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Self-Healing Materials

# A Rapidly Self-Healing Supramolecular Polymer Hydrogel with Photostimulated Room-Temperature Phosphorescence Responsiveness**

*Hui Chen, Xiang Ma,* Shuaifan Wu, and He Tian**

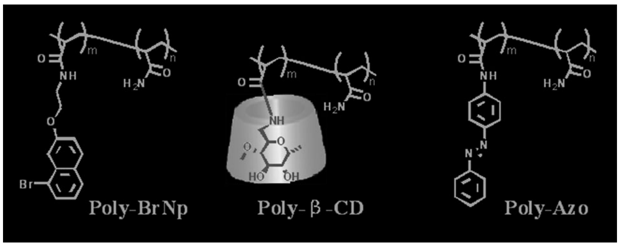
***Abstract:** Development of self-healing and photostimulated luminescent supramolecular polymeric materials is important for artificial soft materials. A supramolecular polymeric hydrogel is reported based on the host–guest recognition between a β-cyclodextrin (β-CD) host polymer (poly-β-CD) and an α-bromonaphthalene (α-BrNp) polymer (poly-BrNp) without any additional gelator, which can self-heal within only about one minute under ambient atmosphere without any additive. This supramolecular polymer system can be excited to engender room-temperature phosphorescence (RTP) signals based on the fact that the inclusion of β-CD macrocycle with α-BrNp moiety is able to induce RTP emission (CD-RTP). The RTP signal can be adjusted reversibly by competitive complexation of β-CD with azobenzene moiety under specific irradiation by introducing another azobenzene guest polymer (poly-Azo).*

Artificial soft materials, based on supramolecular polymerization systems by highly directional noncovalent interactions such as hydrogen bonding, hydrophobic effects, host–guest recognition, π–π interactions, electrostatic interactions, metal–ligand interactions, and so forth,[1,2] are being developed currently to mimic natural biological or vital systems, such as proteins and DNAs, and achieve specific functions. Hydrophilic supramolecular polymers are typical species of such soft materials, which are generally constructed by macrocyclic recognition between host and guest polymeric chains or components in aqueous solution.[3] Development of stimuli-responsive or self-healing supramolecular polymeric materials have drawn much attention recently.[4–15] Other interesting properties for supramolecular polymers are that the monomers of them can be functionalized by introducing various functional moieties with fluorescent emission,[16,17] thermal memory sensing,[18] chirality,[19] redox-feasibility,[20,21] aggregation-induced emission,[22] photochromism,[23] and so forth.

Several examples of hydrophilic self-healing supramolecular polymeric materials by cyclodextrin (CD) recognition in aqueous solution have been reported, the self-healing properties of which were realized by either standing for a longer time,[20] or assembling in specific solvent atmospheres.[24,25] Supramolecular polymers provided with room temperature phosphorescence (RTP) addressing is rarely reported. Herein, we report a supramolecular polymeric hydrogel based on the host–guest recognition between β-CD host polymer (poly-β-CD) and α-bromonaphthalene (α-BrNp) polymer (poly-BrNp) without any additional gelator, which can self-heal quickly within only one minute in air without any additive. Moreover, this supramolecular polymer system can be excited to engender RTP signals based on the inclusion of β-CD macrocycle with α-BrNp moiety. The RTP signal can be adjusted reversibly by competitive complexation with the different photoconfigurations of azobenzene moiety.[26,27]

The structures of poly-β-CD, poly-BrNp, and poly-Azo are shown in Scheme 1, and were prepared by radical binary copolymerization employing acrylamide and monomers containing β-CD, α-BrNp, and azobenzene, respectively (for synthesis details, see the Supporting Information, Figures S1–S3; for the characterization data of polymers, see Table S1). In this work, the concentration of the polymers was represented by the concentration of functional monomers.

The hydrogelation between poly-β-CD and poly-BrNp was easily realized by simply mixing their aqueous solutions together and is based on the supramolecular host–guest recognition interaction between β-CD units and α-BrNp moieties, with a moderate binding constant about $10^3\,\mathrm{L\,mol^{-1}}$[28,29] (Figure 1; see also the Supporting Information, Video S1). A hydrogel was formed after mixing these two aqueous solutions (volume ratio 1:1, both concentrations after mixing are $1\times10^{-2}\,\mathrm{M}$) together and standing for about 15 min. The rheology measurement of this mixture showed that the value of storage modulus ($G'$, more than 300 Pa) was



***Scheme 1.*** Structures of host polymer poly-β-CD and guest polymers poly-BrNp and poly-Azo.

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[*] H. Chen, Prof. X. Ma, Dr. S. Wu, Prof. H. Tian
Key Laboratory for Advanced Materials and
Institute of Fine Chemicals
East China University of Science & Technology
Shanghai 200237 (P. R. China)
E-mail: maxiang@ecust.edu.cn
tianhe@ecust.edu.cn

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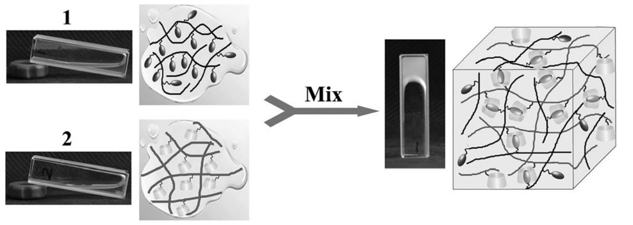

***Figure 1.*** The conversion process to hydrogel by host–guest recognition interaction. Liquid: **1** presents [poly-BrNp] = $2\times10^{-2}$ M, **2** presents [poly-β-CD] = $2\times10^{-2}$ M.

larger than the loss modulus ($G''$, about 200 Pa) over the whole range of the measured strain, indicating the formation of the hydrogel (Supporting Information, Figure S4). Not only the host–guest interaction between β-CD units and BrNp moieties but also the hydrogen bonds between amide groups play important roles in forming the hydrogel, which are conducive to the formation of cross-linked structure. The formed hydrogel was thermally responsive and could realize gel–sol transition by cooling and heating (for details, see the Supporting Information, Figure S5), the transition temperature of which was about 65 °C.

The guest polymer poly-BrNp could engender CD-RTP emission when mixed with β-CD or poly-β-CD in aqueous solution owing to the inclusion effect of β-CD with α-BrNp phosphor.[28] As shown in Figure 2a, addition of β-CD with increasing amount into aqueous poly-BrNp solution engendered the RTP emission, but of a relatively weak intensity. The intensity of the maximum RTP emission shoulders peaks at about 552 nm reached only 74 even after adding 100 equivalents of β-CD. However, the RTP emission intensity of the binary poly-BrNp/poly-β-CD system was much stronger than that of poly-BrNp/β-CD system. As seen in Figure 2b, the RTP intensity increase remarkably upon increasing the amount of poly-β-CD, reaching up to 498 when adding 10 equivalents of poly-β-CD. It has been reported that adding some third component to the BrNp/β-CD system could increase the inclusion binding constant and shield BrNp moiety from oxygen as to enhance the phosphorescence emission.[29,30] The polymeric chains of poly-β-CD might cooperatively stabilize the BrNp/β-CD complex and shield BrNp moiety from oxygen to some extent, and the host–guest interaction between polymer side chains also readily forms a highly cross-linked supramolecular network, which enhances the RTP emission of poly-BrNp/poly-β-CD system. The formed hydrogel by host–guest recognition between poly-BrNp and poly-β-CD of higher concentrations (both are $2\times10^{-2}$ M; Figure 2c) engendered very strong RTP emission with intensity of 889. This was attributed the fact that the polymers in solution had the enhancement effect on the RTP emission and the hydrogel media affected more.[31] The RTP lifetime for the binary poly-BrNp/poly-β-CD system was found about 0.56 ms (Figure 2d).

The RTP emission spectrum of poly-BrNp/poly-β-CD/poly-Azo ternary system is shown in Figure 3a. The fluorescence emission for this system was weak because of the heavy-atom effect of α-BrNp moiety (Supporting Information, Figure S6). At the initial state, this system was excited to engender weak RTP emission peak at about 550 nm, the reason of which was that poly-β-CD preferred to include poly-Azo by forming many pseudorotaxane units between most β-CD macrocycles and azobenzene moieties, while only a small number of β-CDs in the side chain of poly-β-CD complexed with α-BrNp units in poly-BrNp.[26] Interestingly, prolonged UV light irradiation at 365 nm made the RTP emission intensity at 520 nm and 550 nm stronger (Figure 3a). The *trans*-azobenzene units in poly-Azo were photoisomerized to de-thread from the β-CD cavities in poly-β-CD so that more α-BrNp moieties can be included inside, which enhanced the RTP, reaching about 5.3 times its initial state (224 to 42) at the

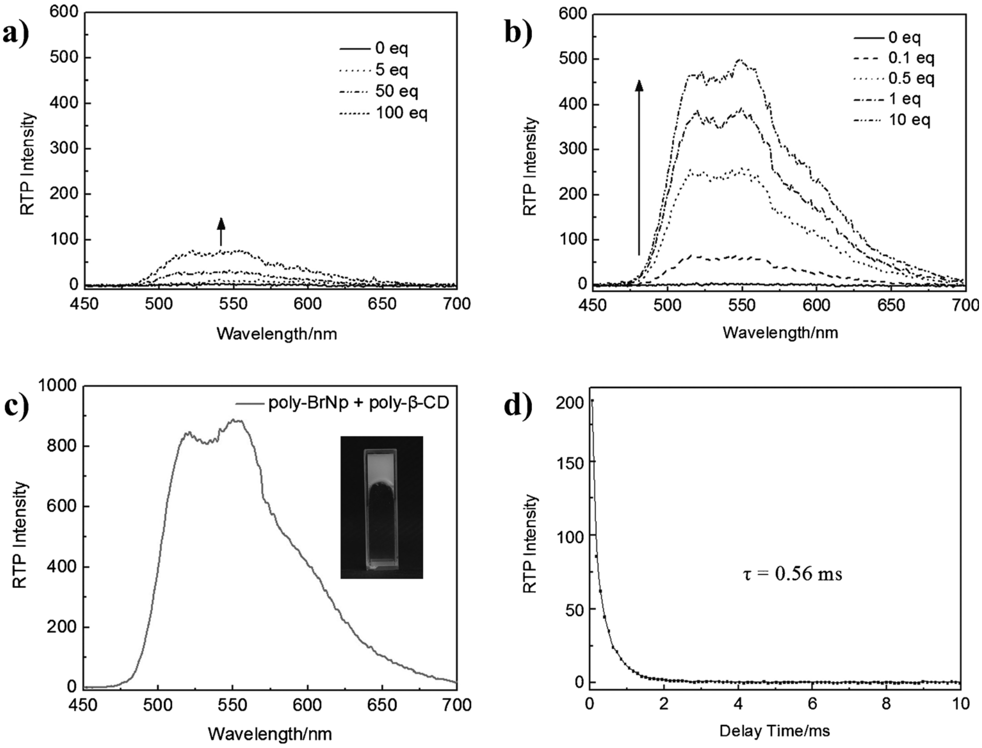

***Figure 2.*** RTP spectra of the binary a) poly-BrNp/β-CD system ([poly-BrNp] = $1\times10^{-5}$ M, [β-CD] = 0, $5\times10^{-5}$, $5\times10^{-4}$, $1\times10^{-3}$ M); b) poly-BrNp/poly-β-CD system ([poly-BrNp] = $1\times10^{-5}$ M, [poly-β-CD] = 0, $1\times10^{-6}$, $5\times10^{-6}$, $1\times10^{-5}$, $1\times10^{-4}$ M); c) poly-BrNp/poly-β-CD hydrogel ([poly-BrNp] = $2\times10^{-2}$ M, [poly-β-CD] = $2\times10^{-2}$ M). Inset: photograph of poly-BrNp/poly-β-CD hydrogel. d) RTP lifetime of the binary poly-BrNp/poly-β-CD system ([poly-BrNp] = $1\times10^{-5}$ M, [poly-β-CD] = $1\times10^{-4}$ M).

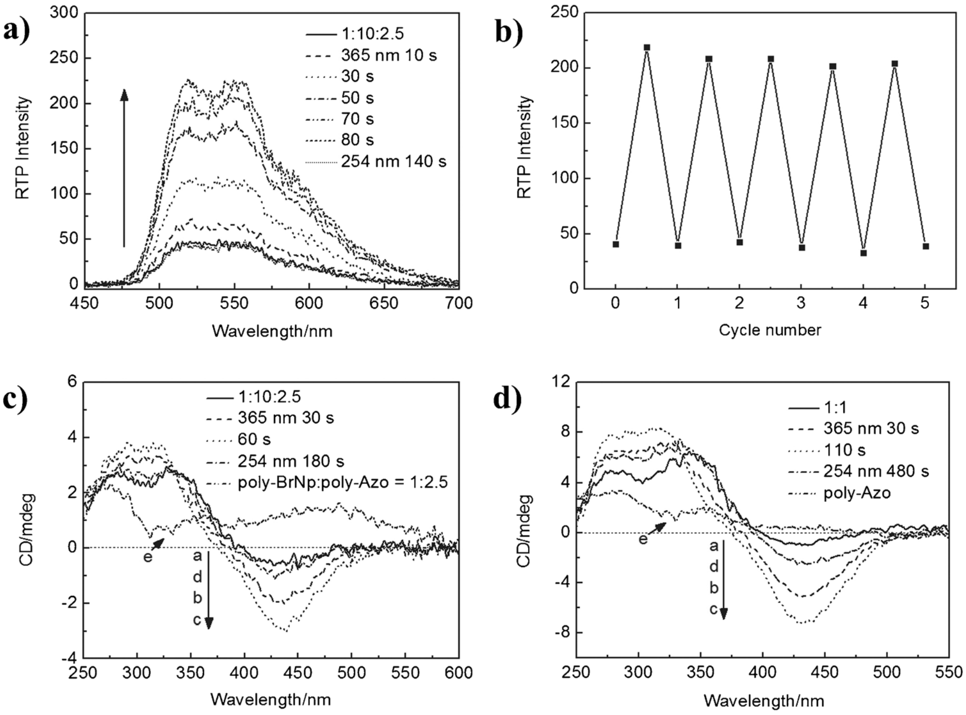

***Figure 3.*** a) RTP spectra of ternary poly-BrNp/poly-β-CD/poly-Azo aqueous solution. ([poly-BrNp] = $1\times10^{-5}$ м, [poly-β-CD] = $1\times10^{-4}$ м, [poly-Azo] = $2.5\times10^{-5}$ м). After irradiation by 365 nm light for 10 s, 30 s, 50 s, 70 s, 80 s; then by 254 nm for 140 s. b) Reversibility of the photostimulated RTP spectrum of the ternary system. Changes in the RTP intensity at 550 nm along with changes in irradiation time and light source. Light sources of 365 and 254 nm were alternated every 80 s and 140 s. c) ICD spectra of poly-BrNp/poly-β-CD/poly-Azo aqueous solution. [poly-BrNp] = $1\times10^{-5}$ м, [poly-β-CD] = $1\times10^{-4}$ м, [poly-Azo] = $2.5\times10^{-5}$ м. After irradiation by 365 nm light for 30 s (b), 60 s (c); then by 254 nm for 180 s (d). d) ICD spectra of binary poly-β-CD/poly-Azo aqueous solution. [poly-β-CD] = [poly-Azo] = $1\times10^{-4}$ м. After irradiation by 365 nm light for 30 s (b), 110 s (c); then by 254 nm for 480 s (d). The poly-Azo aqueous solution (curve e, [poly-Azo] = $1\times10^{-4}$ м) showed no obvious Cotton peak but only the systematic error of the measurement.

photostationary state after irradiation for 80 s. Owing to the *trans–cis* photoisomerization of azobenzene units, they could thread and de-thread into the cavity of β-CD to form pseudorotaxane or not upon irradiation at different UV wavelengths, then the resulting RTP of the competitive poly-BrNp/poly-β-CD assembly could be increased or decreased, which process could be repeated over many cycles with UV irradiation, alternating between 365 and 254 nm (Figure 3b).

The competitive inclusion behavior of this poly-BrNp/poly-β-CD/poly-Azo ternary system was also fully characterized by absorption (Supporting Information, Figure S7) and induced circular dichroism (ICD) spectra. The azobenzene group was known to be included by β-CD to generate ICD signal.[32] As shown in Figure 3c, a positive Cotton peak at about 303 nm and a negative Cotton peak at around 437 nm appeared after mixing the three polymers together at a ratio of 1:10:2.5, which were attributed to the π–π* and n–π* transition bands respectively of azobenzene groups of poly-Azo in *trans* conformation located within β-CD cavities of poly-β-CD.[16] The prolonged irradiation with 365 nm light to this ternary system brought about a gradual intensity increase of both the two Cotton peaks shown in Figure 3c (curves a, b, and c). And the ICD spectral changes could be almost shifted back by irradiation at 254 nm (curve d). The ICD spectrum of the poly-β-CD/poly-Azo exhibited the similar changes under alternative light irradiation at 365 nm and 254 nm (Figure 3d).

The macroscopic self-healing of the usual CD-based self-healing supramolecular polymeric materials reported previously was realized taking relatively longer time (hours, for example),[20,33] and some systems even needing being in wet media.[24,25] Herein, we prepared another hydrogel using the same binary poly-BrNp/poly-β-CD system but of a higher total concentration as $2\times10^{-2}$ м. The rheology measurement of this system showed that the value of storage modulus ($G'$, more than 3000 Pa) was larger than the loss modulus ($G''$, about 1500 Pa) over the whole range of the measured strain, indicating the formation of the hydrogel (Supporting Information, Figure S9) and a better hydrogel intensity than that prepared from the same system of the lower concentration (total concentration $1\times10^{-2}$ м). This hydrogel exhibited superior macroscopic self-healing properties, which could be rapidly realized within only 1 min just in atmosphere. As shown in Figure 4, a piece of poly-BrNp/poly-β-CD hydrogel was cut in half and then the halves were simply put together. After standing for only 1 min, the two pieces re-joined into one piece and the crack disappeared. Then the whole hydrogel piece could be lifted up without breakup (the detailed process of the self-healing experiment could be found in the Supporting Information, Video S2). This hydrogel piece was totally recovered after one hour and restored to its original state both in shape and rheological properties (Supporting Information, Figures S10 and S11). This self-healable supramolec-

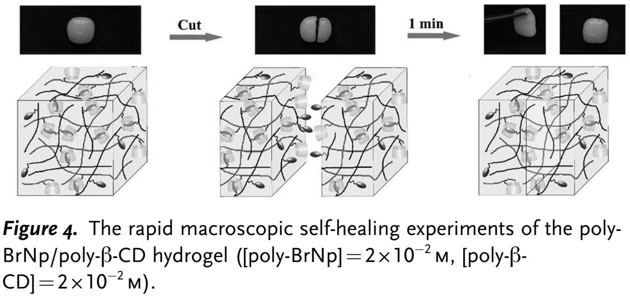

***Figure 4.*** The rapid macroscopic self-healing experiments of the poly-BrNp/poly-β-CD hydrogel ([poly-BrNp] = $2\times10^{-2}$ м, [poly-β-CD] = $2\times10^{-2}$ м).

ular hydrogel was a very simple system without adding any other helpful crosslinking components, gelators, or media.

In summary, a rapid self-healing supramolecular hydrogel system based on host–guest recognition between poly-β-CD and poly-BrNp was successfully prepared. Unlike the previous CD-based supramolecular hydrogel systems, the self-healing of which were realized over a timeframe of hours or under certain conditions such as in wet media, this poly-BrNp/poly-β-CD hydrogel we reported herein could self-heal in macroscopic scale within only one minute and in just air without any additive.

Moreover, the poly-BrNp/poly-β-CD hydrogel engendered enhanced RTP emission owing to the inclusion between β-CD and α-BrNp moieties. When introducing poly-Azo polymer into this binary system in aqueous solution, the RTP emission could be photostimulated by alternative UV irradiation at 365 nm and 254 nm to switch with an intensity change reversibly. This was attributed that the photostimulated *cis–trans* isomerization of the azobenzene units in the system affected the competitive inclusion of β-CD and α-BrNp. This hydrogel system was the first example of supramolecular polymer with RTP function to the best of our knowledge. This rapid self-healing supramolecular hydrogel material would be a smart and potentially applicable soft material in future, which is just like the very recent reported polymers provided with surface-initiated self-healing still realized in metal-free water.[34]

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