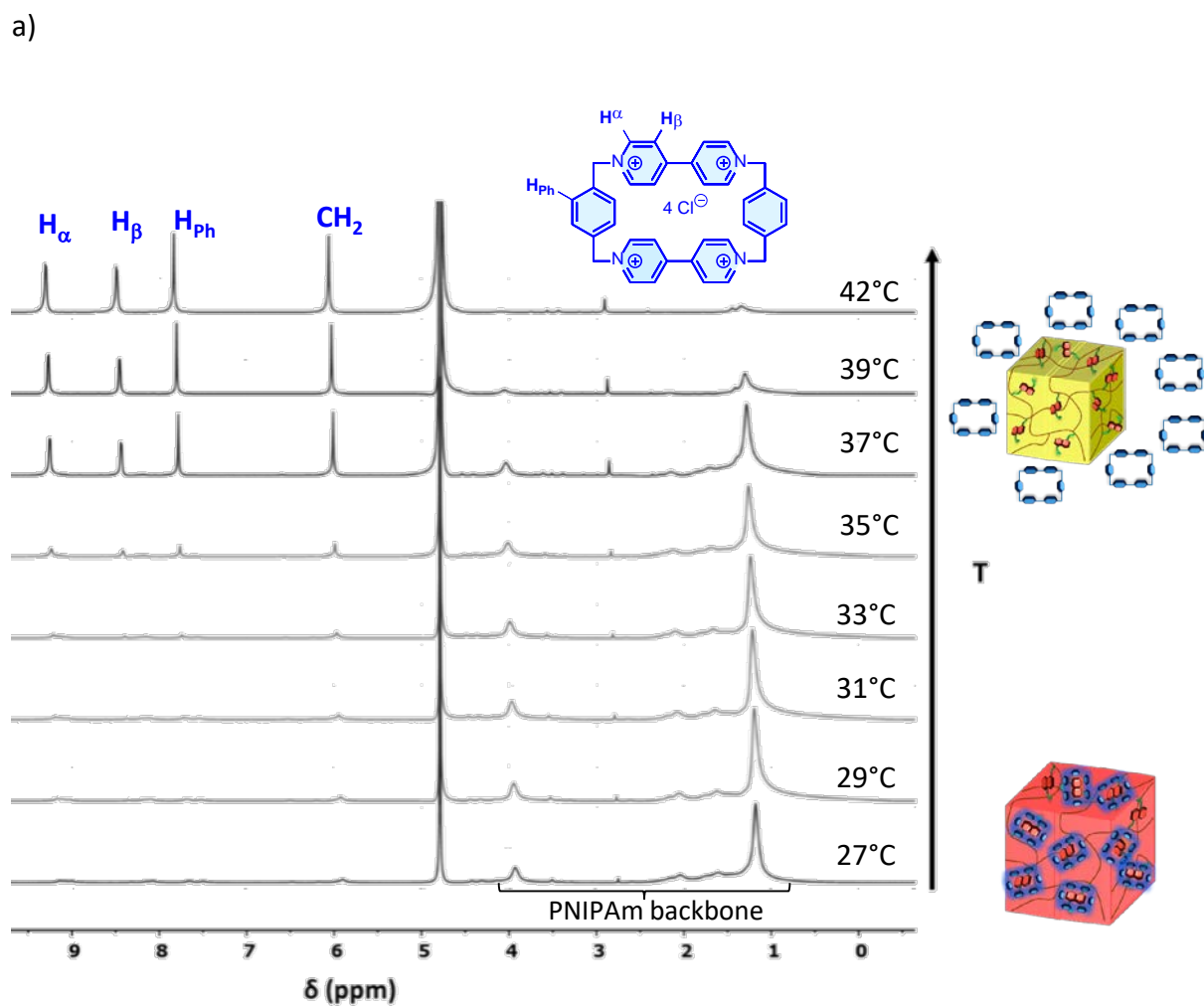


Figure 3. a) $^1\text{H-NMR}$ spectra of Napht-co-PNIPAmGel complexed with $\text{CBPQT}^{4+}, 4\text{Cl}^-$ in D_2O , measured in D_2O at 27°C , 29°C , 31°C , 33°C , 35°C , 37°C , 39°C and 42°C ; b) Photographs of Napht-co-PNIPAmGel. $\text{CBPQT}^{4+}, 4\text{Cl}^-$ at equilibrium swelling (left), and after being heated in water at 50°C for 1 hour (middle) followed by reswelling in fresh cold milliQ water (right).

Based on these observations, we hypothesized that both temperature and exposure time might have an influence on the disassembly of the **Napht.CBPQT⁴⁺,4Cl⁻** complexes in the hydrogels as well as on the diffusion-controlled release of the free **CBPQT⁴⁺,4Cl⁻** into the surrounding medium. Hence, variations in both the temperature and the duration of the heat treatment would lead to a different amount of **CBPQT⁴⁺,4Cl⁻** host retained in the hydrogels. To record these different levels of the retained host in the hydrogels, they can be swollen in fresh water as various degrees of complexation of the **Napht-co-PNIPAmGel** lead to different swelling degrees, as recently shown on naphthalene guests containing poly(*N,N*-dimethylacrylamide) hydrogels.³⁶ Consequently, the difference in swelling between the original complexed hydrogel and the hydrogel that is collected and reswollen in fresh water after heat treatment can be used as an output signal to record the thermal treatment temperature and time, providing information about how long the hydrogel has been exposed to a certain temperature. Even though reswelling in fresh water might not be the most straightforward method for recording an output signal, it represents the first fundamental example of a molecular system that allows monitoring the time and temperature of a heat treatment.

This hypothesized temperature and time dependence of the reswelling behavior of **Napht-co-PNIPAmGel. CBPQT⁴⁺,4Cl⁻** was first evidenced by exposing the complexed hydrogel in excess water (i.e., under equilibrium swelling conditions) to three different heat treatments, namely 10 min at 70 °C (far above VPTT; Q₁), 60 min at 50 °C (above VPTT; Q₂) and 12 h at 35 °C (~VPTT; Q₃). After these heat treatments, the hydrogels were collected from the warm solution and reswollen in fresh demineralized water at 5 °C (Figure 4). The Q_{eq} values of the reswollen hydrogels were found to be lower than the Q_{eq} value of the starting, fully complexed hydrogel (Q₀) at 5 °C, indicating incomplete recomplexation of naphthalene units during the reswelling step and, hence, indicating release of the **CBPQT⁴⁺,4Cl⁻** during the heat treatment. Interestingly, the hydrogels that were exposed to a mild heat treatment (35°C) for a

long time (12h), displayed a much lower reswelling capability compared to that of hydrogels that were subjected to more severe heating (70°C) during shorter times (10 min), while the hydrogel that got an intermediate heat treatment (60 min at 50 °C) revealed an intermediate reswelling capability. This observed trend can be explained by the fact that the hydrogel collapse is more abrupt and hydrogel dehydration is more efficient when the hydrogel is heated to temperatures that are further above the VPTT,³⁷ leading to more efficient entrapment of the non-complexed **CBPQT**⁴⁺,**4Cl**⁻ host molecules inside the uncomplexed hydrogel. As a result, during subsequent reswelling in fresh water, the entrapped hosts lead to reformation of the host-guest complexes resulting in higher reswelling ratios compared to the hydrogel that was heated to a temperature around the VPTT for 12h. In this latter case, the dehydration of the PNIPAM hydrogel is slower and less severe, enabling the uncomplexed **CBPQT**⁴⁺,**4Cl**⁻ host molecules to diffuse outside the dehydrated hydrogel, leading to a much lower amount of restored **Naph.CBPQT**⁴⁺,**4Cl**⁻ complexes upon reswelling in fresh water, and thus to a lower equilibrium reswelling degree.

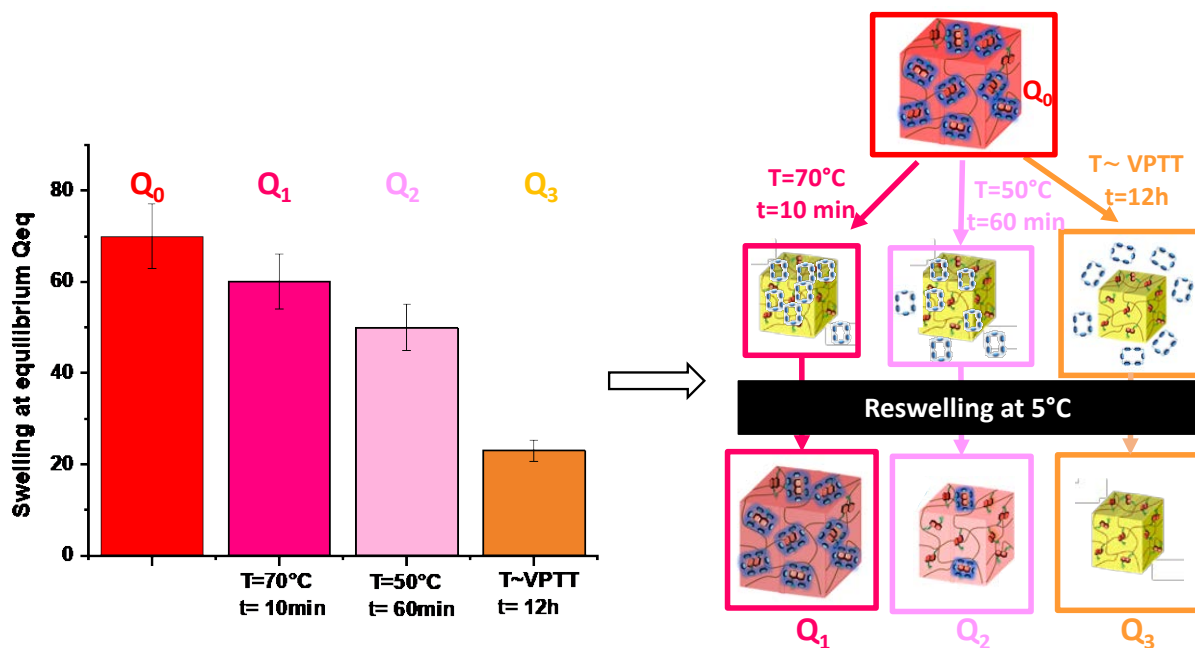


Figure 4. Left: Swelling at equilibrium of fully complexed **Napht-co-PNIPAmGel. CBPQT**⁴⁺,**4Cl**⁻ (Q_0) at 5 °C and of **Napht-co-PNIPAmGel. CBPQT**⁴⁺,**4Cl**⁻ hydrogels that were

reswollen in fresh water at 5 °C after being collected from the warm solutions that were heated for 10 min at 70 °C (Q₁), 60 min at 50 °C (Q₂) and 12 h at 35 °C (Q₃). Right: Schematic illustration of the disassembly of the **Naph.CBPQT⁴⁺,4Cl⁻** complex and the accompanied diffusion-controlled release of the free **CBPQT⁴⁺,4Cl⁻** from the hydrogel upon heating for 10 min at 70 °C, 1 h at 50 °C and 12 h at 35 °C of the hydrogel, followed by reswelling at 5 °C in fresh water.

As a final part of this study, the time memory function was explored more quantitatively by heating fully complexed **Napht-co-PNIPAmGel** hydrogel pieces at different temperatures ranging from close to the phase transition temperature (VPTT = 35°C) up to 60°C for increasing periods of time of 1 h, 5 h, 10 h and 14 h. After the desired time, the hydrogels were collected from the warm water and allowed to reswell in fresh milliQ water below the VPTT at 5 °C for different times up to 96 h. The percentage of decomplexation was calculated from the reswelling Q_{eq} as explained in detail in section S9 of the Supporting Information. All data for these time-temperature memory experiments are summarized in Figure S4 (see Supplementary Information). Based on the evaluation of the reswelling times, it could be concluded that the largest response and variation in Q_{eq}, after heat treatment and reswelling in fresh water, was achieved with 2 hours reswelling time, thus providing the most accurate read-out of the temperature and time memory for the heat treatment hydrogels (see Supplementary Information, section S10).

After determination of the best read-out conditions of the heat-treated **Napht-co-PNIPAmGel** hydrogel, the percentage of decomplexation of the 2h reswollen **Napht-co-PNIPAmGel** hydrogel pieces, that were heated at different temperatures (42 °C, 46 °C, 50 °C and 60 °C) for different times (1 h, 5 h, 10 h and 14 h), were plotted to evaluate the temperature and time memory function (Figure 5). The results clearly demonstrate that the system can report how long it was exposed to a certain temperature as the decomplexation percentage increases with

heating time at all investigated temperatures, thereby representing the first example of a polymeric temperature sensor with a time memory function.

When we take a closer look at Figure 5, it can be observed that heating the complexed **Napht-co-PNIPAmGel** hydrogels pieces slightly above the VPTT (35°C) at 42 °C for 14 hours leads to 80% decomplexation of the **Napht.CPQT⁴⁺,4Cl⁻** complexes. With decreasing heating times, the decomplexation percentage also decreases, showing respectively 35% and 10% after 5 h and 1 h of heating, as expected for diffusion-based release of the uncomplexed **CBPQT⁴⁺,4Cl⁻** host out of the partially dehydrated hydrogel. With increasing heating temperature, up to 46 °C, 50 °C and 60 °C, the time memory function is preserved, whereby the final decomplexation degree after 14 hours of heating steadily decreases with increasing temperature. This is ascribed to the more efficient dehydration of the PNIPAM hydrogels at higher temperatures leading to slower diffusion of the uncomplexed host from the hydrogel to the surrounding medium. As such, we have demonstrated a fundamental proof-of-concept for supramolecular hydrogels as time memory sensors at a certain temperature or as temperature sensors upon exposure to an unknown temperature for 14 hours. It should be noted that the reported system is, however, not capable of independently reporting both temperature and time, and it is restricted to recording the exposure time at a certain temperature or the temperature for a certain exposure time.

Reswelling time = 2 h

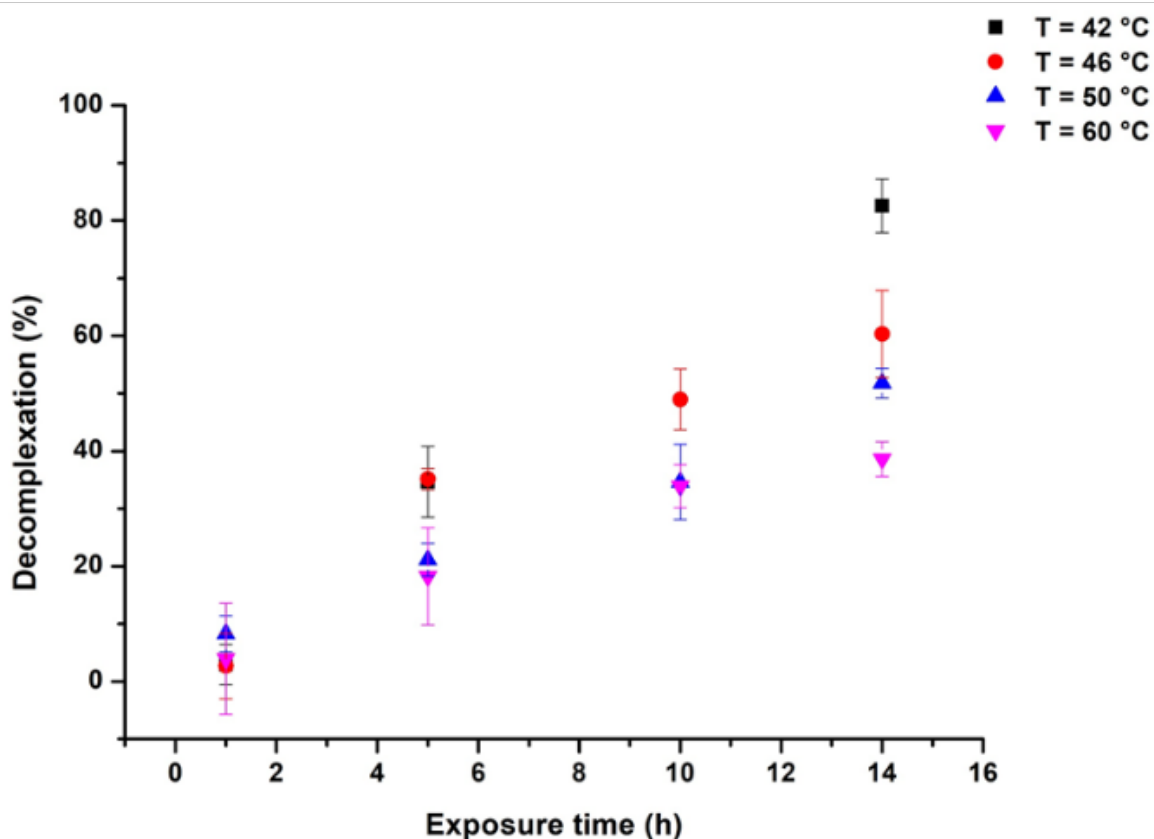


Figure 5. Decomplexation percentages of **Napht-co-PNIPAmGel** after heat treatment at different temperatures: 42 °C (black squares), 46 °C (red circles), 50 °C (blue upward triangles) and 60 °C (purple downward triangles) for different times (1 h, 5 h, 10 h and 14 h), followed by collection of the hydrogel pieces from the warm water followed by reswelling in fresh demineralized water (20 mL) at 5 °C for 2 h. All tests were performed in triplicate.

CONCLUSION

In conclusion, we demonstrated that thermoresponsive hydrogels functionalized with a supramolecular guest molecule and complexed with a tetracationic host could act as temperature sensors capable of recording the time of exposure to a certain temperature. This unprecedented time memory function results from strong hysteresis in the volume-phase transition after being heated above the VPTT due to the disruption of host-guest interactions,

followed by slow diffusion and release of uncomplexed host units from the hydrogel into the surrounding medium. As a result, both the temperature and the heat treatment time exert a kinetic control over the concentration of hosts that are retained in the hydrogel during its volume phase transition. Hence, by means of the reswelling amplitude of the hydrogel in fresh water, it was possible to read out the thermal history of the hydrogel to record the time at a certain temperature or the temperature at a certain exposure time. It should be noted that the proposed system is mainly suitable for single-use sensors, as reuse would require an additional new CBPQT⁴⁺,4Cl⁻ host to replenish the host lost by diffusion. Furthermore, the effectiveness of the concept has so far been established for PNIPAm-based hydrogels and in pure water. To broaden the scope of this concept, future work will aim to demonstrate that other thermosensitive polymer systems with different transition temperature ranges can be used in this context and that this dual memory function can also operate in saline aqueous media. In addition, this general concept could be extended to other stimuli and thus may open new opportunities in developing memory devices based on soft materials. Moreover, in future work, the rather cumbersome reswelling read-out of the system might be replaced with more direct read-out methods, such as UV-vis spectroscopy to determine the degree of decomplexation.

AUTHOR CONTRIBUTION

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. These authors contributed equally.

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SUPPORTING INFORMATION

The Supporting Information is available free of charge at.....

Synthesis and characterization of the Napht-co-PNIPAmGel. The High Resolution Magic Angle Spinning (HR-MAS) NMR spectrum of Napht-co-PNIPAmGel used to determine the Naphthalene content in the hydrogel. Procedure for the complexation of the Napht-co-PNIPAmGel. Determination of equilibrium swelling degree (Qeq) by gravimetric measurement. Determination of Volume Phase Transition Temperature (VPTT) of hydrogels by DSC. Videos showing kinetics of decomplexation and recomplexation of complexed Napht-co-PNIPAmGel. Procedure for the memory experiments of Napht-co-PNIPAmGel.

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