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Jiang, Yingnan; Yang, Xudong; Ma, Cheng; Wang, Chuanxi; Li, Hui; Dong, Fengxia; Zhai, Xiaoming; Yu, Kui; Lin, Quan; Yang, Bai

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# Photoluminescent Smart Hydrogels with Reversible and Linear Thermoresponses

Yingnan Jiang, Xudong Yang, Cheng Ma, Chuanxi Wang, Hui Li, Fengxia Dong, Xiaoming Zhai, Kui Yu,\* Quan Lin,\* and Bai Yang

Polymeric materials with responses to external stimuli are of great interest in a number of applications that require the switch of material properties. For example, thermoresponsive polymers can exhibit coil-to-globule transitions during a change of temperature. Poly(*N*-isopropylacrylamide) (PNIPAM), with a coil-to-globule transition in water at a lower critical solution temperature (LCST) of 32 °C, is one of the candidates and has been widely studied. The coil-to-globule transition of PNIPAM could be a reversible process but not speedy, and the application areas include drug delivery, sensors, color-tunable crystals, and catalysis.<sup>[1]</sup>

Fluorescent PNIPAM hydrogels have recently been reported.<sup>[2]</sup> Usually, various photoluminescent molecules, such as benzofurazan, hemicyanine, carbazole, dicyanomethylene-4*H*-pyran derivatives, and CdTe and ZnS quantum dots, were used to engineer the fluorescent PNIPAM hydrogels. The interactions between the emitters and PNIPAM include physical encapsulation, covalent bonding, and supramolecular interactions. The thermoresponsive fluorescence of the reported PNIPAM-based hydrogels was only active in a very narrow temperature window, which was around the LCST. Little tunability was reported to the thermoresponsive fluorescence.<sup>[2,3]</sup> The sudden change of the emission around the LCST, which was documented as an on–off feature, limits the application of these fluorescent PNIPAM hydrogels. However, there is an outstanding need for fluorescent PNIPAM hydrogels to respond effectively and continuously in a broad temperature window without such an on–off element.

Lanthanide organic complexes, such as Eu(DBM)<sub>3</sub>Phen (DBM = dibenzoylmethide; Phen = 1,10-phenanthroline, have been widely used as luminescent probes and labels in optics and bioanalysis. These complexes exhibit relatively

bright emission with narrow bandwidth, as compared to their corresponding inorganic lanthanide ions.<sup>[4]</sup> However, most of the lanthanide organic complexes are water-insoluble. There is a limited body of literature on the lanthanide organic complexes bound to PNIPAM. For example, in a mixture of tetrahydrofuran and H<sub>2</sub>O or in dimethylformamide, Eu-loaded PNIPAM nanoparticles were formed.<sup>[5]</sup> When water-soluble inorganic lanthanide(III) ions were introduced to a PNIPAM aqueous solution, the resulting product exhibited low luminescence efficiency with a weak response to temperature change.<sup>[6]</sup>

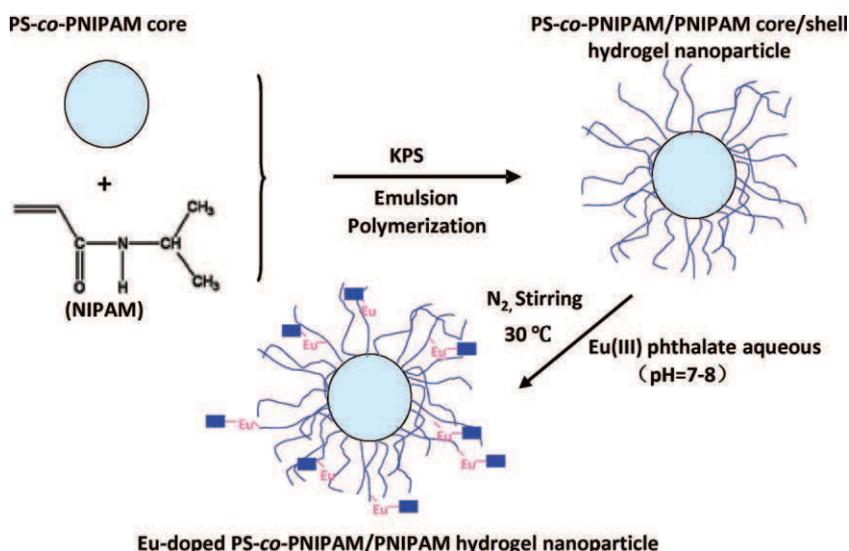
Herein, we report newly developed smart hydrogel nanoparticles with thermoresponsive photoluminescence (PL) at a broad change of temperatures. Such thermoresponses of our bright hydrogels were detected to be linear, reversible, and sensitive regarding the emission intensity but with little change in the emission peak position. The photoluminescent source was the water-soluble europium organic complex Eu(III) phthalate, which was designed to coordinate in the shell of core/shell hydrogel nanoparticles. We designed the core to be poly[styrene-*co*-(*N*-isopropylacrylamide)] (PS-*co*-PNIPAM) and the shell PNIPAM. Thus, our thermoresponsive photoluminescent hydrogels were denoted as Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles. Their temperature-stimulated PL response is considerably different from that of the previously reported PNIPAM hydrogels.<sup>[2,3,6]</sup> These novel photoluminescent nanoparticles with linear and reversible temperature sensitivity should be very promising in various applications.<sup>[1,7]</sup> To the best of our knowledge, these thermoresponsive photoluminescent hydrogels are the first to have their PL intensity reversible, linear, and sensitive to the broad temperature range of 10–50 °C.

**Scheme 1** depicts the synthetic procedure of our Eu-doped PS-*co*-PNIPAM/PNIPAM hydrogel nanoparticles. The PS-*co*-PNIPAM cores were synthesized through surfactant-free emulsion polymerization with potassium persulfate (KPS) as initiator. The core/shell PS-*co*-PNIPAM/PNIPAM nanoparticles were synthesized with a seed emulsion polymerization method. The detailed procedure can be found elsewhere but with modification.<sup>[8]</sup> The Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles with thermoresponsive PL were prepared at ≈30 °C under N<sub>2</sub> with stirring for about 3 h. Both the prepared cores and the core/shell nanoparticles presented very good monodispersity, as shown in Figure S1 in the Supporting Information. The incorporation of the Eu(III) phthalate complex into the PNIPAM shell was found

Dr. Y. N. Jiang, Dr. X. D. Yang, Dr. C. Ma, Dr. C. X. Wang, Dr. H. Li, Prof. F. X. Dong, X. M. Zhai, Prof. Q. Lin, Prof. B. Yang  
State Key Laboratory of Supramolecular Structure and Materials  
College of Chemistry  
Jilin University  
Changchun 130012, P. R. China  
E-mail: linquan@jlu.edu.cn

Prof. K. Yu  
Stacie Institute for Molecular Sciences  
NRC Canada, Ottawa, ON K1A0R6, Canada  
E-mail: kui.yu@nrc.ca

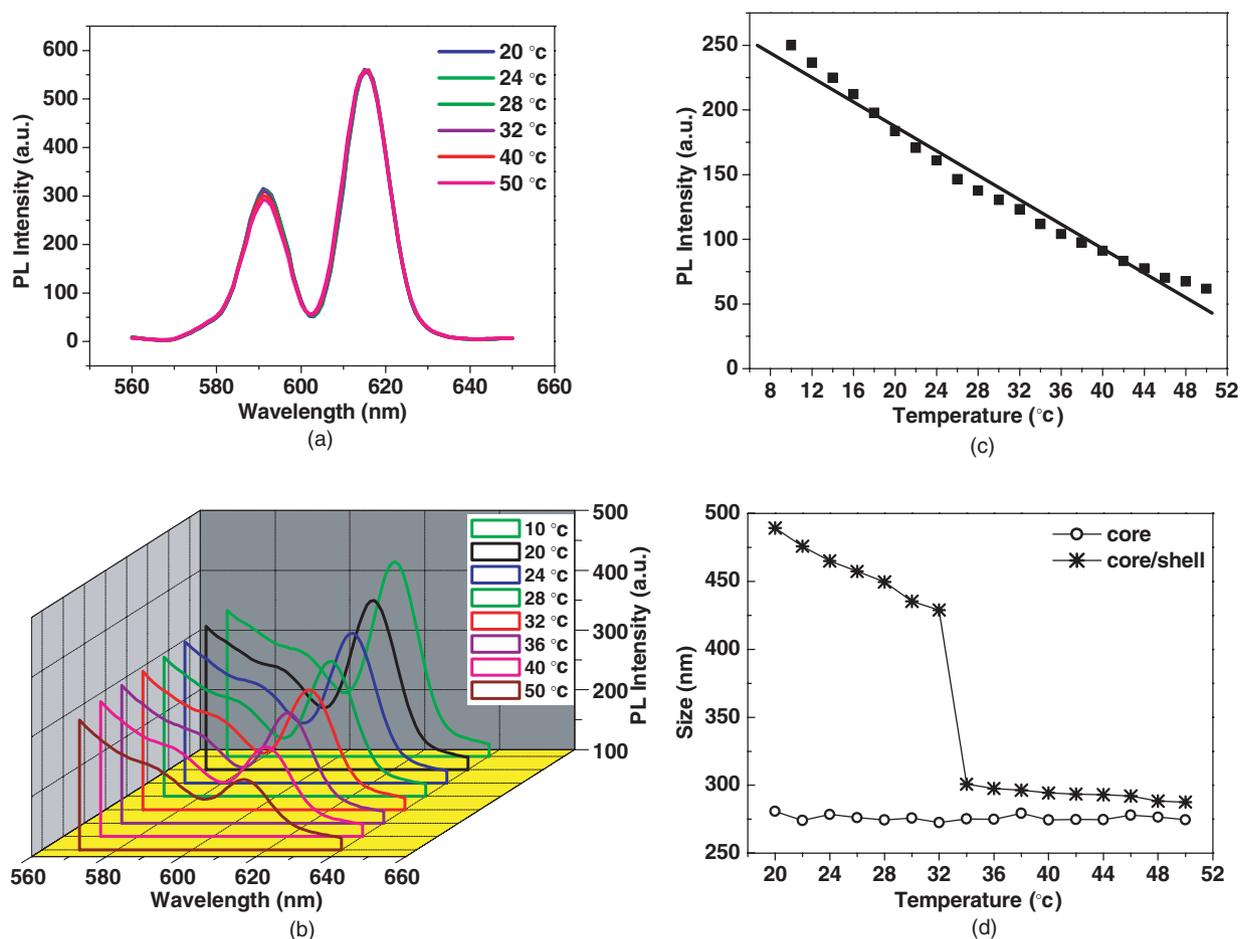
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**Scheme 1.** Schematic drawing of the synthetic route leading to the smart Eu-doped PS-co-PNIPAM/PNIPAM hydrogel nanoparticles exhibiting photoluminescence with linear and reversible thermoresponses.

to be essentially irreversible. It is necessary to point out that the coordination of Eu(III) and the amide bond of PNIPAM has been documented,<sup>[6]</sup> and our IR data are given in Figure S2 in the Supporting Information. Note that 30 °C was found to be an appropriate reaction temperature, at which hydrophilic PNIPAM chains swell without the presence of a coil-to-globule transition. Accordingly, the Eu(III) phthalate complex could be coordinated with the PNIPAM chains at different places. The Eu-doped PS-co-PNIPAM/PNIPAM nanoparticles prepared at  $\approx 25$  °C exhibited much lower PL than those prepared at  $\approx 30$  °C; the loading of the Eu complex was much less at  $\approx 25$  °C than that at  $\approx 30$  °C.

**Figure 1a** shows the PL spectra of an Eu(III) phthalate aqueous solution, acquired during an increase of the temperature. Obviously, the emission properties



**Figure 1.** PL spectra of a) Eu(III) phthalate and b) Eu-doped PS-co-PNIPAM/PNIPAM hydrogel nanoparticles in water, collected during the indicated increases in temperature ( $\lambda_{\text{ex}} = 395$  nm). c) Apparent linear relationship of the baseline-corrected PL intensity at  $\approx 614$  nm versus temperature; the concentration of the nanoparticles was  $\approx 0.26\%$  (by weight) and that of Eu(III) phthalate  $\approx 0.13\%$  (by the feed molar ratio of the Eu complex to shell monomer). d) DLS measurements of the core and Eu-doped PS-co-PNIPAM/PNIPAM nanoparticles in water, collected during the increase in temperature.

were not temperature sensitive. The Eu complex exhibits two emission peaks at  $\approx 590$  and  $\approx 615$  nm, with an intensity ratio of  $\approx 0.53$ .

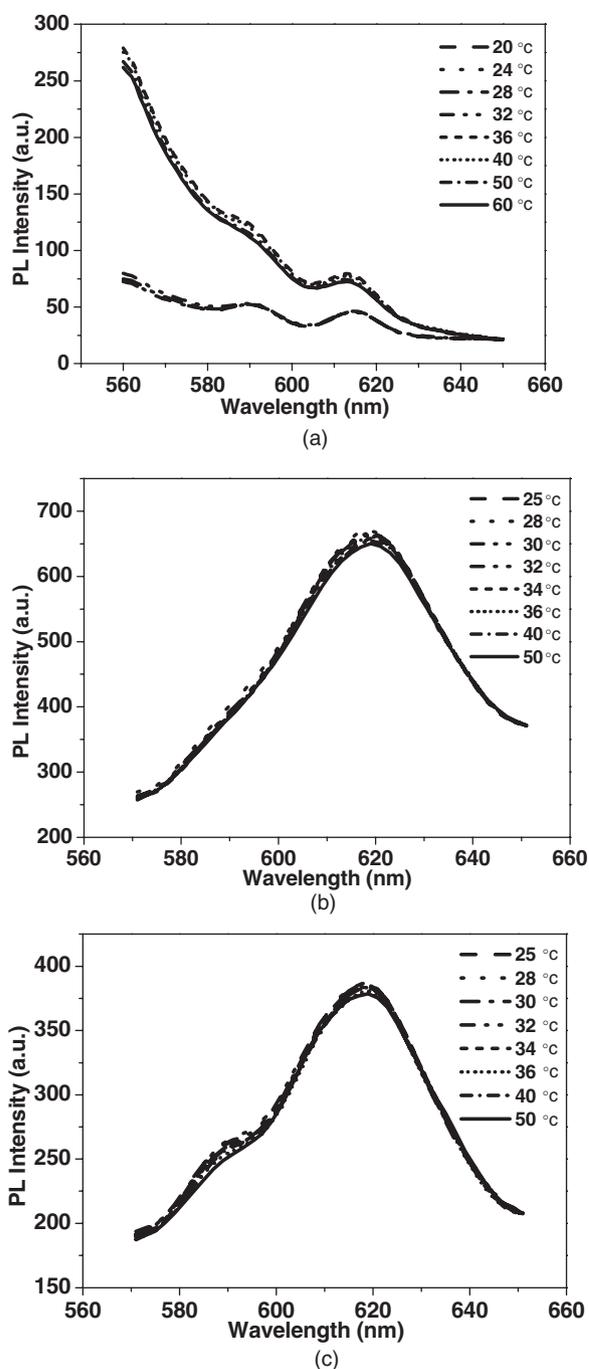
Figure 1b shows the PL spectra of an aqueous solution of the smart Eu-doped PS-*co*-PNIPAM/PNIPAM hydrogel nanoparticles, collected during an increase of the temperature. The two PL peak positions of the smart nanoparticles change little, but the intensity ratio changes to  $\approx 0.12$ . Here, the baseline-corrected PL intensity is dealt with. It is interesting that the PL intensity decreased gradually when the temperature was increased from 10 to 50 °C. Careful analysis shows that the intensity change of the emission at  $\approx 614$  nm exhibited a linear relationship (Figure 1c).

Evidently, Figure 1c shows a linear relationship of the thermoresponsive PL intensity. Therefore, our Eu-doped PS-*co*-PNIPAM/PNIPAM hydrogel nanoparticles exhibit completely different thermoresponsive PL from that of the previously reported PNIPAM-based hydrogels. The latter presented either a sudden increase or a sudden decrease of their PL around the LCST.<sup>[2,3,6]</sup> Each PL spectrum collected with a 2 °C increase from 10 to 50 °C is presented in Figure S3 in the Supporting Information.

To understand the change of the PL intensity, dynamic light scattering (DLS) was used to examine the sizes of the PS-*co*-PNIPAM core and Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles in water during the increase in temperature from 20 to 50 °C. Apparently, as shown in Figure 1d, there was little change in the size of the core nanoparticles but a decrease in the size of the Eu-doped core/shell nanoparticles. In particular, a significant decrease in the hydrodynamic size of the Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles took place when the temperature was changed from 32 to 34 °C. Such a decrease can be easily understood by the phase transition of the PNIPAM shell. Surprisingly, no precipitation was observed for both the core and Eu-doped core/shell emulsions (Figure S4, Supporting Information), under the conditions of pH 7 with NaCl 0 mM. Also, see the Supporting Information (Figure S4) for the absence or presence of precipitation observed for both the core and Eu-doped core/shell emulsions under different conditions, namely pH 11 with NaCl 0 mM and pH 7 with NaCl 200 mM.

Accordingly, it is easy to understand that for one Eu-doped PS-*co*-PNIPAM/PNIPAM microsphere during the increase of temperature, the Eu(III) phthalate loaded on the PNIPAM chains became closer and closer, thus leading to the decrease of the emission intensity. It is our core/shell structure design that results in such a sensitively linear thermoresponse of the emission intensity.

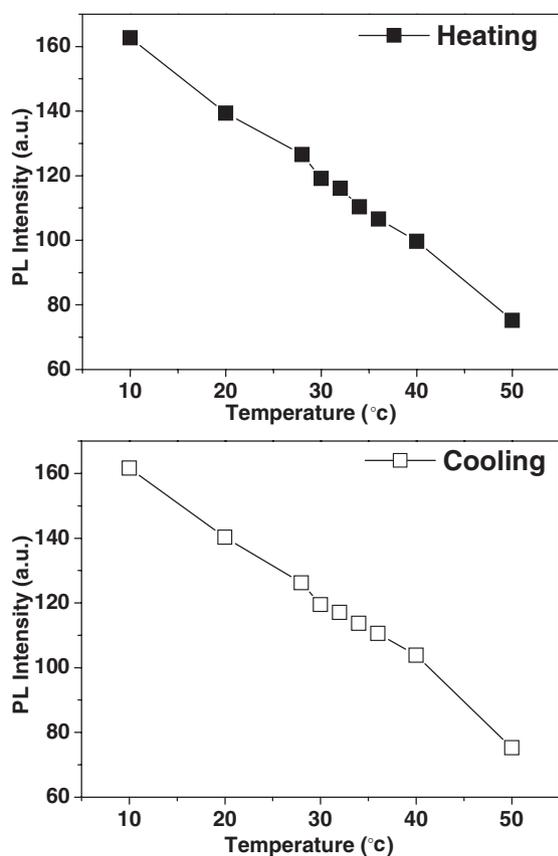
To confirm our understanding of the thermoresponsive PL of the core/shell structure, as shown in Figure 2, we investigated the thermoresponsive PL of linear PNIPAM polymers with Eu(III) phthalate coordinated (Figure 2a), PS-*co*-PNIPAM nanoparticles containing Eu(III) phthalate, which was introduced during the formation of the nanoparticles (Figure 2b), and PS-*co*-PNIPAM/PNIPAM core/shell nanoparticles with Eu(III) phthalate introduced during the synthesis of the core (Figure 2c). A sudden change of the PL was observed for the aqueous solution in Figure 2a when the temperature was increased from 32 to 36 °C, which indicated



**Figure 2.** PL spectra of aqueous solutions of: a) linear PNIPAM with Eu(III) phthalate coordinated; b) PS-*co*-PNIPAM nanoparticles with Eu(III) phthalate encapsulated, which was introduced into the nanoparticles during the polymerization; and c) PS-*co*-PNIPAM/PNIPAM core/shell nanoparticles with Eu(III) phthalate encapsulated in the core.

that a phase transition took place. For this solution, little PL change was observed in the two temperature windows of 20 to 32 °C and 36 to 60 °C. More interestingly, there was little PL change for the solutions shown in Figure 2b,c during the temperature change from 25 to 50 °C.

Finally, we would like to point out that the photoluminescent thermoresponse of our core/shell structure is repeatable and reversible according to the increase and/or decrease of



**Figure 3.** PL intensity of the Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles in water, when the temperature was increased from 10 to 50 °C (top) and subsequently decreased from 50 to 10 °C (bottom). The PL intensity was obtained at  $\approx 614$  nm, with the excitation at 395 nm. The concentration of the nanoparticles was 0.26% (by weight) and that of Eu(III) phthalate  $\approx 0.06\%$  (by the feed molar ratio of the Eu complex to shell monomer).

temperature. One example is shown in **Figure 3**, in which the Eu-doped PS-*co*-PNIPAM/PNIPAM hydrogel nanoparticles were subjected to heating (top) and subsequent cooling (bottom). The change of the PL intensity of the hydrogels in water was fully autoreversible. The PL spectra are presented in Figure S5 in the Supporting Information. Also, see Figure S6 for another example of the autoreversible PL during multiple heating and cooling cycles. Such autoreversible PL as a result of the thermoresponse enables the Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles to have potential in various applications, such as PL thermometers, biosensors, and optical sensors.

In conclusion, we have successfully designed and synthesized smart hydrogels that exhibit linear and reversible photoluminescent thermoresponses in the temperature range of 10 to 50 °C. These thermosensitive photoluminescent hydrogels consist of Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles, and their unprecedented photoluminescent thermoresponse is different from that of previously reported PNIPAM-based photoluminescent hydrogels. Our novel core/shell hydrogels are excellent candidates as PL thermometers, and also have potential in applications such as optical sensing and biosensing. The present design and synthesis of

the photoluminescent PNIPAM-based hydrogels with reversible and linear thermoresponses bring insight into a universal approach to functional hydrogels with reversible and linear responses to external stimuli.

## Experimental Section

**Preparation of the PS-*co*-PNIPAM Cores:** The PS-*co*-PNIPAM nanoparticles were synthesized by emulsifier-free emulsion copolymerization. NIPAM ( $\approx 0.5$  g, 4.4 mmol; Acros) was dissolved in deionized water ( $\approx 15$  mL) in a 250-mL three-necked round-bottomed flask equipped with a stirrer, a condenser, and a nitrogen inlet. Afterward, styrene ( $\approx 5.0$  mL, 50.0 mmol) and deionized water ( $\approx 175$  mL) were added to the reaction flask. Under a  $N_2$  atmosphere, the mixture was stirred at room temperature for  $\approx 30$  min to remove oxygen, and the temperature was increased to 70 °C (and maintained for  $\approx 10$  min). An initiator solution of KPS ( $\approx 0.1$  g) in water ( $\approx 10$  mL) was swiftly injected into the reaction mixture. The reaction was allowed to proceed for  $\approx 8$  h (at 70 °C under  $N_2$  with stirring). The prepared PS-*co*-PNIPAM nanoparticles were purified three times by centrifugation and dispersion in deionized water. Note that the present study does not address the effect of the size of the core affecting the performance of the final photoluminescent core/shell hydrogels (see preliminary data shown in Figure S8, Supporting Information).

**Preparation of the PS-*co*-PNIPAM/PNIPAM Core/Shell Nanoparticles:** The PNIPAM shells were grafted on the purified PS-*co*-PNIPAM nanoparticles by seed polymerization. The purified PS-*co*-PNIPAM nanoparticles were dispersed in deionized water ( $\approx 185$  mL) in a 250-mL three-necked round-bottomed flask. NIPAM ( $\approx 4.5$  g, 39 mmol) was added to the reaction flask. Similarly, under a  $N_2$  atmosphere, the mixture was stirred at room temperature for  $\approx 30$  min to remove oxygen, and the temperature was increased to 70 °C (and maintained for  $\approx 10$  min). An initiator solution of KPS ( $\approx 0.1$  g in  $\approx 15$  mL water) was swiftly injected into the reaction mixture. The reaction was allowed to proceed for  $\approx 8$  h (at 70 °C under  $N_2$  with stirring). Again, the resulting PS-*co*-PNIPAM/PNIPAM hydrogel nanoparticles were purified three times by centrifugation and dispersion in deionized water. The purified core/shell nanoparticles were dispersed in  $\approx 200$  mL water, as a stock solution.

**Preparation of the Eu Complex:** The water-soluble europium organic complex Eu(III) phthalate was prepared via the reaction of  $EuCl_3$  ( $\approx 0.54$  g, 1.4 mmol) with phthalic acid ( $\approx 0.48$  g = 2.9 mmol) in water ( $\approx 10$  mL). The aqueous solution was kept at pH  $\approx 7-8$  by the dropwise addition of a NaOH solution ( $\approx 0.1$  M) under vigorous stirring. The reaction mixture was diluted to  $\approx 100$  mL, as a stock solution. For simplicity, the Eu complex obtained by the reaction of  $EuCl_3$  and phthalic acid in the present study is termed Eu(III) phthalate.

**Preparation of the Eu-Doped PS-*co*-PNIPAM/PNIPAM Hydrogel Nanoparticles:** Water-soluble Eu(III) phthalate ( $\approx 0.95$  mL stock solution) was mixed with the PS-*co*-PNIPAM/PNIPAM microspheres ( $\approx 10$  mL stock solution) in a 100-mL round-bottomed flask. The reaction mixture was stirred at 30 °C under  $N_2$  for 3 h. Finally, the prepared Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles were purified once by centrifugation. The purified Eu-doped PS-*co*-PNIPAM/PNIPAM nanoparticles were dispersed in  $\approx 25$  mL water, as a stock solution.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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