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A Luminescent Thermometer Based on Linearly Thermo-responsive Copolymer and Polyoxometalates

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Electronic Supplementary Information

Abstract A novel switchable luminescent thermometer based on thermo-responsive triblock copolymer poly(ethylene glycol)-*b*-poly(acrylamide-*co*-acrylonitrile-*co*-dimethylaminoethylmethacrylate) (PEO₁₁₃-*b*-P(AAm₂₆₄-*co*-AN₁₁₂-*co*-DMA₈)) and Eu-containing polyoxometalate (Eu-POM) was successfully constructed. The copolymer synthesized by RAFT exhibited a linear response to temperature variations in aqueous media, which was quite different from the uncharged copolymer P(AAm-*co*-AN) having a specific upper critical solution temperature (UCST). Eu-POM was surrounded around thermo-responsive blocks through electrostatic interactions, and its luminescence could be finely tuned due to the sensitivity of copolymer to the temperature variation. In cold water, POMs were trapped in highly hydrophobic cores, exhibiting an intense emission. With the upraising of temperature, the emission intensity presented a gradual decrease and showed a linear correlation with temperature. When the complex solution cooled down, the luminescence could also be perfectly restored. This temperature-luminescence correlation could be held for numerous trials, showing a potential application in thermometer.

Keywords Luminescent thermometer; Block copolymer; Polyoxometalate; UCST

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INTRODUCTION

Development of water-soluble smart polymeric materials that are sensitive to temperature has been a tremendous research topic in recent decades.^[1–4] Their smart nature stems from the switchable hydrophilic-hydrophobic properties under the perturbation of temperature, which makes them hold great potential of applications in both academic and industry.^[5,6] In contrast to the best known polymers exhibiting a lower critical solution temperature (LCST) behavior, far less attention has been paid to polymers with an upper critical solution temperature (UCST), which could undergo micelles dissociation/association upon alternative heating/cooling cycles. In principle, this phase transition with heating-enhanced solubility should be desirable for practical applications such as drug releases. In most cases, the documented UCST polymers were designed on basis of either ionic interaction or hydrogen bonding.^[7–13] Zwitterionic polymer featured with strong electrostatic interactions between anionic and cationic groups are the early examples to be found to display UCST behaviors.^[14] The attraction between the polymer

chains undergoes a sufficient shift at elevated temperature, resulting in better solubility in aqueous solution. However, the temperature-sensitive interactions are vulnerable to salts in solution, and dissociative ions would be preferentially attracted by zwitterionic polymer chains, which leads to a detention or loss of UCST properties and limits further applications in thermo-responsive systems.

Recently, Agarwal *et al.* made a notable contribution that uncharged random copolymers poly(acrylamide-*co*-acrylonitrile) (P(AAm-*co*-AN)) synthesized by free radical polymerization exhibited drastic UCST-type physical properties in water or electrolyte solution, and the cloud point could be tuned by varying the composition of monomers.^[15,16] Zhao *et al.* investigated three types of amphiphilic copolymer by coupling P(AAm-*co*-AN) block with polystyrene (PS), poly(dimethylacrylamide) (PDMA), or electrolyte polymers of poly(*N,N*-dimethylaminoethyl methacrylate) (PDMAEMA).^[17] The micelles formed in aqueous solution also showed diverse temperature-response with tunable UCSTs. Later on, they incorporated the electrolyte unit acrylic acid (AAc) or 4-vinylpyridine (4VP) into P(AAm-*co*-AN), and found that a small change in pH would lead to a large shift in phase transition temperature, which demonstrated a new UCST-type polymer-based approach for pH detection.^[18] Besides, amphiphilic copolymers PEG-P(AAm-*co*-AN) dis-

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playing a UCST phase transition could encapsulate hydrophobic drugs at low temperature and achieve a drug delivery upon heating.^[19,20] These researches surely would extend the application range of thermo-responsive polymers.

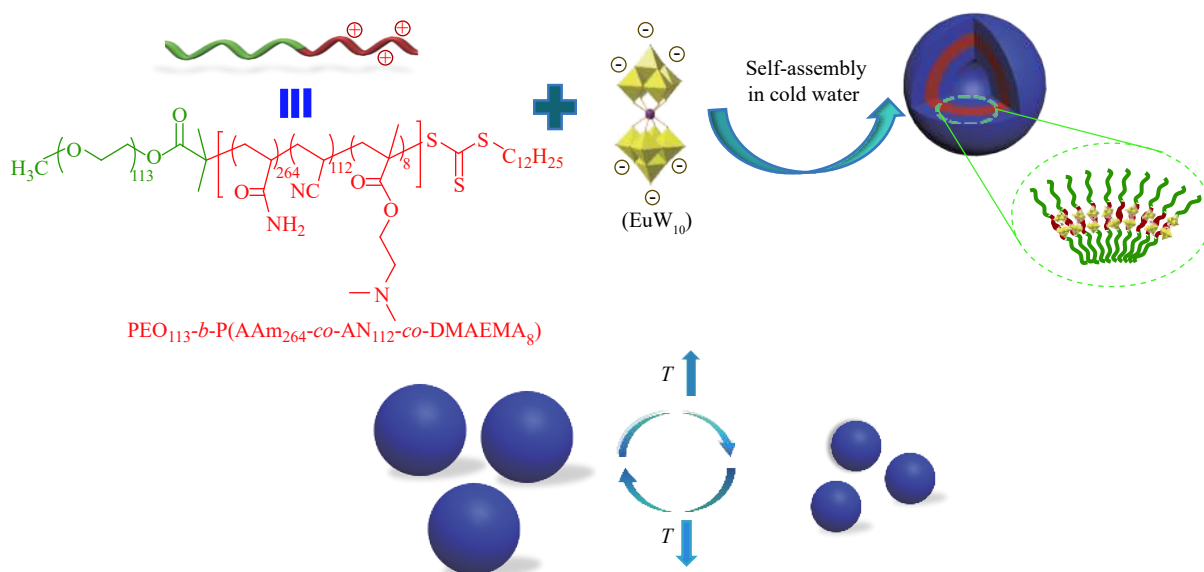
Polyoxometalates (POMs), as a class of discrete anionic transition metal oxide clusters, hold promising applications in the field of catalysis, electrooptics, and medicines.^[21–23] Luminescent lanthanide-containing POMs (Ln-POMs , $\text{Ln} = \text{Dy}, \text{Eu}$) have been systematically studied in our previous work by electrostatic assembly with stimuli-responsive copolymers. Acid or CO_2 was used to make the copolymer protonated, and as a result, the anionic POMs were encapsulated in hydrophobic coacervate core through the strong electrostatic attraction, leading to an enhancement in luminescence intensity. Moreover, the luminescence could also be restored by the addition of base or N_2 .^[24,25] As the UCST-type polymer is highly dehydrated in cold water, it would be a good candidate to encapsulate Ln-POM and provide a hydrophobic environment. Moreover, the hydrophobicity of the copolymer could be tuned by temperature variations, and thus a thermo-responsive luminescent hybrid system would be constructed by combination of the UCST-type copolymer and Ln-POMs , where POMs would be a good luminescent probe for sensing temperature changes. To the best of our knowledge, most polymeric thermo-responsive luminescence sensors were established by coupling sensitive molecules into LCST copolymer backbones.^[26–28] There has been hardly any report on modulating the luminescence of a dissociative molecule by applying inorganic-organic hybrids based on UCST copolymers.

In the present work, a novel temperature-dependent luminescent sensor was built by electrostatic co-assembly of the UCST-type copolymer $\text{PEO}_{113}\text{-}b\text{-P(AAm}_{264}\text{-co-AN}_{112}\text{-co-DMA}_8\text{)}$ and luminescent EuW_{10} (Scheme 1). The copolymer was successfully synthesized by RAFT with AAm and AN serving as the thermo-responsive segments and DMA being

employed as a weak electrolyte to immobilize POMs. Unexpectedly, both the copolymer and the hybrid complex in aqueous solution displayed a linear response when monitoring transmittance as a function of temperature, which is quite different from the case of classic P(AAm-co-AN) with a specific phase transition temperature UCST. The luminescence intensity of the hybrid complex was dramatically enhanced in cold water and gradually decreased with up-raising temperature. As the temperature was recovered, the luminescence could also be perfectly restored, which indicated a good reversed thermo-sensitivity upon heating/cooling cycles.

RESULTS AND DISCUSSION

The UCST-type copolymer $\text{PEO}_{113}\text{-}b\text{-P(AAm}_{264}\text{-co-AN}_{112}\text{-co-DMA}_8\text{)}$ was synthesized and characterized according to the literature,^[17] and details were presented in the electronic supplementary information (ESI). The copolymers P(AAm-co-AN) have been reported to have a sharp UCST in water behavior, and the phase transition temperature could be tuned by varying the composition of monomers. However, with the monomer DMA incorporated into the polymerization, a copolymer with unique thermo-responsive property was obtained. In order to clearly investigate the phase transition behavior, UV-Vis transmittance spectra of the copolymer aqueous solution at 550 nm were tracked. As illustrated in Fig. 1, with the upraising temperature from 5 °C to 55 °C, the transmittance of $\text{PEO}_{113}\text{-}b\text{-P(AAm}_{264}\text{-co-AN}_{112}\text{-co-DMA}_8\text{)}$ copolymer solution increased linearly, which is quite different from the behavior of P(AAm-co-AN) copolymers reported.^[29] When the the solution was cooled down, its transmittance also decreased linearly. We have checked the turbidity variation of the polymer solutions in various concentrations. Similar to the thermal behavior of the solution at 5 $\text{mg}\cdot\text{mL}^{-1}$, the one with a higher concentration of $\sim 10 \text{ mg}\cdot\text{mL}^{-1}$ still exhibited obvious linear response to tempe-



Scheme 1 Schematic illustration of a novel temperature-dependent luminescent sensor based on UCST-type copolymer $\text{PEO}_{113}\text{-}b\text{-P(AAm}_{264}\text{-co-AN}_{112}\text{-co-DMA}_8\text{)}$ and luminescent EuW_{10} , and its thermal response to temperature variations

ture, while the one with a lower concentration of $\sim 1 \text{ mg} \cdot \text{mL}^{-1}$ displayed certain change with temperature as well (Fig. S2 in ESI). The UCST behavior of P(AAm-co-AN) was based on hydrophobic interactions and hydrogen bonding between polymer chains. When a few charged DMA units were incorporated into the polymer backbone, the UCST phenomenon may be brought down to a level that is unobservable. Under such a circumstance, with the insertion of weak electrolyte DMA into PEO₁₁₃-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈), the interactions between polymer chains were partially interrupted, resulting in a dull response to temperature. Similarly, PEO₁₁₃-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex solution displayed nearly the same thermo-responsive pattern in one heating and cooling cycle with a slight hysteresis in cooling process. Addition of EuW₁₀ did not exert obvious effect on the thermo-responsive properties of the copolymers.

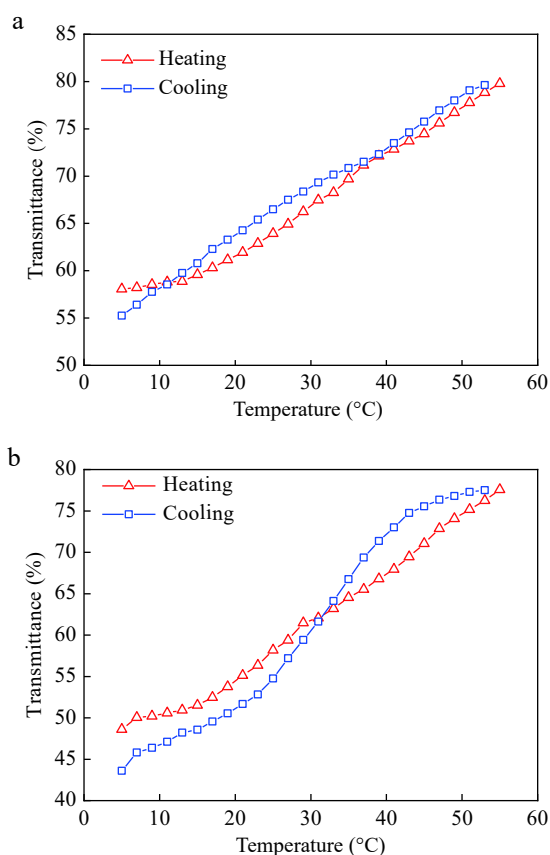


Fig. 1 Turbidity curves of (a) PEO₁₁₄-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈) and (b) PEO₁₁₄-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex in aqueous solution ($c_{\text{copolymer}} = 5 \text{ mg} \cdot \text{mL}^{-1}$, $c_{\text{EuW}_{10}} = 0.3 \text{ mg} \cdot \text{mL}^{-1}$)

Transmission electron microscopy (TEM) and dynamic light scattering (DLS) measurements upon heating and cooling were performed to investigate the co-assembly behavior of PEO₁₁₃-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ in solution. At low temperature, vesicles were formed in solution with an average diameter of 255 nm as revealed by TEM images in Fig. 2(a). Real-time dynamic light scattering was then used to track the variations in aggregates size as a func-

tion of temperature. As the copolymer/EuW₁₀ complex solution was heated from 5 °C to 55 °C, the hydrodynamic radius (R_h) of aggregates manifested a continuous decrease from 135 nm to 55 nm (Fig. 2b). Since the copolymer became more hydrophilic and the electrostatic interaction between polymer chains and EuW₁₀ was gradually weakened during the heating process, as a consequence, a decrease in aggregates size was observed. The micelles still existed in hot water as the complex solution was not completely transparent. With the temperature alternatively changed between 35 and 5 °C, R_h could be restored, displaying reversible dissociation/association of vesicles.

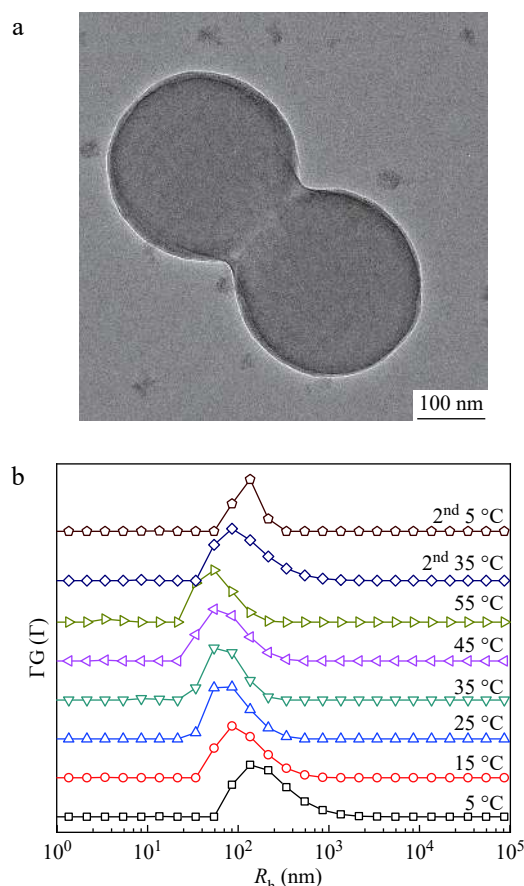


Fig. 2 (a) TEM images of PEO₁₁₄-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex at temperature of 5 °C; (b) Temperature-dependent DLS curves of PEO₁₁₄-*b*-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex in solution ($c_{\text{copolymer}} = 1.63 \text{ mg} \cdot \text{mL}^{-1}$, $c_{\text{EuW}_{10}} = 0.1 \text{ mg} \cdot \text{mL}^{-1}$)

The luminescence intensity of anionic EuW₁₀ would be greatly enhanced by electrostatic co-assembly with the cationic copolymers into core-shell micelles or vesicles according to our previous work.^[24,25,30] In the current work, due to the high hydrophobicity of the thermo-responsive copolymer at low temperature, it is inferred that the copolymer would provide enough hydrophobic surroundings for EuW₁₀ and the weak electrolyte DMA in copolymer could immobilize EuW₁₀ to co-assemble into vesicles. As demonstrated in Fig. 3(a) and Fig. S3(a) (in ESI), compared with original EuW₁₀, the luminescent intensity of the complex solution

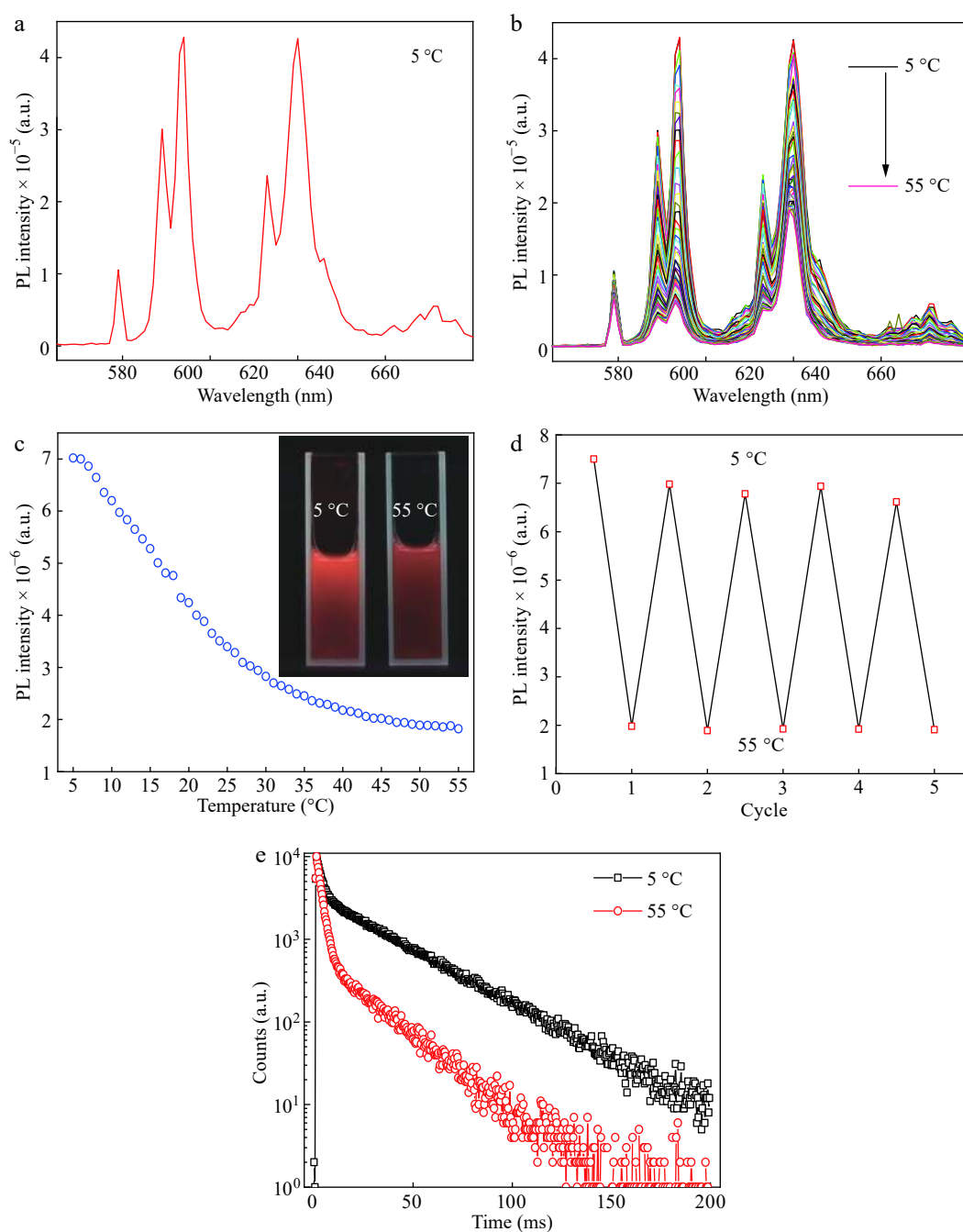


Fig. 3 (a) Fluorescent spectra of PEO₁₁₄-b-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex in cold water at 5 °C; (b) Temperature-dependent luminescence spectra of PEO₁₁₄-b-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex solution; (c) Total integral PL intensity of PEO₁₁₄-b-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex solution (Inset was the photograph of luminescent complex solution at 5 and 55 °C, respectively); (d) Reversible switch of the luminescence intensity of PEO₁₁₄-b-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex by alternating heating/cooling treatment; (e) Decay curves of PEO₁₁₄-b-P(AAm₂₆₄-co-AN₁₁₂-co-DMA₈)/EuW₁₀ complex at 5 and 55 °C ($\lambda_{\text{ex}} = 254 \text{ nm}$, $c_{\text{copolymer}} = 1.62 \text{ mg} \cdot \text{mL}^{-1}$, $c_{\text{EuW}_{10}} = 0.1 \text{ mg} \cdot \text{mL}^{-1}$)

was greatly enhanced in cold water. The integration ratio of two characteristic peaks $I_{4F9/2 \rightarrow 6H_{13/2}}/I_{4F9/2 \rightarrow 6H_{15/2}}$ was calculated to be 1.50, which is comparable with that of EuW₁₀ in solid state, indicating the luminescent EuW₁₀ was successfully located in hydrophobic cores.^[31,32] Temperature variable luminescence of the complex solution was also recorded in Figs. 3(b) and 3(c). With temperature rising up from 5 °C to 55 °C, a dramatic decrease in PL intensity was ob-

served. The emissive color of complex solution changed from bright to dark red. Interestingly, the profile of emissive intensity as a function of temperature could be divided into two different patterns. At the first stage of temperature from 5 °C to 35 °C, the decreasing rate was relatively fast and linear. However, in the stage from 35 °C to 55 °C, it became much lower but still kept in line, probably due to the sensitivity of luminescence to the copolymer thermal behavior. As

shown in Fig. 1(b), the changing rate of turbidity decreased in the high temperature range, especially in cooling process, which slowed down the declining rate of luminescence intensity. The absolute quantum yields were also characterized to descend from 1.61% to 0.45%. Meanwhile, the decay lifetime was largely shortened (Fig. 3e) with the long lifetime decaying from 3.3 ms (88.4%) to 2.2 ms (49.0%). Besides, due to the invertible phase transition of copolymer in response to temperature, the photoluminescent thermoresponse of the complex could be numerous repeated (Fig. 3d), which endows this complex with potentials in various applications, such as PL thermometer and optical sensors.

To better understand the mechanism of luminescent chromism of the complex on temperature, a series of control experiments were performed. For the original EuW₁₀ solution in Fig. S3(a) (in ESI), the temperature change showed negligible impact on its luminescence. When mixing EuW₁₀ with copolymer PEO-*b*-P(AAm-*co*-AN), the luminescence intensity could be enhanced to some extent, and also decreased gradually with the upraising temperature (Fig. S3b in ESI).

However, the intensity changes provided by the copolymer PEO-*b*-P(AAm-*co*-AN) were hardly comparable to that of PEO₁₁₄-*b*-P(AAm₂₆₄-*co*-AN₁₁₂-*co*-DMA₈), indicating that the introduction of DMA to immobilize EuW₁₀ around the UCST-type copolymer was absolutely necessary. Taking all these results into consideration, we suggested that both DMA and AAm-*co*-AN made their contributions, *i.e.* the weak electrolyte DMA caught the luminescent EuW₁₀ and temperature-sensitive segments AAm-*co*-AN afforded the hydrophobic surroundings. As EuW₁₀ was located in the dense cores of vesicles, the water bound to Eu³⁺ would be expelled out, giving rise to great enhancement of photoluminescence intensity. Along with the upraising temperature, the hydrophobicity effect provided by the copolymer on EuW₁₀ was weakened, and consequently EuW₁₀ was exposed to water, leading to the decrease of luminescent intensity.

To explore the possibility of complex in practical application as a thermometer, the dynamic range of the sensitivity of luminescence intensity to temperature was detected. As we can see in Fig. 3(c), the decreasing curve of total PL intensity is relatively linear in the temperature range from 5 °C to 35 °C. Hereby, *in situ* luminescence detection was repeated for three times at this heating stage. Surprisingly, the PL intensity fluctuation of complex was quite narrow, and the total PL intensity at each temperature point could be linearly fitted with a correlation coefficient of 0.99 (Fig. 4). This high sensitivity surely would make the thermo-responsive luminescent complex a good candidate for application as sensors.

CONCLUSIONS

In this work, we have successfully constructed a hybrid luminescent thermal sensor by mixing thermo-responsive copolymer PEO₁₁₄-*b*-P(AAm₂₆₄-*co*-AN₁₁₂-*co*-DMA₈) with EuW₁₀. The copolymer showed an unexpectedly linear response to temperature upon cycled heating and cooling. Benefitted from both electrostatic interaction and hydrophobicity provided by the copolymer in cold water, EuW₁₀

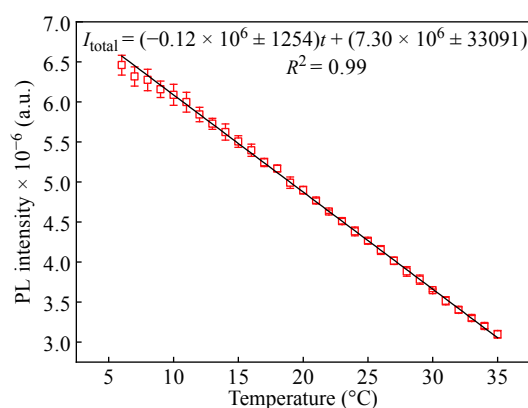


Fig. 4 PL intensity with error bar of PEO₁₁₄-*b*-P(AAm₂₆₄-*co*-AN₁₁₂-*co*-DMA₈)/EuW₁₀ complex in the temperature range from 5 °C to 35 °C. Insert was the linearly fitted equation for the PL intensity of PEO₁₁₄-*b*-P(AAm₂₆₄-*co*-AN₁₁₂-*co*-DMA₈)/EuW₁₀ complex ($c_{\text{copolymer}} = 1.62 \text{ mg} \cdot \text{mL}^{-1}$, $c_{\text{EuW}_{10}} = 0.1 \text{ mg} \cdot \text{mL}^{-1}$)

was restricted in highly hydrophobic cores, leading to a dramatic enhancement in luminescence intensity. With an increase of temperature, the hydrophobic interaction provided by the copolymer was gradually weakened, and a decrease in emission was clearly observed. As the temperature was lowered, the luminescence could also be reversibly restored. Furthermore, this luminescence-temperature correlation between 5 and 35 °C could be linearly repeated, which suggested a good promising application in thermometer or sensors.

Electronic Supplementary Information

Electronic supplementary information (ESI), which includes the experimental section, is available free of charge in the online version of this article at [10.1007/s10118-019-2287-z](https://doi.org/10.1007/s10118-019-2287-z).

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