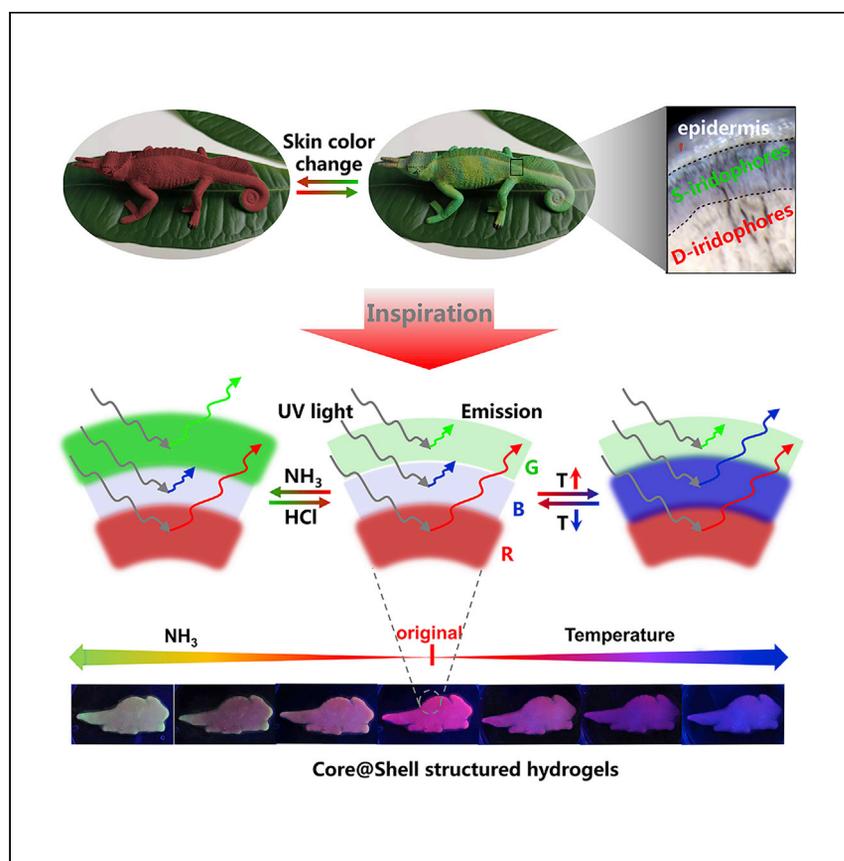


Article

A panther chameleon skin-inspired core@shell supramolecular hydrogel with spatially organized multi-luminogens enables programmable color change



Inspired by the core@shell structure of natural chameleon skin, Lu et al. report fabrication of responsive core@shell-structured multi-luminogen hydrogels that display programmable emission color changes and desirable excitation wavelength-dependent emission properties. This opens the possibility of utilizing a bioinspired core@shell structure to develop multi-color fluorescent systems with promising applications, such as sensing and anti-counterfeiting.

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Highlights

Core@shell-structured hydrogels with spatially organized multi-luminogens are fabricated

Multiresponsive wide emission color tunability is achieved

Potential uses for sensing and anti-counterfeiting are demonstrated

Article

A panther chameleon skin-inspired core@shell supramolecular hydrogel with spatially organized multi-luminogens enables programmable color change

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SUMMARY

Organization of different iridophores into a core@shell structure constitutes an evolutionary novelty for panther chameleons that allows their skins to display diverse color change. Inspired by this natural color-changing design, we present a responsive core@shell-structured multi-luminogen supramolecular hydrogel system that generates a programmable multi-color fluorescent change. Specifically, red Eu^{3+} -amidopicolinate (R) luminogen is incorporated into the core hydrogel, while blue naphthalimide (B) and green perylene-tetracarboxylic acid (G) luminogens are grown into two supramolecular shell hydrogels. The intensities of G/B luminogens could then be controlled independently, which enables its emission color to be programmed easily from red to blue or green, nearly covering the full visible spectrum. Because of the differential excitation energies between these luminogens, a desirable excitation wavelength-dependent fluorescence is also achieved. Colorful materials with a patterned core@shell structure are also demonstrated for anti-counterfeiting, opening up the possibility of utilizing a bio-inspired core@shell structure to develop an efficient multi-color fluorescent system with versatile uses.

INTRODUCTION

Soft multicolor material systems capable of emitting differently colored fluorescence and light upon stimulation play important roles in promising applications, such as stretchable electronics, dynamic camouflaging robots, sensing, and anti-counterfeiting.^{1–9} To construct these color-changing soft materials, a convenient design is to simultaneously incorporate two or more responsive luminogens (e.g., metal complexes,^{10–14} nanoparticles,^{15–17} or organic fluorophores^{18–38}) that can alter the overlap of their fluorescence spectra in response to external stimuli in a controllable way into one single elastomer/hydrogel matrix. On the other hand, animals have a drastically different structure design that enables their soft skins to display dazzling colors or fluorescence. One of the most famous examples is the panther chameleon, which has amazing control over its skin colors for camouflage, mood expression, or thermoregulation upon environmental changes. As reported previously,³⁹ panther chameleon skin consists of two thick layers of iridophore cells, S-iridophores and D-iridophores, that are assembled into a core@shell structure (Figures 1A and 1B).⁴⁰ The key feature of this core@shell design is that guanine nanocrystals of different sizes and shapes are organized spatially into these two distinct layers, which can exhibit an efficient optical functional synergy through independent tuning of the lattice of these guanine nanocrystals upon environmental stimuli. As a result,

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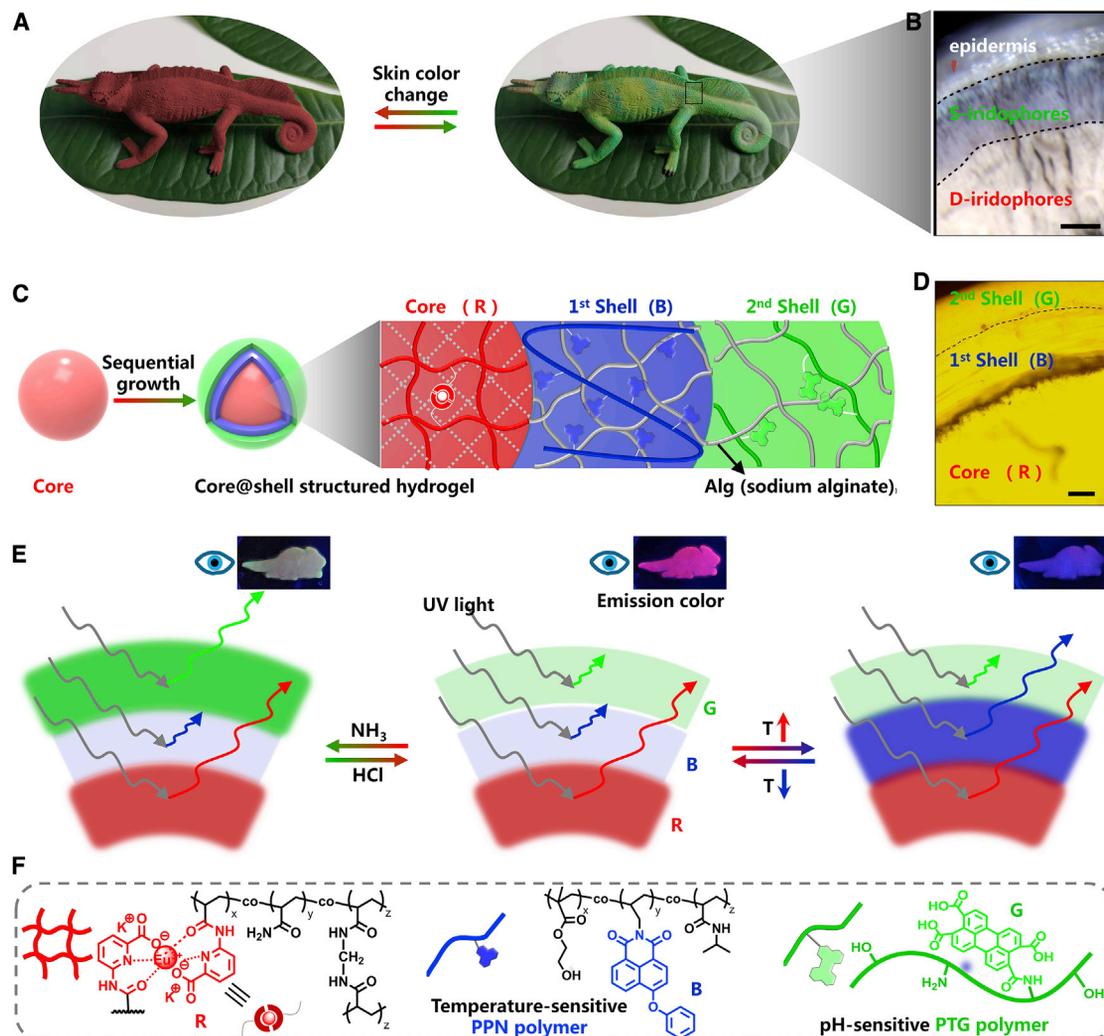


Figure 1. Biological inspiration and multicolor material system design

(A) The reversible skin color change process of a real chameleon.

(B) Cross-section image of panther chameleon skin (reproduced from Teyssier et al.³⁹).

(C) Illustration showing the core@shell-structured multicolor fluorescent polymeric hydrogel, which was prepared by sequential growth from a red fluorescent core hydrogel. In this core@shell structure, R/G/B luminogens are organized spatially into different hydrogel layers.

(D) Optical micrograph of the core@shell-structured hydrogel sample.

(E) Illustrations showing the mechanism for temperature/pH-responsive fluorescence color change of the core@shell-structured hydrogel sample.

(F) Chemical structures of the materials.

complex and rapid skin color changes of panther chameleons are usually observed during social interactions (e.g., male contests or courtship). Inspired by this biological architecture, we wanted to find out whether it is possible to mimic this unique core@shell structure in artificial color-changing materials where different luminogens are organized spatially into different core and shell layers. Such a novel core@shell layout is believed to not only allow a wide choice of luminogens without the necessity to consider their compatibility in one single matrix but also mostly eliminate the complex photophysical processes (e.g., resonance energy transfer, excimer emission, and especially concentration quenching of fluorescence) that are highly dependent on the separation distance between different luminogens.^{41–44} Moreover, this unique design is also favorable for continuously regulating the intensity of each luminogen by varying its concentration or using external stimuli. These

advantages are essential for development of robust panther chameleon skin-like artificial multicolor materials with programmable diverse color changes, especially those whose fluorescence color could be adjusted to nearly cover the full visible spectrum. In addition to improved material properties, this bio-inspired core@shell design is also appealing from an economic point of view because a precious luminogen-doped shell can be coated over an inexpensive core to reduce the consumption of expensive luminogens compared with a preparation of the same amount of a homogeneous material.

To prove this hypothesis, here we report a unique multi-luminogen supramolecular hydrogel system with programmable diverse color changes in which different red/green/blue (R/G/B) luminogens are organized spatially into the chameleon-inspired core@shell structure. The system we developed is based on supramolecular fluorescent polymeric hydrogels because polymeric hydrogels, as highly water-swollen quasi-solids, feature a unique tissue-like modulus, intrinsic soft wet nature, and usually good biocompatibility.^{45–64} Consequently, soft wet polymeric hydrogels with color-changing features are very similar to natural systems such as chameleon skins. Moreover, introduction of multicolor fluorescence moieties into smart polymeric hydrogels has the potential to integrate the merits of hydrogels and fluorescent materials and, hence, enable promising applications such as chemosensors, anti-counterfeiting, or soft actuators/robotics.⁶⁵

To fabricate a supramolecular core@shell structure, we propose to sequentially grow the conformal blue and green fluorescent hydrogel shells onto a red fluorescent core hydrogel. As shown in Figures 1C, 1D, and 1F, the red fluorescent Eu^{3+} -amidopicolinate complex (R) was chosen as the luminogen to functionalize the core hydrogel because of its bright fluorescence and high emission stability. The aggregation-induced emissive (AIE) blue naphthalimide (B) luminogen is grafted to a thermo-responsive poly(4-phenoxy-N-allyl-1,8-naphthalimide-co-N-isopropyl acrylamide-co-hydroxyethyl methacrylate) (PPN) polymer in the first shell layer, and the pH-sensitive green perylene tetracarboxylic acid (G)-grafted gelatin (PTG) polymer is organized into the second shell layer. In this biomimetic core@shell structure, each luminogen is incorporated separately into a different layer, which is the key difference from the previously reported multicolor hydrogels that are prepared by simultaneous introduction of multiple luminogens into one homogeneous matrix.^{12,13,23,24,65} Because of this unique supramolecular core@shell layout, the fluorescence intensity of B/G luminogens can be regulated independently by varying their concentrations in the shell hydrogels or utilizing temperature or pH variations by external stimulation while avoiding complex photophysical interactions. As a consequence, the fluorescence color of the prepared chameleon-shaped core@shell hydrogels can be programmed easily from red to green/blue in response to pH/temperature stimuli (Figure 1E), nearly covering the full visible spectrum. Additionally, highly promising but difficult-to-realize excitation wavelength-dependent fluorescence color change was achieved because of the differential excitation energies between the red luminogen and green/blue luminogens. On the basis of these promising properties, their potential for producing colorful materials with a patterned core@shell structure for anti-counterfeiting are explored.

RESULTS

Growth of the core@shell-structured supramolecular hydrogel system

The key step for preparing chameleon-inspired multi-luminogen supramolecular hydrogel system is fabrication of core@shell polymer structures. Figures 2A–2C depicts the preparation procedure, which is inspired by the inside-out growth type

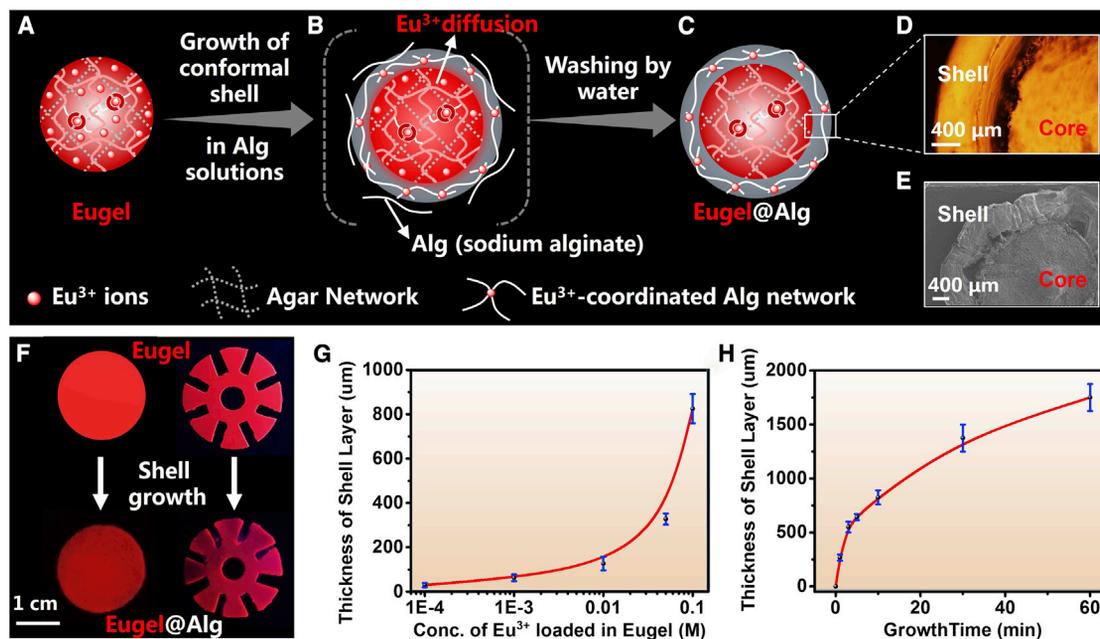


Figure 2. Fabrication of Eugel@Alg hydrogels

(A) First the Eu³⁺-loaded core hydrogel (Eugel) is prepared. The core gel is then incubated in aqueous solutions of sodium alginate (Alg). (B and C) During this time, Eu³⁺ gradually diffuses outward to form a crosslinked Alg polymer hydrogel shell around the core gel (B), resulting in core@shell-structured Eugel@Alg hydrogels (C). (D) Optical micrograph of the Eugel@Alg hydrogel sample. (E) SEM image of a freeze-dried Eugel@Alg sample. (F) Photos of Eugel@Alg hydrogel samples prepared from regularly and irregularly shaped Eugel (taken under a 254-nm UV lamp). (G) Shell layer thickness of Eugel@Alg as a function of Eu³⁺ concentration loaded in the core hydrogel under the given conditions (the concentration of the Alg solution is 2 wt %, and the growth time is 10 min). (H) Shell layer thickness of Eugel@Alg as a function of growth time under the given conditions (the concentration of the Alg solution is 2 wt %, and the Eu³⁺ concentration loaded in the core hydrogel is 0.1 M). The results and error bars were calculated according to three independent experiments.

of onions and eggs.⁴⁰ First, the red fluorescent core hydrogel (Eugel) was synthesized by radical polymerization of potassium 6-acrylamidopicolinate (K6APA), acrylamide (AAm), methylene bisacrylamide in the presence of agar polymer, followed by incubation in aqueous Eu³⁺ solutions (Figure S1). K6APA is a specially designed monomer bearing an amidopicolinate ligand that can efficiently chelate Eu³⁺ to form red fluorescent lanthanide complexes via an antenna effect.¹³ Because of its double network structure,⁵⁸ the core hydrogel has satisfying mechanical properties and can be cut into various shapes (e.g., a disk-like shape). The disk-shaped core hydrogel with a diameter of 20 mm (about 1-mm thickness) was then incubated in aqueous Eu³⁺ solutions of various concentration (~10⁻⁴–0.1 M) for at least 30 min. During this time, excess Eu³⁺ ions diffuse into the disk-shaped core hydrogel, in which not only the grafted picolinate ligands are chelated but free Eu³⁺ ions also coexist. In this way, the Eu³⁺-loaded Eugel was prepared (Figure 2A). Next, this Eugel was incubated in a growth solution consisting of an aqueous solution of sodium alginate (Alg), which is an ionic biopolymer bearing a high-density pendent carboxylate groups. Spontaneous diffusion of Eu³⁺ from the core hydrogel into the surrounding solution induces instant gelation of Alg via Eu³⁺-Alg complexation. As a consequence, a shell layer of cross-linked Alg polymer hydrogel was formed around the Eugel, resulting in a well-defined Eugel@Alg hydrogel. As shown in Figure 2B, the complexation-induced shell growth begins at the interface and advances in a radial direction outward because of the gradual outward diffusion of Eu³⁺ from

the core hydrogel. This type of growth is called a diffusion-induced interfacial polymerization process. When a layer of sufficient thickness is formed (*vide infra*), the Eugel@Alg hydrogel was taken out of the growth solution and washed with deionized water to remove any free Alg (Figure 2C). The distinct core@shell structure of the Eugel@Alg hydrogel that was grown in a confined geometry (as illustrated in Figure S2) was observed directly by microscope (Figure 2D) and characterized further by scanning electron microscopy (SEM) of a freeze-dried sample (Figure 2E). The core and shell layer have a porous structure, suggesting cross-linked polymer networks. The reason why the core and shell layers seems to be partially separated in this SEM image is that both hydrogel layers have largely differential volume shrinkage ratios in the freeze-drying process. The core-shell interaction is strong enough to bind these two hydrogel layers together because there are a high density of hydrogen bonds and metal coordination interactions between the polymer chains in the core and shell hydrogel layers. The grown shell layer appears to be quite similar for regularly and irregularly shaped core hydrogel samples (Figure 2F). The shell layer thickness can be controlled systematically by modulating the diffusion-induced interfacial polymerization kinetics. As summarized in Figures 2G and 2H, it was found that the shell thickness increased with increasing amounts of Eu^{3+} loaded in the core hydrogel, whereas prolonging the growth time enlarged the shell thickness up to 1,700 μm within 60 min. Note that the as-prepared core@shell hydrogels are brittle but very stable and cannot be dissolved in water solutions even after being immersed for 7 days (Figure S3) because the formed Eu^{3+} -Alg complexation crosslinks are quite stable under ambient conditions. Besides Eu^{3+} , many other metal ions were loaded into the core hydrogel to test the universality of the fabrication method. As shown in Figure S4, we found that various divalent/trivalent metal ions (Zn^{2+} , Ca^{2+} , Cu^{2+} , Fe^{3+} , and Al^{3+}) can be used to grow core@shell hydrogels because they all induce gelation of Alg via metal coordination interactions.

The two-luminogen supramolecular hydrogel systems

The adjustable shell thickness (~ 0 –1,700 μm), together with the conformal core@shell structure, makes the proposed diffusion-induced interfacial polymerization suitable for subsequent preparation of nearly arbitrarily shaped core@shell supramolecular multicolor hydrogels. To demonstrate these capabilities, we first considered preparation of core@shell hydrogels with a temperature-sensitive red-to-blue emission color response (Figure 3A) by employing mixed solutions of Alg (1 wt %) and PPN (~ 0.5 –5 mg/mL) as growth solutions to coat the red fluorescent core hydrogel (Eugel loaded with 0.1 M Eu^{3+}). In a typical experiment, the Eugel was placed into a mixed Alg/PPN solution for 10 min, during which Eu^{3+} diffused outward to crosslink Alg polymer chains to grow the hydrogel shell layer. The high-density O/N-containing groups along the PPN chain form plenty of hydrogel bonds with the crosslinked Alg network, distributing this AIE PPN homogeneously within the shell hydrogel. Figure 3B shows photos of the as-prepared Eugel@PPNx hydrogels (x denotes the PPN concentration in milligrams per milliliter in the Alg/PPN growth solutions) at 20°C (below LCST [lower critical solution temperature] of PPN). Because of the fluorescence spectrum overlap of the core and shell layers, the emission color of Eugel@PPNx hydrogels turns gradually from red to purplish red and then to blue with increasing PPN concentrations from 0.5–5 mg/mL under 254 nm UV illumination. As expected, all of these Eugel@PPNx hydrogels displayed a thermo-responsive fluorescence response (Figures 3B and S5). Among them, the Eugel@PPN2.5 sample displayed a distinct thermo-triggered “purplish red to blue” emission color change (Figures S6 and S7), which was purplish red fluorescent at 20°C but emitted blue light at 50°C. This was evidenced by their fluorescence spectra (Figure 3C), in which the broad blue emission band around 437 nm increased significantly, whereas the narrow red emission band

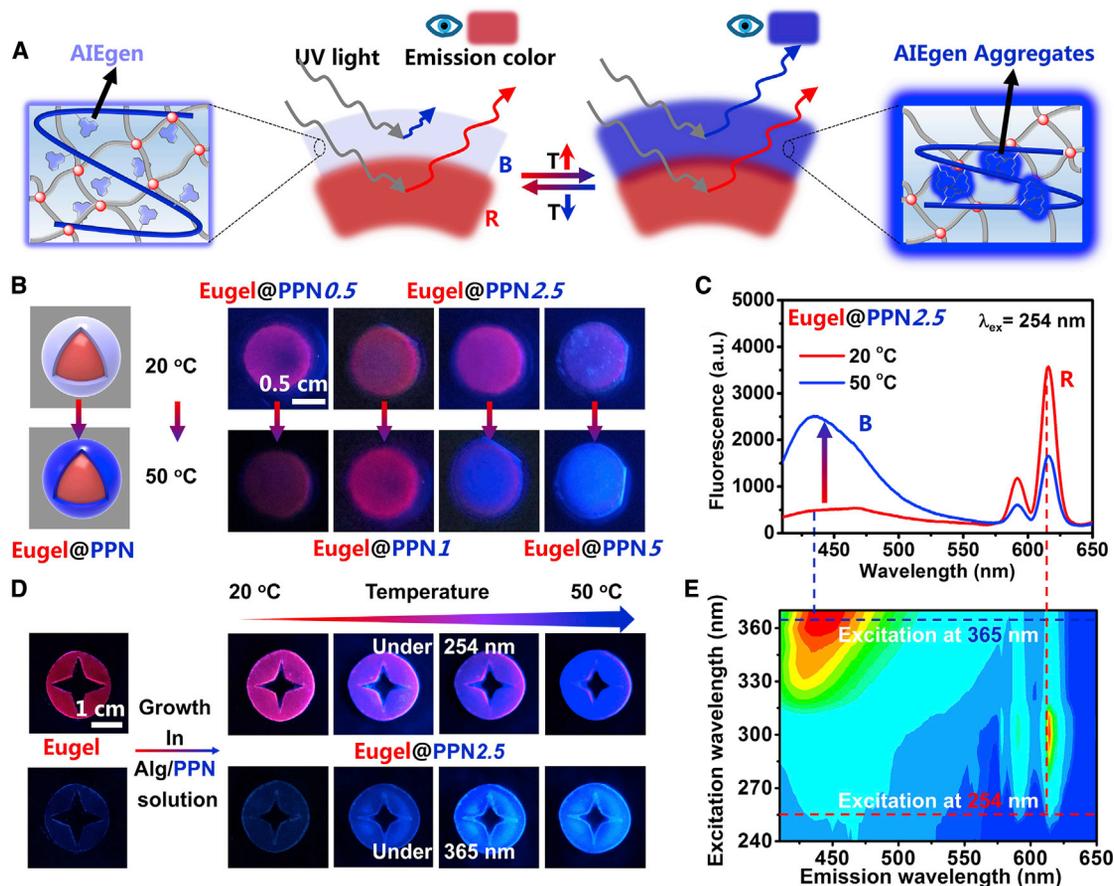


Figure 3. Study of the Eugel@PPN hydrogel

(A) Illustrations showing the mechanism of the thermo-responsive red-to-blue fluorescence color change of Eugel@PPN hydrogel.
 (B) Photos of Eugel@PPNx samples at 20°C and 50°C (taken under a 254-nm UV lamp), prepared by growth in various Alg/PPN growth solutions (x denotes the PPN concentration in the growth solutions).
 (C) Fluorescence spectra of Eugel@PPN2.5 recorded at 20°C and 50°C (excitation at 254 nm).
 (D) Photos of Eugel and Eugel@PPN2.5 in response to a temperature change from 20°C to 50°C.
 (E) Excitation fluorescence mapping of Eugel@PPN2.5 under ambient conditions (20°C).

centered at 617 nm declined in intensity. This interesting “purplish red to blue” fluorescence color change is ascribed to heat-induced heavier aggregation of the substituted naphthalimide AIEgens that are grafted into the thermo-responsive poly(N-isopropyl acrylamide),⁶⁶ which resulted in large blue emission enhancement of the PPN polymer at 50°C (above LCST of PPN polymer; Figure 3A).

Of particular interest, the highly appealing but rarely reported excitation wavelength-dependent emissive (Ex-De) property was also observed for our Eugel@PPNx hydrogels. As shown in Figure 3D, the as-prepared Eugel@PPN2.5 hydrogel was purplish red fluorescent under 254-nm illumination but emitted weak blue light under 365-nm illumination. Similar results were also noted for the Eugel@PPN1 hydrogel (Figure S5). To further investigate this interesting Ex-De phenomenon, the excitation fluorescence spectra of the Eugel@PPN2.5 hydrogel were recorded at room temperature (~20°C). As illustrated in Figures 3E and S8, it was found that the primary fluorescence band of Eugel@PPN2.5 around 617 nm was evident under an excitation wavelength of 254–320 nm but nearly disappeared when excited by UV light over 320 nm. Similar Ex-De performance was also observed for Eugel@PPN2.5

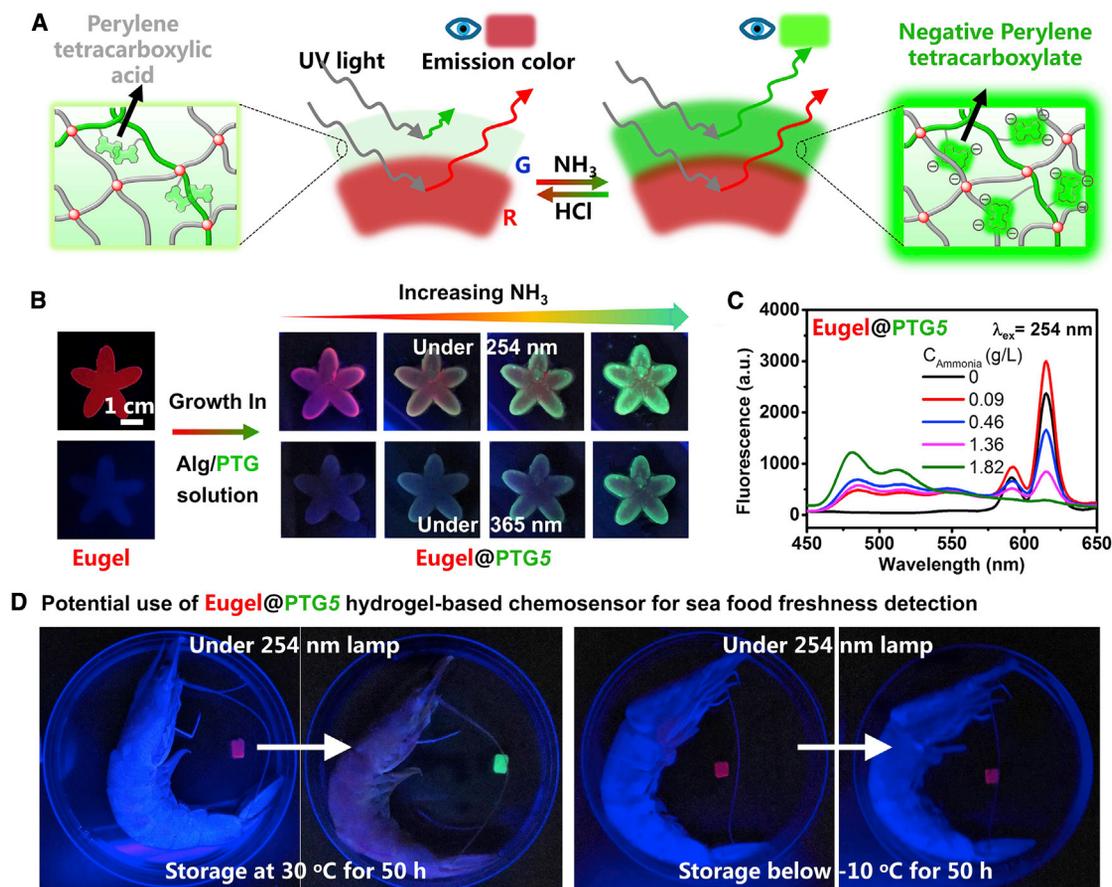


Figure 4. Study of Eugel@PTG hydrogels

(A) Illustrations showing the mechanism of NH_3 -triggered red-to-green fluorescence color change of Eugel@PTG hydrogels. (B and C) Photos of Eugel and Eugel@PTG5 in the presence of increasing NH_3 (B) and the corresponding fluorescence spectra (C) (excitation at 254 nm). (D) PL (photoluminescence) photographs of Eugel@PTG5-based chemosensors for amine vapors produced by shrimp stored at 30°C and -10°C for 50 h.

above LCST of PPN. Such a thermo-triggered emission color change and Ex-De response could be cycled because of the reversible phase transition behavior of the AIE-active PPN polymer in the shell layer (Figure S9). Such a unique Ex-De feature is believed to derive from different excitation energies of the blue and red luminogens, which are organized separately in the shell and core hydrogel. As reported in our previous work,⁶⁶ AIE-active naphthalimide dye has a primary absorption band around 365 nm and exhibits blue light emission when excited at 365 nm or higher-energy 254 nm UV light. In contrast, the Eugel core was only highly red-light-emitting when excited at 254 nm but nearly non-fluorescent under lower-energy 365-nm light excitation because the picolinate chromophore has only a small conjugation unit that has no absorbance band above 300 nm.¹³

Besides temperature-responsive Eugel@PPN, a pH-sensitive Eugel@PTG example (Figures 4A and 4B) was also prepared by placing the Eugel core hydrogel into the Alg/PTG solution for 10 min. During this time, Eu^{3+} diffused outward to crosslink Alg and PTG polymer chains as the shell hydrogel. To realize a pH-triggered red-to-green color change, the concentration of PTG polymer in the growth solution was optimized to be 5 mg/mL. As shown in Figure 4B, the optimized Eugel@PTG5 appeared red under 254 nm, but changed gradually to yellowish and then green upon exposure to NH_3 , which turned on the green fluorescence of the shell hydrogel by

reacting with the perylene tetracarboxylic acid luminogens to form highly fluorescent perylene tetracarboxylate moieties (Figure 4A). This distinct red-to-yellow-to-green fluorescence color change was consistent with the corresponding fluorescence spectra of Eugel@PTG5 in the presence of increasing NH_3 concentrations (Figure 4C). Because low-concentration NH_3 is sufficient to transform the perylene tetracarboxylic acid luminogens into the highly fluorescent perylene tetracarboxylate moieties, it is estimated that the fluorescence color change of Eugel@PTG5 will become visible when the pH of the core shell is above 9. Similar emission color changes were also observed for Eugel@PTG5 upon exposure to other basic compounds, such as Et_3N and NaOH (Figures S10 and S11). Moreover, because the green luminogens in the shell hydrogel can be excited by 365-nm or higher-energy 254-nm UV light,³⁸ an interesting excitation wavelength-dependent emission color change was also realized for Eugel@PTG (Figures 4B and S10–S12).

The obtained Eugel@PTG5 hydrogel, characterized by its hydrophilic matrix and the pH-sensitive emission color change, encouraged us to explore its potential use as a food spoilage chemosensor. As mentioned above, the red emission color of Eugel@PTG5 changed to green upon exposure to various amine vapors, accompanied by a ratiometric fluorescence intensity response. This result indicates the potential of Eugel@PTG5 to detect seafood freshness because biogenic volatile amine vapors (e.g., NH_3) from microbial growth are a well-known indicator of shrimp and fish spoilage.²⁵ Test stripes made of Eugel@PTG5 were sealed with fresh shrimp or fish in packing boxes and then stored at different temperatures for 50 h (Figures 4D and S13). It was found that the color change could be barely distinguished by the naked eye for the sample stored at low temperature (below -10°C), whereas a vivid red-to-green emission color change was observed for the sample stored at 30°C , indicating spoilage of the seafood.

A multi-luminogen supramolecular Eugel@PPN2.5@PTG5 system with programmed diverse color change

A more advanced core@dual-shell-structured supramolecular hydrogel system with a programmable diverse emission color change to cover nearly the full visible spectrum was demonstrated via proposed diffusion-induced interfacial polymerization. Figure 5A illustrates the synthetic procedure of Eugel@PPN2.5@PTG5, with Eu^{3+} -crosslinked Alg/PPN and Alg/PTG networks as the inner and outer hydrogel shell, respectively. In a typical experiment, a freshly prepared disk-shaped Eugel@PPN2.5 was first incubated in aqueous Eu^{3+} solutions to load Eu^{3+} in the first shell layer and then transferred into mixed solutions of Alg (1 wt %) and PTG (5 mg/mL) to grow the second shell hydrogel. This two-step growth process could be traced directly by microscopy (Figures 5B and S14), which clearly showed dual concentric hydrogel layers around the core. The SEM images (Figure 5C) suggest formation of a supramolecular cross-linked polymer network in the core and shell layers. Besides disk and rectangle shapes (Figure S15), conformal core@dual-shell samples were also prepared by starting from a core hydrogel with an irregular shape, such as inspired by a snowflake (Figure S16) or chameleon (Figure 5F). Because the B and G luminogens confined spatially in these two shells are sensitive to different triggers, the as-prepared Eugel@PPN2.5@PTG5 proved to be responsive to pH and temperature. Figure 5D depicts its fluorescence spectra in response to the subtle interplay of pH and temperature stimuli. In agreement with the fluorescence spectra, the as-prepared Eugel@PPN2.5@PTG5 hydrogel has a primary emission band around 617 nm and emits red light under 254-nm UV light irradiation. Nevertheless, upon increasing the temperature to 50°C , the broad emission band centered at 437 nm increased significantly (Figure S17A), triggering a noticeable red-to-blue emission color

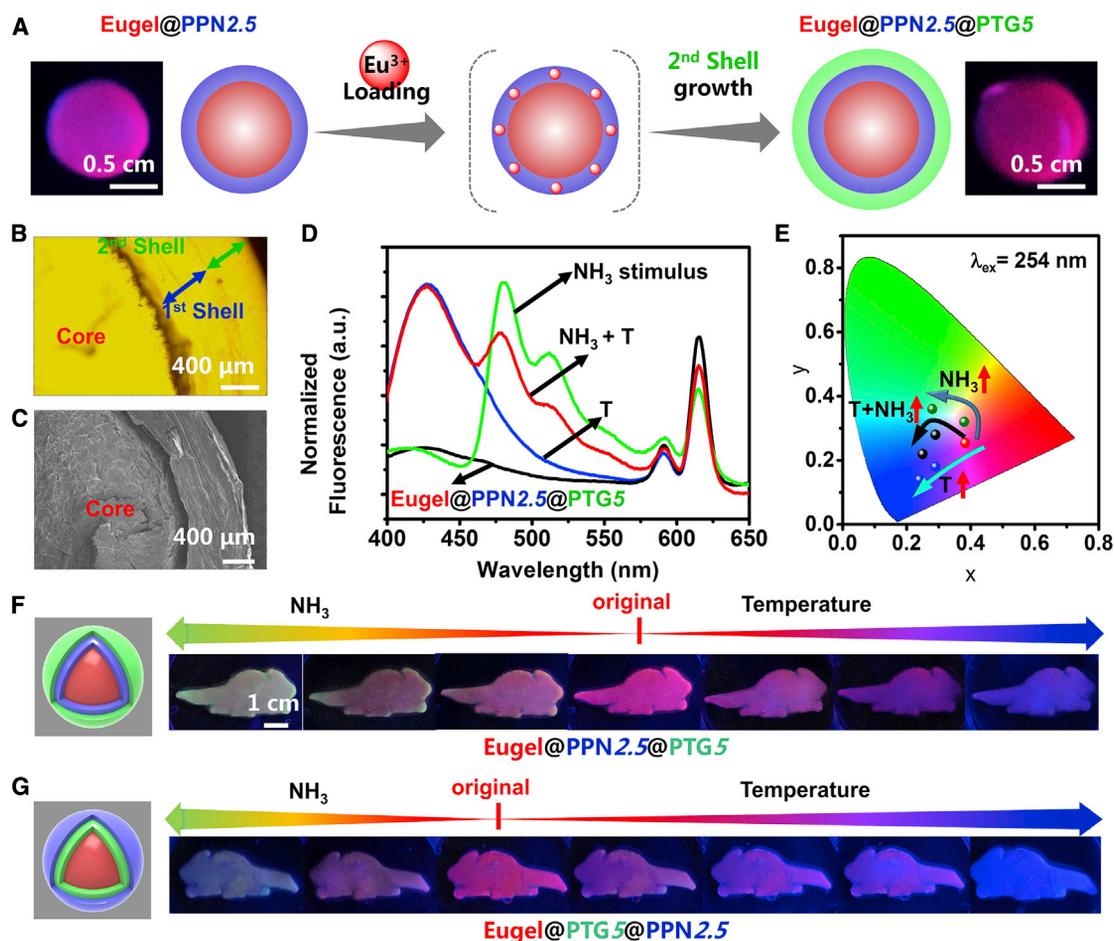


Figure 5. Fabrication of core@dual-shell-structured hydrogels

(A) Schematics showing the synthetic procedure of Eugel@PPN2.5@PTG5 fabrication by starting from Eugel@PPN2.5. The photos in the inset were taken under a 254-nm UV lamp.
 (B and C) Optical micrograph of the as-prepared Eugel@PPN2.5@PTG5 sample (B) and SEM image of the freeze-dried sample (C).
 (D) Fluorescence spectra of Eugel@PPN2.5@PTG5 in response to interplay between NH₃ and temperature (T) stimuli.
 (E) NH₃/T-triggered fluorescence color change of Eugel@PPN2.5@PTG5 shown in a CIE (Commission Internationale de l'Éclairage) 1931 chromaticity diagram.
 (F and G) Photos showing the NH₃/T-responsive fluorescence color change of Eugel@PPN2.5@PTG5 and Eugel@PTG5@PPN2.5, which were prepared from the same chameleon-inspired core gel.

change. Exposure to NH₃ resulted in the appearance of perylene tetracarboxylate emission bands (Figure S17B) and a red-to-green emission color change. Remarkably, when triggered simultaneously by high temperature and NH₃, the blue and green emission bands were turned on (Figure S17C). These results demonstrate the wide emission color tunability of the Eugel@PPN2.5@PTG5 hydrogel to cover nearly the full visible spectrum in response to subtle interplay of temperature and NH₃ stimuli (Figures 5E and 5F). Furthermore, another core@dual-shell hydrogel example, Eugel@PTG5@PPN2.5 with an inverted shell layer structure, was constructed (Figure 5G). In this design, the pH-responsive Alg/PTG hydrogel was employed as the inner shell and protected by the outer Alg/PPN shell, making the PTG polymer less efficiently responsive to the NH₃ stimulus. As a result, the pH-triggered emission color change of Eugel@PTG5@PPN2.5 was not as obvious as that of Eugel@PPN2.5@PTG5. These results highlight that the growth order of shell hydrogel layers plays an important role in the design of core@multi-shell multicolor hydrogels.

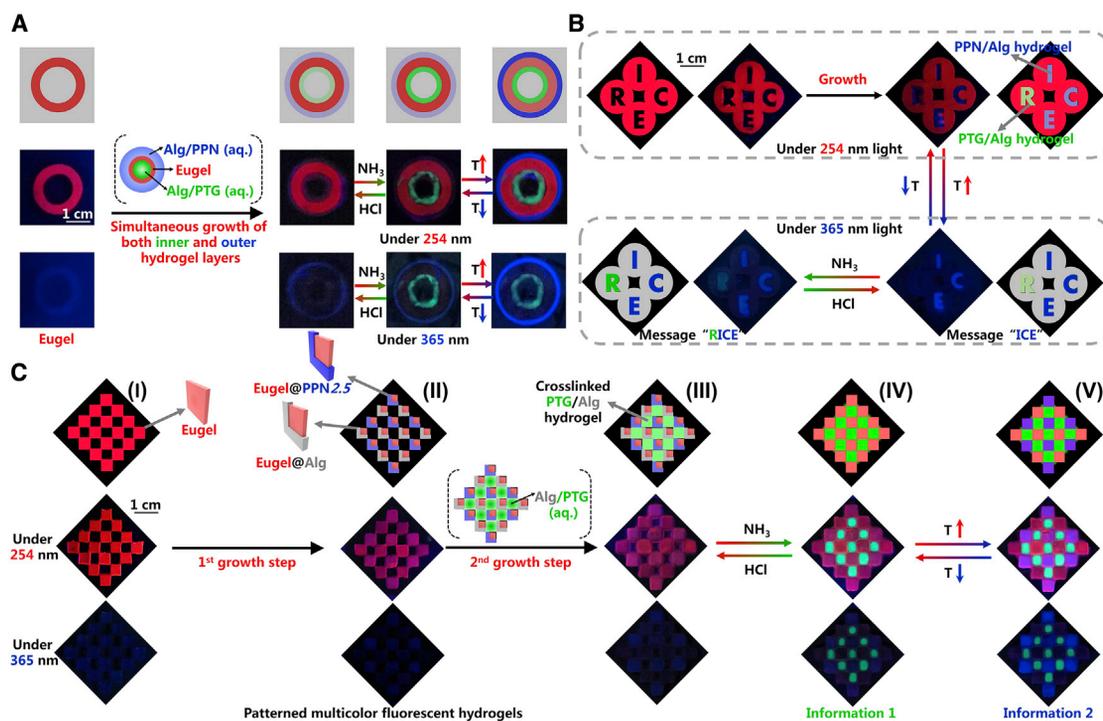


Figure 6. Growth of multicolor fluorescent materials with a patterned supramolecular core@shell structure for anti-counterfeiting applications

(A) Preparation of a responsive bicolor/tricolor fluorescent ring by starting from a ring-shaped Eugel hydrogel as the template to simultaneously grow inner and outer hydrogel layers. In a typical experiment, the Alg/PTG solution and Alg/PPN solution were placed into and out of the ring-shaped Eugel hydrogel template for 10 min.

(B) Preparation of the soft anti-counterfeiting system with on-demand information decryption by employing a letter-shaped Eugel hydrogel as the template. In a typical growth experiment, the Alg/PTG solution was placed into the "R" region for 10 min, whereas the Alg/PPN solution was placed into the "I," "C," and "E" regions.

(C) Fabrication of a complex multicolor fluorescent pattern via a two-step growth procedure (see supplemental experimental procedures for details). Briefly, in the first growth step, the Eugel hydrogel blocks in the first, third, fifth, and seventh lines were exposed to Alg/PPN solution for 10 min, whereas the rest of hydrogel blocks were exposed to the Alg solution. In the second growth step, the Alg/PTG solution was placed into the gaps between these core@shell-structured hydrogel blocks for 30 min.

Multicolor fluorescent materials with a patterned supramolecular core@shell structure for anti-counterfeiting applications

The above results indicate that the chameleon-inspired supramolecular hydrogels prepared using an easy growth procedure result in conformal core@shell structures with wide emission color tunability and excitation wavelength-dependent emission. These unique advantages encouraged us to explore their potential applications to grow complex and diverse pattern-based colorful materials for controlled fluorescence color display and anti-counterfeiting. As a proof of concept, we first used a ring-shaped Eugel hydrogel as the template to simultaneously grow inner and outer hydrogel layers according to the procedures shown in Figure 6A. The fluorescent ring obtained after 10 min of growth could be switched to different types of bicolor or tricolor fluorescent rings upon environmental changes (temperature, pH, or UV illumination). Similarly, it is possible to grow a soft anti-counterfeiting system by employing patterned letters of the Eugel hydrogel as a template (Figure 6B). Typically, the Alg/PTG solution was placed into the "R" region to grow the crosslinked Alg/PTG hydrogel, whereas the Alg/PPN solution was placed into the "I," "C," and "E" regions to grow the crosslinked Alg/PPN hydrogel. Under 365-nm UV light, the word "ICE" (information 1) with intense blue emission appeared at 50°C, whereas further exposure to NH₃ led to a different message, "RICE" (information 2) by turning on the green fluorescence of the letter "R". In this way, different

information could be disclosed under different conditions for our anti-counterfeiting system, greatly improving the security of encoded texts.

Growth of a more complex multicolor fluorescent pattern from the Eugel core hydrogel was performed using a two-step growth procedure, as shown in Figure 6C. First, square Eugel hydrogel blocks were placed together (Figure 6C, I). The Eugel hydrogel blocks in the first, third, fifth, and seventh lines were then transformed to core@shell-structured Eugel@PPN2.5 hydrogels by growth of a thermo-responsive blue fluorescent shell in the Alg/PPN solution, whereas the rest of hydrogel blocks were transformed to Eugel@Alg hydrogels by growth of a non-fluorescent shell in the Alg solution. In the second growth step, the Alg/PTG solution was placed into the gaps between these core@shell-structured hydrogel blocks, as illustrated in Figure 6C, II. After this two-step growth, a complex multicolor fluorescent pattern was obtained. As can be seen in Figure 6C, III, only red fluorescent patterns displayed under 254-nm UV light, and no pattern was noticed under 365-nm UV light. Interestingly, exposure to NH_3 resulted in red and green patterns (Figure 6C, IV), whereas further temperature increases led to more complex tricolor fluorescent patterns (Figure 6C, V) under 254-nm illumination. The whole message, the Chinese character 中 (Zhong), appeared gradually under 365-nm UV light in response to sequential pH and temperature changes. Thus, by stepwise growth of thermo-responsive blue and pH-responsive green fluorescent hydrogel shells around the Eugel core hydrogel, flexible patterned materials with the capacity for colorful information encryption and on-demand decryption were constructed and hold great potential for anti-counterfeiting.

DISCUSSION

We demonstrated the first chameleon skin-like core@shell-structured multi-luminogen supramolecular hydrogel system, whose fluorescence color can be adjusted continuously over a wide color range in response to environmental changes. The material was prepared using a red Eu^{3+} -amidopicolinate luminogen-grafted core hydrogel as a template, followed by growth of a blue naphthalimide or green perylene tetracarboxylic acid luminogen-functionalized temperature/pH-responsive shell hydrogel via a bioinspired diffusion-induced interfacial polymerization method. Because of the controlled fluorescence spectral overlap of the core and shell hydrogels, the as-prepared Eugel@PPN and Eugel@PTG hydrogels displayed not only a programmable “red to blue or green” emission color change but also desirable excitation wavelength-dependent emission properties when triggered by temperature or pH change. Furthermore, an advanced core@dual-shell-structured Eugel@PPN@PTG system was fabricated via sequential shell growth, whose emission color could be adjusted dynamically to cover nearly the full visible spectrum, which has not been achieved previously. These interesting properties further encouraged construction of a soft hydrogel chemosensor for seafood freshness detection as well growth of patterned, colored materials for anti-counterfeiting.

Spatial organization of multi-luminogens into different core and shell hydrogel layers is the key novelty for the present chameleon skin-inspired multicolor material system, in contrast to many reported multicolor fluorescent hydrogels in which multiple luminogens are introduced into one single homogeneous hydrogel matrix. As demonstrated in this study, this novel core@shell layout does not require careful choice of luminogen pairs, nor does it require an elaborative design or regulation of the complex photophysical interactions (e.g., resonance energy transfer, excimer emission, fluorescence self-quenching) between different luminogens to realize

controlled fluorescence spectral overlap. Moreover, because each luminogen is incorporated separately into a different layer, the fluorescence intensity of every luminogen can be controlled independently and continuously by certain external stimuli. As a result, a wide variety of luminogens can be used synergistically to fabricate multicolor fluorescent materials without considering their compatibility in one single material matrix. These advantages are definitely important for future construction of robust multicolor material systems with so far unachievable performance, such as the desirable excitation wavelength-dependent emission properties demonstrated here.

Finally, the proposed diffusion-induced interfacial polymerization to prepare core@shell materials proves to be general. As shown in Figure S3, a number of common divalent and trivalent metal ions (e.g., Zn^{2+} , Ca^{2+} , Cu^{2+} , Fe^{3+} , and Al^{3+}) can be used to grow the core@shell structure as long as they can induce gelation of Alg via metal coordination interactions. In fact, the shell material is not restricted to bio-based Alg; other natural or synthetic polymers (e.g., sodium polyacrylate and carboxymethyl chitosan) that have the ability to chelate with metal ions can also be used to construct similar core@shell materials (Figure S18).

This study opens the possibility of utilizing the bioinspired core@shell structure to construct artificial color-changing material systems. We believe that the wide color tunability of the novel core@shell-structured materials and the versatility of the proposed diffusion-induced interfacial polymerization method are attractive to researchers. Many new types of core@shell-structured materials with expanded functionalities are expected to be constructed in the near future, with many potential applications, such as chemosensing, bioimaging, information encryption, and biomimetic color-changing soft actuators and robotics.

EXPERIMENTAL PROCEDURES

Resource availability

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Tao Chen (tao.chen@nimte.ac.cn).

Materials availability

6-acrylamidopicolinic acid (6APA), PPN, and PTG were prepared and characterized in our previous work.^{38,66}

Data and code availability

All data supporting the findings of this study are available from the lead contact upon request.

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at <https://doi.org/10.1016/j.xcrp.2021.100417>.

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AUTHOR CONTRIBUTIONS

W.L. and T.C. conceived the idea and designed the experiments. W.L. conducted the experiments with assistance from M.S., H.Q., and R.W. H.L. and B.W. synthesized the PPN and PTG polymers, respectively. W.L., T.C., S.W., J.Z., G.Y., P.T., and Y.W. contributed to analysis and discussion of the results. W.L. and T.C. co-wrote the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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