

## Mimicking Color-Changing Organisms to Enable the Multicolors and Multifunctions of Smart Fluorescent Polymeric Hydrogels

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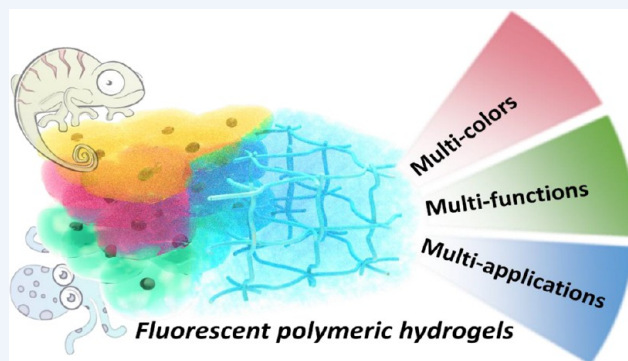
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**CONSPECTUS:** Fluorescent polymer hydrogels (FPHs) are of significant interest for diverse emerging applications such as visualized sensing, smart display, camouflaging skins, soft actuators/robots, because they can synergize the features of classic fluorescent polymers and hydrogels. With great efforts in the past decades, the major challenge in this field has been believed to be not whether a given FPH of interest can be prepared but how to fabricate robust FPHs with multicolor tunability and multifunctional synergy. Such materials will conceptually minimize the contribution of passive materials to the mass and size of the final system, holding great potential to facilitate multiple applications. To this end, one promising way is to learn from the Nature that has superb capability to forge delicate or sometimes beyond-imagination materials. Chameleons and cephalopods serve as typical examples, which are famous for not only diverse skin color adaptability under changing environmental demands, but also synergistic skin color and body gesture changes to communicate, warn, camouflage, etc. Biological studies revealed their structural color-changing capacity derives from different types of skin chromatophores and their rational multilayer arrangement in under-skin tissues. Besides, their superb ability to heterogeneously integrate soft tissues with disparate functions into topology-optimized architectures has led to various multifunctional performances. Such natural strategies, if replicated and implemented in artificial systems, would significantly benefit and advance the development of robust FPHs for various applications.



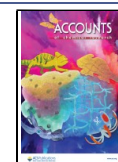
In this Account, we summarize the key advances of smart FPHs mainly achieved by our groups. We start by introducing the unique hierarchical multilayer structures of skin chromatophores in structural color-changing reptiles, followed by an in-depth discussion on how a rational integration of bioinspiration and man-made design makes it possible to largely expand the fluorescence color-changing range of smart FPHs to almost cover the whole visible spectrum. Then, to closely mimic the multifunctional behaviors of chameleons and cephalopods, we further develop efficient strategies to introduce supramolecular interactions or heterogeneously integrating smart FPHs with other soft materials with disparate functions, producing a number of multifunctional fluorescent polymeric hydrogel systems. These robust FPHs can find many frontier applications, including bioinspired synergistic color/shape switchable hydrogel actuators/robots, smart systems with on-demand fluorescent patterning capacities for displaying or information encryption, as well as robust chemosensors for important food or environmental analytes. We expect that the discussion presented in this Account would promote better understanding of the discoloration systems in nature, and advance the development of bioinspired color-changing materials.

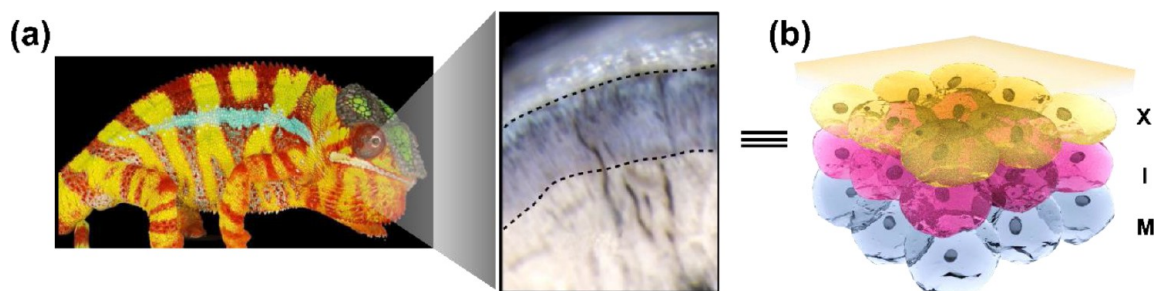
### KEY REFERENCES

- Shi, H.; Wu, S.; Si, M.; Wei, S.; Lin, G.; Liu, H.; Xie, W.; Lu, W.; Chen, T. Cephalopod-inspired design of photomechanically modulated display systems for on-demand fluorescent patterning. *Adv. Mater.* 2022, 34, 2107452.<sup>1</sup> This study draw inspiration from the bioelectromechanical display mechanism of cephalopods to develop a conceptually new photomechanically modulated fluorescent system, which enables the on-demand display of multicolor fluorescent patterns via an NIR-light-regulated actuating process.
- Wu, S.; Shi, H.; Lu, W.; Wei, S.; Shang, H.; Liu, H.; Si, M.; Le, X.; Yin, G.; Theato, P.; Chen, T. Aggregation-induced emissive carbon dots gels for octopus-inspired shape/color synergistically adjustable actuators. *Angew.*

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**Figure 1.** (a) Photograph of a color-changing reptile and lateral view of the multilayer skin. Adapted with permission from ref 24. Copyright (2015) NPG. (b) Illustration showing the organization of xanthophores (X), iridophores (I), and melanophores (M) into a vertical multilayer structure.

*Chem., Int. Ed.* **2021**, *60*, 21890–21898.<sup>2</sup> Robust aggregation-induced emissive multicolor carbon dot polymeric hydrogel systems were synthesized and designed to construct one artificial soft swimming robot with an octopus-like synergistic shape/color change and directional swimming motion.

- Le, X.; Shang, H.; Yan, H.; Zhang, J.; Lu, W.; Liu, M.; Wang, L.; Lu, G.; Xue, Q.; Chen, T. A urease-containing fluorescent hydrogel for transient information storage. *Angew. Chem., Int. Ed.* **2021**, *60*, 3640–3646.<sup>3</sup> A urease-containing smart fluorescent polymeric hydrogel is presented as an information storage material that self-destructs after decryption in response to an environmental stimulus.
- Wei, S.; Lu, W.; Le, X.; Ma, C.; Lin, H.; Wu, B.; Zhang, J.; Theato, P.; Chen, T. Bioinspired synergistic fluorescence-color-switchable polymeric hydrogel actuators. *Angew. Chem., Int. Ed.* **2019**, *58*, 16243–16251.<sup>4</sup> Lanthanide-coordinated smart multicolor fluorescent polymeric hydrogels were synthesized and used to fabricate anisotropic soft actuators exhibiting chameleon-inspired simultaneous color-shifting and shape-morphing behavior.

## 1. INTRODUCTION

Smart fluorescent polymeric hydrogels (FPHs) have been heavily researched in the past decade and recognized as rising stars of luminescent materials because they can offer the combined merits of hydrogels<sup>5–11</sup> and fluorescent polymers,<sup>12</sup> including a soft, wet nature, tissue-like modulus, and tunable luminescence/volume. Smart FPHs are thus of significant interest in diverse frontier fields, e.g., sensors, actuators, robots, and displays.<sup>13–16</sup> To produce color-changing FPHs, the most popular way relies on the physical doping or covalent grafting of two or more responsive fluorophores (mainly fluorescent proteins, organic fluorophores, lanthanide complexes, and luminescent nanoparticles) into one cross-linked polymer matrix,<sup>17</sup> resulting in numerous color-changing FPHs that respond to different environmental stimuli (e.g., temperature, pH, solvent, and light).<sup>18–23</sup> However, owing to the inherent nature of this classic strategy, different types of fluorophores are usually randomly organized in most of these reported FPHs. To a large extent, it leads to unpredictable and complex photophysical processes (resonance energy transfer, excimer emission, aggregation-caused quenching, etc.) that are highly dependent on the separation distance between different fluorophores, possibly introducing deficiencies such as narrow fluorescence color tunability, poor color-changing sensitivity, and difficult-to-interpret mechanisms. Still, multifunctional FPHs are scarce but highly expected because of their potential to conceptually eliminate the contribution of passive materials

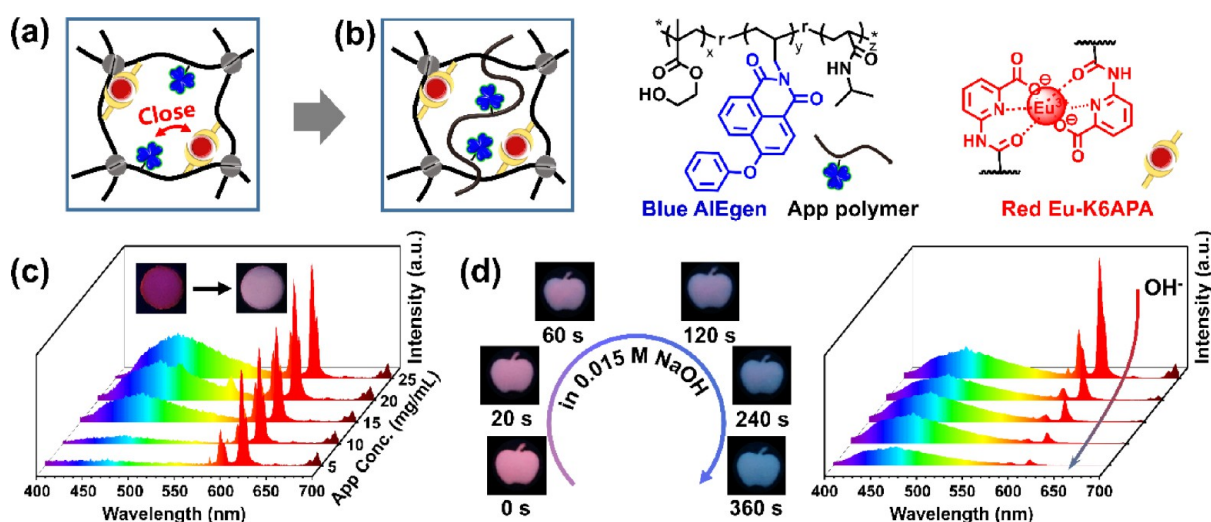
to the mass and size of the final systems for frontier applications.

One promising approach to expanding the multiple colors and functionalities of FPHs is to learn from nature, which is recognized for producing masterful color-changing organisms perfected by millions of years of evolution.<sup>24,25</sup> Chameleons and cephalopods are typical examples in which different types of chromatophores and their rational multilayer arrangement in under-skin tissues lead to amazing structural color-changing performances beyond additive behavior, allowing for sensitive and diverse skin color responses upon environmental changes. Moreover, their superb ability to heterogeneously integrate soft tissues with disparate functions into topology-optimized architectures has led to as-yet-unimagined performances, such as synergistic skin color and body morphology changes for communicating, warning, or camouflaging purposes under dynamic environmental demands. All of these key findings can provide inspiring clues for the development of multicolor and multifunctional FPHs.

Nevertheless, the construction of multicolor and multifunctional FPHs is not easily guaranteed by simply mimicking the natural structures or mechanisms because these natural color changes rely on the structural color derived from light diffraction<sup>24</sup> but not fluorescence color. In other words, what nature offers is only inspiration rather than a direct solution. Therefore, an orchestrated combination of natural inspiration and rational design is always needed. According to this concept, we have been heavily engaged in this field and recently fabricated many bioinspired FPHs with wide color tunability or multifunctional synergy. In this Account, we will provide a focused discussion of this topic, from which one can see how an orchestrated integration of bioinspiration and rational design enables us to efficiently realize the multiple colors and functionalities of smart FPHs for multiple frontier applications. Finally, we summarize these studies to present the remaining challenges and opportunities facing this field.

## 2. BIOINSPIRED MULTICOLOR FPHS

Color change is widespread in numerous kinds of reptiles throughout the world. Many of them have evolved to exhibit facultative crypsis, whereby multiresponsive rapid and diverse skin color changes are employed to match the dynamically changeable environmental background. Such robust skin color adaptability of reptiles is quite intriguing. A microscopic observation of soft, wet dermal skin has identified several types of chromatophores (Figure 1), including xanthophores, iridophores, and melanophores.<sup>24,25</sup> Usually, these pigment-containing cells are arranged into a vertical multilayer structure with xanthophores in the uppermost layer, iridophores in the



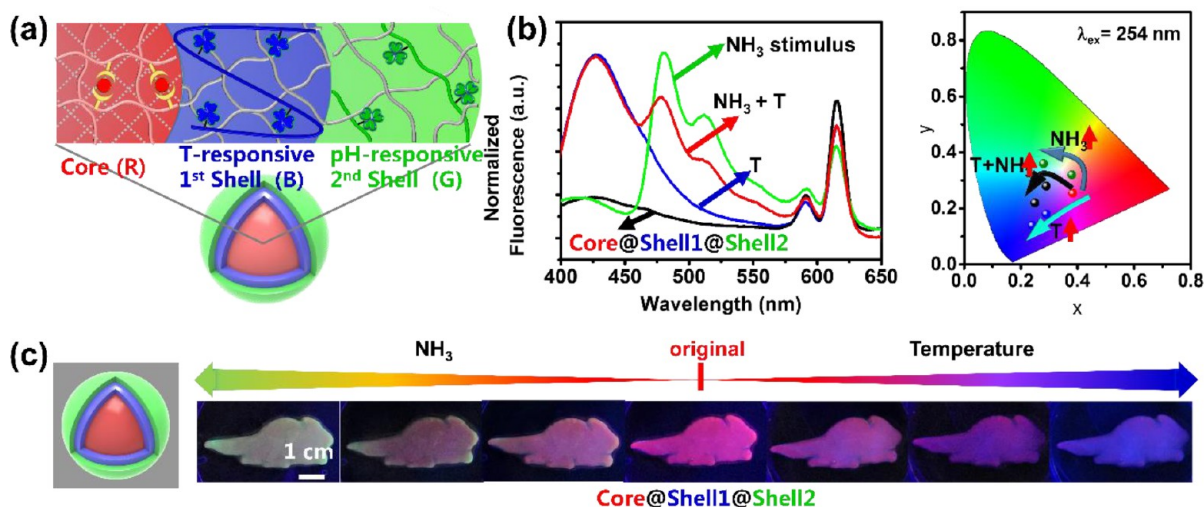
**Figure 2.** Structural illustration of (a) one classic FPH via random copolymerization and (b) our bioinspired semi-IPN FPH. (c) Fluorescence spectra of this semi-IPN hydrogel with increasing AIEgen concentration. (d) Photographs showing the NaOH-triggered continuous fluorescence color change and the corresponding fluorescence spectra. Adapted with permission from ref 26. Copyright (2022) Wiley-VCH.

intermediate layer, and melanophores in the basal layer. When the surrounding background changes, differential dispersion/aggregation responses of pigment granules within chromatophores arise, and sometimes the spatial arrangement of chromatophore layers is varied or even reversed, resulting in a multitude of skin colors. For example, a yellowish-to-brown skin color change is produced in reptiles after expanding the iridophore layer to be thicker and shrinking the melanophore layer to be thinner. The reptile skin frequently turns green if the vertical order of xanthophores and iridophores is reversed. Skin with black coloration is contributed only from the melanophore layer.

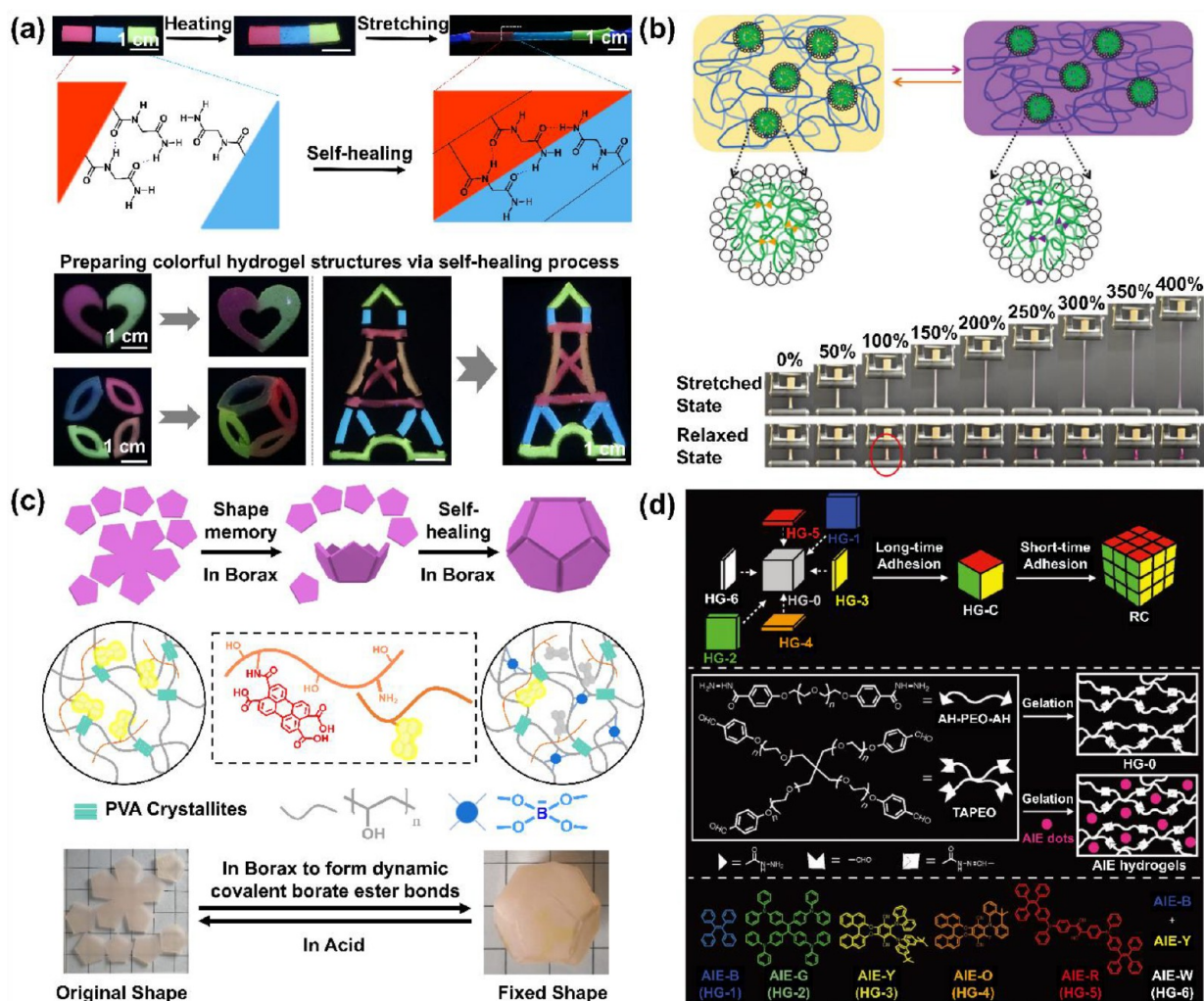
In contrast to natural reptile skins, most artificial FPHs, despite having a similar modulus and a soft, wet nature, show much poorer multicolor adaptability.<sup>17</sup> Careful comparison studies lead us to conclude the following: (1) There are different responsive behaviors between chromatophores and fluorophores. As discussed above, each type of skin chromatophore usually exhibits relatively independent dispersion/aggregation behavior upon stimulation, indicating that the color-mixing proportions of different chromatophores can be largely adjusted to produce diverse skin colors. As for most FPHs, two or more responsive fluorophores are physically doped or covalently grafted into one polymer network (Figure 2a), potentially resulting in complex photophysical interactions between different fluorophores. Consequently, it becomes challenging to independently and continuously regulate the fluorescence intensity of each fluorophore by varying its concentration or using external stimuli. (2) There are different structure design bases between natural reptile skins and artificial FPHs. Compared with the vertical multilayer structure of skin chromatophores, different fluorophores are usually randomly distributed in the hydrogel matrix. Therefore, a careful choice of specially screened fluorophore pairs is always required to ensure their compatibility in a single matrix. Moreover, given that the distances between these coexisting fluorophores are quite close ( $\sim 10$  nm or less) in FPHs, it is also difficult to selectively turn on/off the emission intensity of certain fluorophore without significantly affecting the intensities of others. For all of these reasons, the color mixing proportions of different fluorophores in artificial FPHs are

difficult to vary independently by using environmental stimuli. It thus remains challenging to construct chameleon-like FPHs with continuously changeable fluorescence color over a wide gamut, especially those whose fluorescence color could be engineered to cover the full visible spectrum.

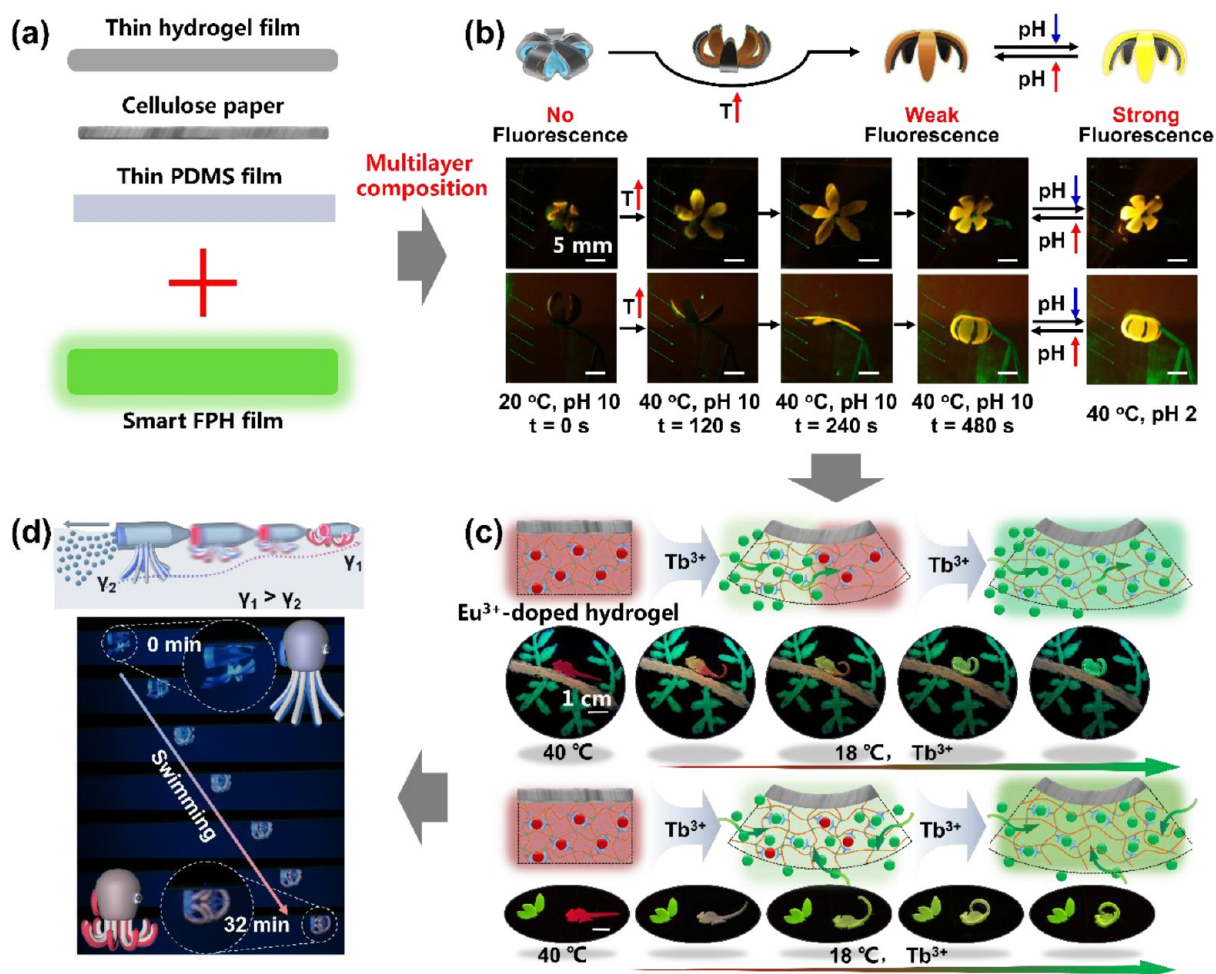
With these discussions, we first mimicked the independently responsive behaviors of different skin chromatophores to propose an innovative FPH example whose emission color could be continuously regulated from red to blue.<sup>26</sup> Its material design is depicted in Figure 2b, in which the aggregation-induced blue-emissive-substituted naphthalimide (4-phenoxy-*N*-allyl-1,8-naphthalimide, AIEgen) and red-light-emitting  $\text{Eu}^{3+}$ -potassium 6-acrylamidopicolinate (Eu-K6APA) molecules are organized separately into different polymer chains of one polymer network. Such a rational design is favorable to the coexistence of hydrophobic AIEgens and hydrophilic Eu-K6APA in the same hydrogel by first incorporating AIEgens into hydrophilic poly(*N*-isopropylacrylamide) (PNIPAM) chains and then forming semi-interpenetrating network (semi-IPN) with Eu-K6APA-grafted poly(*N*-acryloyl glycineamide). Importantly, the blue AIEgens and red Eu-K6APA in the obtained hydrogels were found to be orthogonally responsive. As summarized in Figure 2c, after elevating the concentration of AIEgen-grafted PNIPAM polymer (APP, 0 to 20 mg/mL), the blue emission intensity at 475 nm increases proportionally, owing to the heavier aggregation of hydrophobic AIEgens without affecting the red intensity of Eu-K6APA at 614 nm. A noticeable red-to-white color shift was thus observed with increasing AIEgen content. Similarly, a NaOH-triggered wide and continuous fluorescence color change from red to pink and finally blue was also realized because Eu-K6APA is gradually decomposed in alkaline solutions to completely quench its red fluorescence within several minutes, while the blue emission of AIEgens is only slightly influenced (Figure 2d). In this way, the fluorescence intensities of these two different fluorophores are capable of being independently and continuously controlled by varying the concentration or using external stimuli. Nevertheless, this bioinspired hydrogel structural design, despite being efficient, seems to be limited to smart FPHs containing only two types of fluorophores because the hydrogel system may become too



**Figure 3.** (a) Structural illustration of our bioinspired core@shell FPH. (b) Its fluorescence spectra in response to different environment stimuli and the color changes shown in a CIE 1931 chromaticity diagram. (c) Their corresponding photographs. Adapted with permission from ref 27. Copyright (2021) Elsevier.



**Figure 4.** (a) Self-healing FPH system via multiple hydrogen-bonded cross-links. (b) Mechanically strong FPH system by using self-assembled micelles to dissipate energy. (c) Shape memory and self-healing FPH system based on dynamic covalent borate ester bonds between PVA and borax. (d) Self-healing multicolor FPH system via dynamic acylhydrazone bonds. Adapted with permission from ref 26 (copyright 2022, Wiley-VCH), ref 30 (copyright 2017, Wiley-VCH), ref 33 (copyright 2019, Wiley-VCH), and ref 34 (copyright 2019, Wiley-VCH).



**Figure 5.** (a) Modular design principle for multilayered FPH systems. (b) Bilayer hydrogel actuator with thermoresponsive physical folding/unfolding deformation and on–off fluorescence switching behavior. (c) Hydrogel actuator displaying chameleon-like synergistic multifluorescence color changes and 3D body movements for camouflage. (d) Soft hydrogel robot with octopus-like synergistic shape/color changes and directional swimming motion. Adapted with permission from ref 36 (copyright 2018, Wiley-VCH), ref 4 (copyright 2019, Wiley-VCH), and ref 2 (copyright 2021, Wiley-VCH).

complicated and bring about some unexpected events when three or more kinds of fluorophores are involved.

Furthermore, we explored the possibility of utilizing the bioinspired vertical multilayer structure to largely expand the multicolor adaptability of smart FPHs with three kinds of fluorophores. To this end, a diffusion-induced interfacial polymerization process was proposed to produce core@shell-structured FPHs<sup>27</sup> in which the red-light-emitting Eu-K6APA-grafted core hydrogel was used as a template for the sequential growth of a temperature-responsive blue fluorescent hydrogel as the first shell layer and a pH-responsive green fluorescent hydrogel as the second shell layer. In this biomimetic multilayer structure illustrated in Figure 3a, red Eu-K6APA, blue AIEgens, and green perylene tetracarboxylic acid fluorogens (PTgens) are spatially organized into three distinct core or shell layers. Because the spatial distances between different luminogens are large enough to completely avoid any photophysical event between each other, the fluorescence intensities of blue AIEgens and green PTgens in the core@shell hydrogels can be regulated independently in response to environmental temperature or pH changes, respectively (Figure 3b). Therefore, the chameleon-shaped core@shell

hydrogel is capable of behaving like a real chameleon to display continuously adjusted fluorescence color from red to green and even blue (Figure 3c) when exposed to different external stimuli. Additionally, this bioinspired core@shell structural design also brings about other promising advantages, such as the rarely realized excitation-wavelength-dependent fluorescence color tunability owing to the differential excitation energies between red Eu-K6APA and green/blue luminogens. Besides this core@shell structural design, a double-layer hydrogel structure, in which each fluorophore is spatially separated in a distinct layer, has also been utilized to construct smart multicolor FPHs.<sup>28</sup>

The assembly of different skin chromatophores into a vertical multilayer structure represents an evolutionary novelty for natural color-changing reptiles, which allows their skins to exhibit diverse color changes.<sup>24</sup> Inspired by this finding, we proposed to prepare core@shell-structured FPHs by spatially organizing different fluorophores into several distinct hydrogel layers. This is the key difference in the present hydrogel when compared to the previously reported FPHs. As discussed above, this bioinspired multilayer design does not require an elaborate regulation of the complex photophysical events

between different types of fluorophores for the purpose of achieving controlled emission spectral overlap. Moreover, such a multilayer layout largely weakens the necessity to consider the compatibility of different types of fluorophores in one hydrogel matrix. This means that a wide variety of fluorogens can potentially be combined to produce robust multicolor hydrogels with as-yet-unachievable performances, which has been previously unimaginable. Therefore, it is believed that there is still great untapped potential for this bioinspired multilayered structural design.

### 3. BIOINSPIRED MULTIFUNCTIONAL FPHs

Besides multicolor tunability, natural soft, wet skins of color-changing organisms have also evolved to have many other superb abilities such as self-healing features, adaptive 3D shape transformations, and so on. It is usually through the multifunctional synergy of these features that allows them to efficiently adapt dynamic environmental changes, which are their essential survival traits. For example, the damaged chameleon/octopus skins are capable of self-healing to the initial state within several days.<sup>26</sup> Such natural multifunction synergistic behaviors, if successfully replicated, would significantly enrich the functionalities of artificial soft, wet FPHs. To this end, two primary strategies have recently been devoted to developing multifunctional FPHs.

#### 3.1. Introduction of Supramolecular Interactions or Dynamic Covalent Bonds

Supramolecular interactions are highly dynamic upon stimulation and have become the molecular basis for many promising functions such as self-healing and mechanical toughness.<sup>29</sup> The rational introduction of supramolecular interactions into smart FPHs will thus endow them with extra functions. For example, we have recently utilized multiple hydrogen bonds between the grafted glycinamide moieties as supramolecular cross-links to present one multicolor polymeric hydrogel system (Figure 4a).<sup>26</sup> Owing to the thermo-triggered reversible dissociation/recombination of hydrogen bonds, several multicolor FPH blocks were fully healed together at elevated temperature and even firmly adhered into meaningful multicolor objects. Meanwhile, Zheng,<sup>30</sup> Chen,<sup>31</sup> and Qu<sup>32</sup> have reported several mechanically strong FPH systems by accommodating the hydrophobic fluorophores into self-assembled micelles with good energy-dissipating efficiency (Figure 4b).

Besides supramolecular interactions, dynamic covalent bonds have also been employed to produce multifunctional FPHs. In an example shown in Figure 4c,<sup>33</sup> we first combined crystalline domains and hydrogen bonds between poly(vinyl alcohol) (PVA) and fluorescent perylene tetracarboxylic acid-grafted gelatin to present one mechanically strong FPH. When deformed by hands and exposed to borax solutions to form dynamic covalent borate ester bonds, its temporary shape was quickly fixed and facily recovered to the initial shape after being placed in acid solutions to trigger the dissociation of these covalent bonds. Additionally, a self-healing feature was also observed, as is evidenced by the fact that different hydrogel blocks were quickly healed together in borax solutions. As a result, a complex 3D hydrogel dodecahedron was constructed on the basis of collective shape memory and self-healing features. In parallel, dynamic acylhydrazone bonds (Figure 4d)<sup>34</sup> and phototriggered coumarin interlinking

interactions<sup>35</sup> were employed to construct self-healing FPHs, which could even be reshaped upon stimulation.

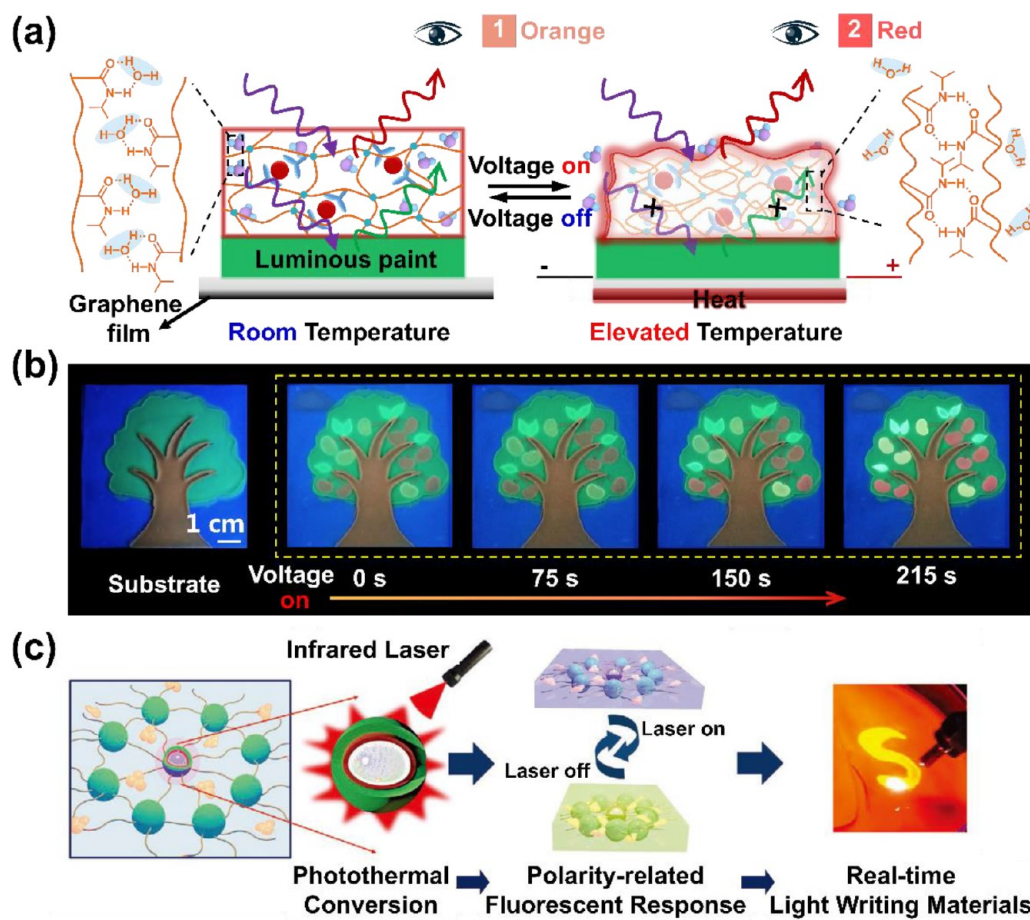
#### 3.2. Multilayer Interfacial Composition

Another noteworthy aspect of chameleons is their powerful capacity to heterogeneously integrate soft color-changing skins with other under-skin tissues into topology-optimized multilayer architectures, which leads to the synergistic color change and body deformation for camouflaging via efficient environment background matching.<sup>17</sup> This finding provides us important inspiring clues for developing a series of synergistic shape/fluorescence color switchable hydrogel systems. Figure 5a illustrates the modularly designed bilayer structure, in which smart FPH was interfacially composited with another hydrogel film with differential swelling ratios or static cellulose paper/elastomer films. In the first attempt, a pH-responsive perylene bisimide-functionalized hydrogel layer was integrated with another graphene oxide-incorporated PNIPAM hydrogel layer to produce a bilayer actuator, which exhibits thermoresponsive physical folding/unfolding deformation and on-off fluorescence switching behavior (Figure 5b).<sup>36</sup> To further mimic the synergistic multicolor switching and shape-deforming functions of chameleons, Eu<sup>3+</sup>/Tb<sup>3+</sup> coordinated multicolor poly-(NIPAM-co-K6APA) hydrogels were synthesized and interfacially assembled with static cellulose paper.<sup>4</sup> Note that the fluorescence colors of these lanthanide coordinated hydrogels could be widely adjusted with exposure to acidity/alkalinity or metal ions. Therefore, the obtained chameleon-shaped hydrogel actuators are capable of behaving like natural chameleons and exhibiting multicolor changes and 3D body movements for camouflage (Figure 5c) when responding to a subtle interplay of several environmental stimuli such as temperature, pH, and chemicals. On this basis, we demonstrated that the Marangoni effect could be employed as an ideal driving force to promote the directional locomotion of bilayer FPH/elastomer actuators by preloading a low-surface-tension solvent (e.g., glycol) in the gel layer.<sup>2</sup> As a result, simultaneous shape/color changes and directional swimming motion were demonstrated (Figure 5d), exactly resembling the multifunction synergistic behaviors of octopi that quickly swim away and simultaneously alter skin colors and body shapes to escape from predators. Following similar design principles, a number of elegant multilayer or gradient-structured FPH actuators have been further programmed to display various types of complicated 3D shape-deforming functions and diverse emission-color switching capacities.<sup>37–42</sup> This progress clearly highlights that it is possible to engineer robust fluorescent hydrogel systems with multiple responsiveness and programmable functionalities by assembling specially selected materials into bioinspired multilayered structures.

### 4. MULTIPLE FRONTIER APPLICATIONS

#### 4.1. Smart Display

Many marine mollusks and fishes are capable of exhibiting responsive red, orange, or green biofluorescence, which serves as a light lure to attract prey and mates or functions as a display strategy for warning and communicating in low-light deep-sea environments.<sup>43</sup> One famous example is the Atolla jellyfish that exists in a quasi-solid hydrogel state and has the superb ability to display dazzling bioluminescent patterns to scare off predators. Inspired by this interesting phenomenon, we utilized the interfacial composition of thermoresponsive FPH, a luminous paint layer, and a conductive graphene film to



**Figure 6.** (a) Schematic illustration of color-changing mechanism for the electrically powered multicolor fluorescent hydrogel device and (b) its use for the on-demand display of a fluorescent painting named “a cherry tree”. (c) Illustration showing the photothermally induced fluorescence response for a real-time light-writing display. Adapted with permission from ref 44 (copyright 2021, American Chemical Society) and ref 46 (copyright 2021, Wiley-VCH).

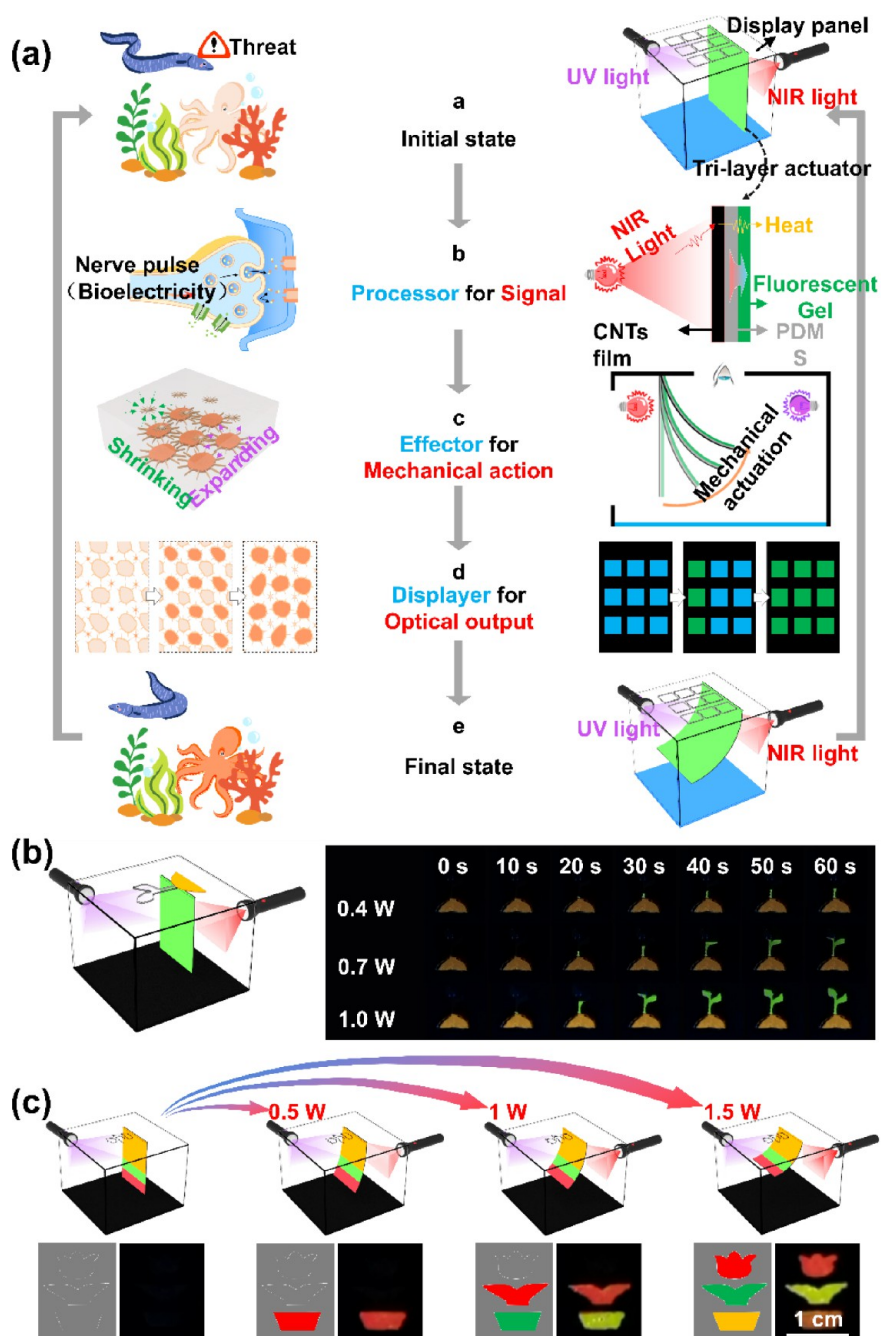
produce an electrically powered multicolor fluorescent hydrogel device.<sup>44</sup> As shown in Figure 6a, upon applying voltage to a graphene film, Joule heat was generated to trigger the phase transition of FPH, leading to the overlapping color change of the whole device. Because the electrical stimulus is easily regulated in terms of amplitude and duration, the generated Joule heat can be controlled in a local and real-time manner, which enables precise and local multifluorescence color control at low voltage. Consequently, a fluorescent painting named “a cherry tree”, which was prepared by using luminous paint to construct the tree and different-colored hydrogels to prepare fruits and leaves, could be dynamically displayed upon applying voltage (Figure 6b). All of these advantages further encouraged us to demonstrate an artificial Atolla jellyfish that is capable of interacting with a model predator and displaying switched fluorescent patterns for an alarming purpose. Besides electricity, light and force stimuli have also been used to trigger fluorescence color changes of hydrogels for smart display applications.<sup>45</sup> In a study shown in Figure 6c, Zhang and co-workers utilized the photothermal effect of liquid metal nanoparticles to achieve real-time and reversible light writing that enables the on-demand display of different fluorescence information.<sup>46</sup>

Despite these advances, the pattern display capacity of artificial systems is still far inferior to that of natural cephalopod skins, which features a concerted integration of

spatial/temporal precision for multicolor patterns and reversible/rapid switching upon stimulation. Biological studies reveal that the cephalopod skin colors/patterns are switched by the bioelectricity-controlled mechanical contraction and expansion of chromatophores. This finding inspired us to mimic this natural bioelectromechanical display mechanism and construct a new-concept photomechanically modulated display system.<sup>1</sup> As shown in Figure 7a, it consists of one tethered NIR-light-responsive trilayer fluorescent gel actuator and the other top suspended display panel with a hollow window. When paired with customized display panels, various multicolor fluorescent patterns were on-demand displayed by remotely applying NIR light to deform the tethered fluorescent actuator. Importantly, the deformation extent of the actuator could be continuously adjusted by varying the NIR-light power, and the composition of the gel layer could be flexibly varied. All of these characteristics make it possible to explore this conceptually new display device for dynamic color-changing painting applications (Figure 7b,c).

#### 4.2. Data Encryption

A responsive pattern displaying features of fluorescent materials are also suitable for anticounterfeiting applications. In this respect, smart multicolor FPHs are desired because they enable dynamic multicolor displays of encrypted information to ensure high security levels. In one recent study, we grafted substituted naphthalimide and light-responsive spirocyan

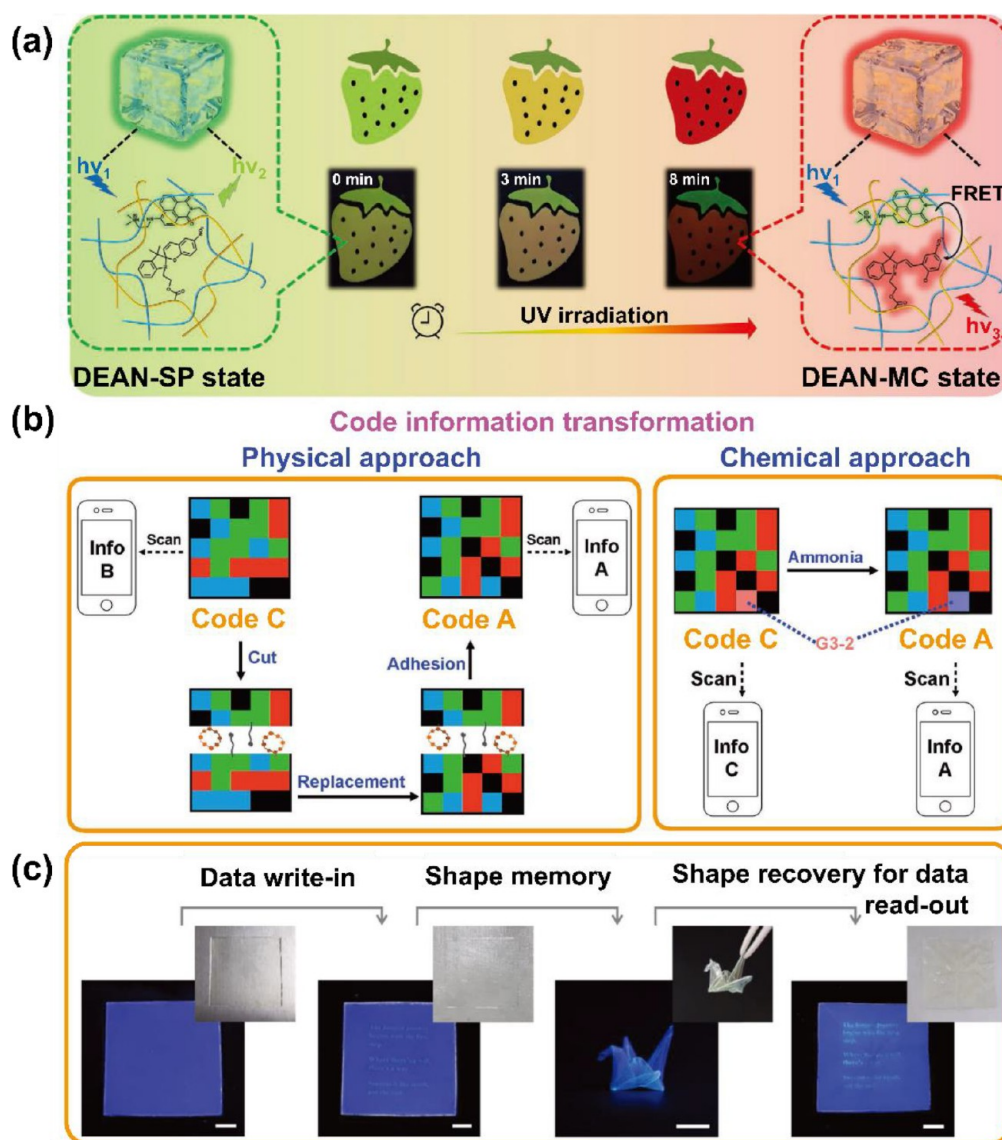


**Figure 7.** (a) Schematic illustration of the cephalopod-inspired photomechanically modulated display system. (b, c) On-demand display of dynamic color-changing painting by varying the NIR-light power to adjust the extent of deformation of the trilayer fluorescent gel actuator. Adapted with permission from ref 1. Copyright (2022) Wiley-VCH.

fluorophores into the heterogeneous networks of one fluorescent organohydrogel (Figure 8a).<sup>47</sup> Such a system thus allows for multistage fluorescence-color changes from green to yellow and finally to red by efficiently varying the fluorescence resonance energy transfer (FRET) process between two fluorophores under UV light irradiation. Consequently, the on-demand encryption of multicolor fluorescent patterns was realized with increasing irradiation time, significantly raising the difficulty of data decryption. Along this line, a number of smart FPHs with diverse responsiveness and programmable fluorescence changes have been designed for multistage information encryption, greatly enriching the potential tool box against data forging.<sup>1,48–51</sup>

Recently, there has been increasing interest in utilizing the multifunctional synergistic behaviors of smart FPHs for efficient switching between different fluorescent patterns that correspond to different information. One typical example was reported by Sessler, Huang, and co-workers (Figure 8b).<sup>52</sup> Three distinct fluorescent (blue, green, and red) hydrogels were engineered to bear tetracationic receptor-anion recognition motifs, which ensured efficient but reversible physical adhesion between different hydrogel blocks. Therefore, various multicolor fluorescent codes were readily produced by rationally adhering several different hydrogel blocks. Remarkably, these codes were capable of being switched by replacing some building blocks with others, thus allowing for the rapid





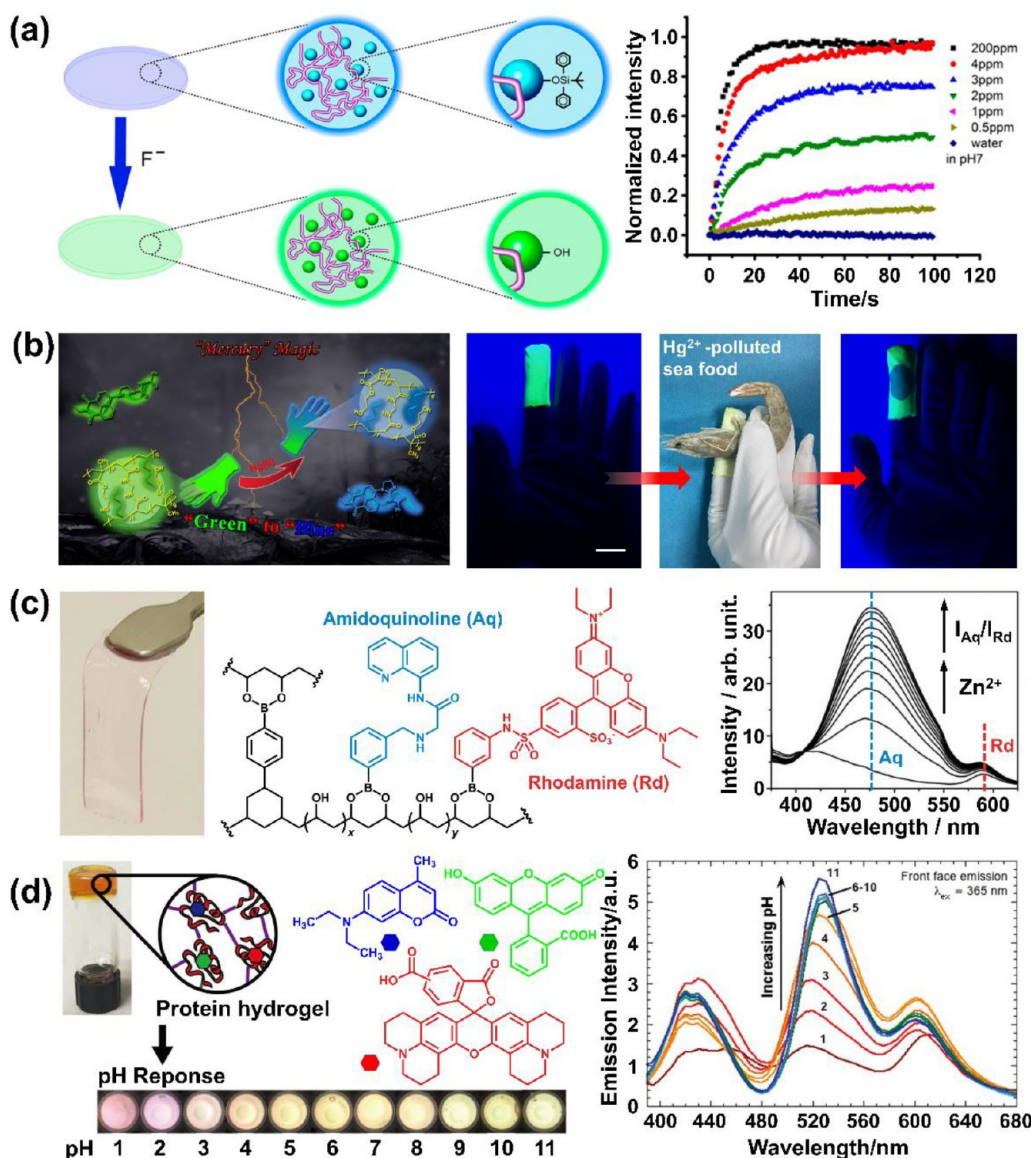
**Figure 8.** (a) On-demand encryption of multicolor fluorescent patterns by efficiently controlling the FRET process between substituted naphthalimide and spiropyran fluorophores in response to UV light irradiation. (b) Facile switching of various multicolor fluorescent codes by replacing some hydrogel building blocks with others via a self-healing process. (c) High-level information encryption by encoding data inside 3D hydrogel structures via a shape memory process. Adapted with permission from ref 47 (copyright 2021, Wiley-VCH), ref 52 (copyright 2018, Wiley-VCH), and ref 56 (copyright 2021, Wiley-VCH).

switching between different information. Zhao and Li et al. further expanded this strategy by employing hydrogel blocks with light-triggered ON–OFF switchable luminescence.<sup>53</sup> Tang and Ji also advanced this concept by using a “Codes in Code” method to achieve improved data storage capacity.<sup>54</sup> Additionally, multifunctional FPHs can also be used to enhance the encryption security levels.<sup>55</sup> For example, Wu incorporated the photoresponsive donor–acceptor fluorophores into a cross-linked poly(1-vinylimidazole-*co*-methacrylic acid) network to present a robust FPH system, which combines the features of high toughness and temperature-triggered shape memory owing to high-density thermoresponsive intra/inter-chain hydrogen bonds.<sup>56</sup> On the basis of the synergistic effect of these appealing functions, fluorescent patterns of interest could be photowritten on 2D hydrogel sheets and then programmed into specific 3D configurations (Figure 8c). Information encrypted inside such 3D hydrogel structures is decrypted only after triggering their shape

recovery to 2D hydrogel sheets. Note that the specially pre-designed procedures to trigger shape recovery are usually unknown to the public, indicating the superior encryption security of the multifunctional FPH-based 3D anticounterfeiting platform compared to that of their traditional 2D counterparts.

### 4.3. Sensing

Smart FPHs with an analyte-specific fluorescence response are highly desired for sensing uses because they integrate the advantages of a liquid phase in situ detecting environment of solution sensors and the facile portability of solid film sensors. Importantly, ultrafast substance exchange with surrounding aqueous analyte solutions is usually guaranteed by their highly hydrophilic 3D polymeric network, resulting in improved detection efficiency. For instance, Yang et al. realized the ultrafast  $F^-$  detection within 15 s by burying a  $F^-$ -specific fluorescent probe in a hydrogel matrix (Figure 9a).<sup>57</sup> Similarly,



**Figure 9.** (a) FPH probe for ultrafast  $F^-$  detection in drinking water. (b) Wearable fluorescent hydrogel-coated gloves for reporting  $Hg^{2+}$ -polluted sea food by directly touching them. (c, d) Ratiometric fluorescent hydrogel chemosensors for  $Zn^{2+}$  (a higher  $I_{Aq}/I_{Rd}$  value with increasing  $Zn^{2+}$ ) and pH by simultaneously introducing the sensing molecule and another static reference fluorophore into the hydrogel matrix. Adapted with permission from ref 57 (copyright 2013, American Chemical Society), ref 61 (copyright 2019, Wiley-VCH), ref 63 (copyright 2014, RSC), and ref 64 (copyright 2017, Wiley-VCH).

numerous turn-on/turn-off fluorescent hydrogel sensors have been presented for important analytes such as  $Cu^{2+}$ ,  $Cd^{2+}$ , and perchlorate.<sup>58–60</sup> Moreover, FPHs with an analyte-triggered ratiometric fluorescence response are more expected for ensuring accurate detection. To this end, we offered one efficient chemosensor in which the thiourea-containing fluorescent molecules (NDBCB) were covalently grafted into hydrophilic hydrogel-coated flexible paper/textile films (Figure 9b).<sup>61</sup> The grafted NDBCB moieties are green-light-emitting but specifically react with  $Hg^{2+}$  to produce blue-light-emitting guanidine derivatives. A  $Hg^{2+}$ -specific color-changing chemosensor was thus constructed and integrated into hydrogel-coated wearable gloves that potentially report  $Hg^{2+}$ -polluted seafood by direct touch. Given that there are only a few fluorophores with analyte-triggered color changes, a more popular method is to pair the sensing molecule with a

reference fluorophore to realize a ratiometric response.<sup>62</sup> Figure 9c,d shows two typical examples, which paired sky-blue amidoquinoline and red rhodamine fluorogens for  $Zn^{2+}$ <sup>63</sup> and tricolor fluorophores for  $H^+$ .<sup>64</sup>

## 5. CONCLUSIONS AND OUTLOOK

We have summarized the recent progress in the bioinspired fabrication of multicolor and multifunctional FPHs for multiple frontier applications such as displays, encryption, and sensing. As detailed in these stories, the evolutionally optimized hierarchical structures and discoloration mechanisms of natural color-changing organisms have provided important inspiring clues for the preparation of robust artificial fluorescent hydrogels. Nevertheless, despite these advances, the related studies are still believed to be in their infancy. These as-prepared materials can just behave similarly to their

natural counterparts, but their multiresponsive color-switching performances and levels of multifunctional collaboration are still far inferior to that of the natural color-changing skins. Innovative collaborations from people of different backgrounds are highly expected in order to produce robust color-changing hydrogels that can compete with or even surpass the natural skins.

In the future, constant effort will be needed for the following issues. First, bioinspired structural color hydrogels with great prospects have also been reported.<sup>65,66</sup> Robust hydrogels with both fluorescence and structural color-changing properties will be highly desired. Second, it is necessary to obtain a deeper understanding of the molecular basis of natural color-changing processes. These studies will provide continuous inspiration for the innovative development of artificial hydrogels with rapid/sensitive color-switching capacities. Finally, it is known that the high-level multifunctional synergistic behavior of chameleons/cephalopods comes from the correct arrangement of color-changing skins and other soft tissues with disparate functions into heterogeneous topology-optimized structures.<sup>17</sup> Therefore, the future integration of smart FPHs with other soft materials (e.g., organogels<sup>47</sup> and elastomers<sup>2</sup>) via advanced processing methods (e.g., 3D printing) is expected to lead to enhanced or beyond-imagination performance. Meanwhile, application-oriented research should also be encouraged. It is especially important to construct custom-tailored multicolor/multifunctional fluorescent polymeric hydrogel devices according to the specific requirements of one certain application. Such studies are essential to promoting the exciting advance and long-term development of smart FPHs.

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