

## REVIEW

# Progress in aggregation-induced emission-active fluorescent polymeric hydrogels

Wei Lu<sup>1,2,3</sup> | Shuxin Wei<sup>1,2</sup> | Huihui Shi<sup>1,2</sup> | Xiaoxia Le<sup>1,2</sup> | Guangqiang Yin<sup>1</sup> | Tao Chen<sup>1,2</sup> <sup>1</sup> Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Chinese Academy of Sciences, Ningbo Institute of Materials Technology and Engineering, Ningbo, China<sup>2</sup> School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing, China<sup>3</sup> Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology, Guangzhou, China**Correspondence**Tao Chen, Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.  
Email: tao.chen@nimte.ac.cn**Funding information**

National Natural Science Foundation of China, Grant/Award Numbers: 52073297, 21774138, 51773215; Key Research Program of Frontier Sciences, Chinese Academy of Sciences, Grant/Award Number: QYZDB-SSW-SLH036; Youth Innovation Promotion Association of Chinese Academy of Sciences, Grant/Award Number: 2019297; Open Fund of Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology, Grant/Award Number: 2019B030301003

**Abstract**

Aggregation-induced emission (AIE)-active fluorescent polymeric hydrogels (FPHs) are the marriage of AIE-active materials and polymeric hydrogels. Different from the widely studied AIE-active materials that are primarily used in solution or dry solid state, they feature a three-dimensional crosslinked polymer network that can absorb water without dissolving. Consequently, they are known to bear many advantageous properties such as soft wet nature, tissue-like mechanical strength, biocompatibility, biomimetic self-healing feature, facilely tailored structure, as well as responsive fluorescence and volume/shape changes, thus representing a promising category of luminescent materials with many frontier uses. This Review is intended to give a systematic summary of the recent progress in this young but flourishing research area, with particular focus on their design and preparation. Current challenges and future outlooks in this field are also discussed in order to attract new interests and inspire more efforts.

**KEYWORDS**

aggregation-induced emission, fluorescence, polymeric hydrogel

**INTRODUCTION**

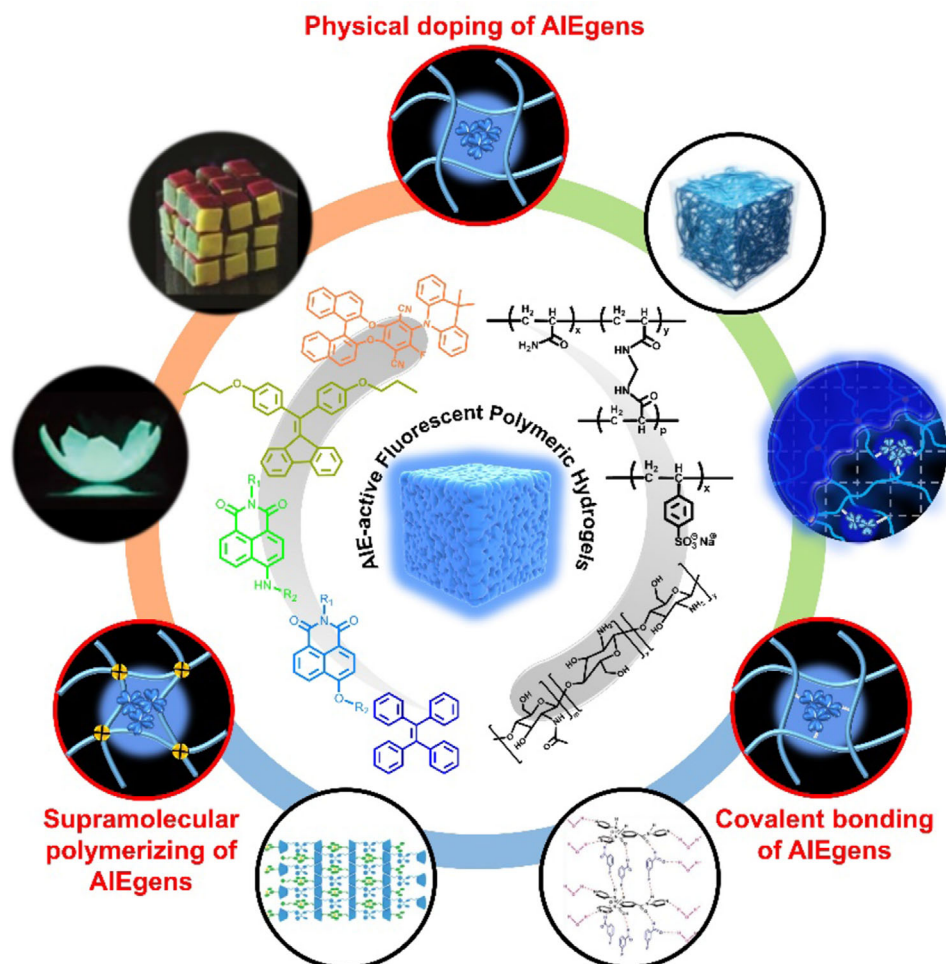
In nature, a large number of marine mollusk shells and tissues are found to exist in quasi-solid hydrogel state, and have evolved to utilize intelligent luminescent behavior for communication, camouflage, or reproduction purposes.<sup>[1,2]</sup> One typical example is Atolla Jellyfish that was reported to exhibit remarkable bioluminescent intensity change when there is threat perception. Inspired by these interesting natural systems, great efforts have been devoted to introducing fluorescent moieties into polymeric hydrogels to produce fluorescent polymeric hydrogels (FPHs) with tunable fluorescence color/intensity property.<sup>[3–12]</sup> As a marriage of polymeric hydrogels and fluorescent materials, FPHs potentially integrate the merits of both materials, including intrinsic soft wet nature, tissue-like mechanical strength, biocompatibility, biomimetic self-healing feature, facilely tailored structure, as well as responsive fluorescence, and volume/shape

changes.<sup>[13–15]</sup> These appealing properties make FPHs unique from the widely investigated fluorescent polymeric materials that are primarily used in solution or dry solid state. It thus presents an attractive opportunity to broaden the list of fluorescent materials and expand into many potential frontier uses, including smart display, optical sensing, bioimaging, bio-inspired soft actuators/robotics, information coding, and encryption.<sup>[16–18]</sup>

Among various potential building blocks for FPHs, the fluorophores with aggregation-induced emission (AIE) nature are of particular research interest.<sup>[19,20]</sup> First of all, most AIEgens are known to be hydrophobic organic molecules with nonplanar propeller-shaped configuration, which are nearly nonfluorescent as the molecular state, but emit intense light as the aggregate state. Consequently, largely enhanced fluorescence can be ensured in the hydrophilic hydrogel matrix where the spontaneous aggregation of AIEgens restricts their intramolecular motions. Second, since the

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2021 The Authors. *Aggregate* published by John Wiley & Sons Australia, Ltd on behalf of South China University of Technology and AIE Institute



**SCHEME 1** Schematic illustration showing the synthetic strategy of aggregation-induced emission (AIE)-active fluorescent polymeric hydrogels (FPHs)

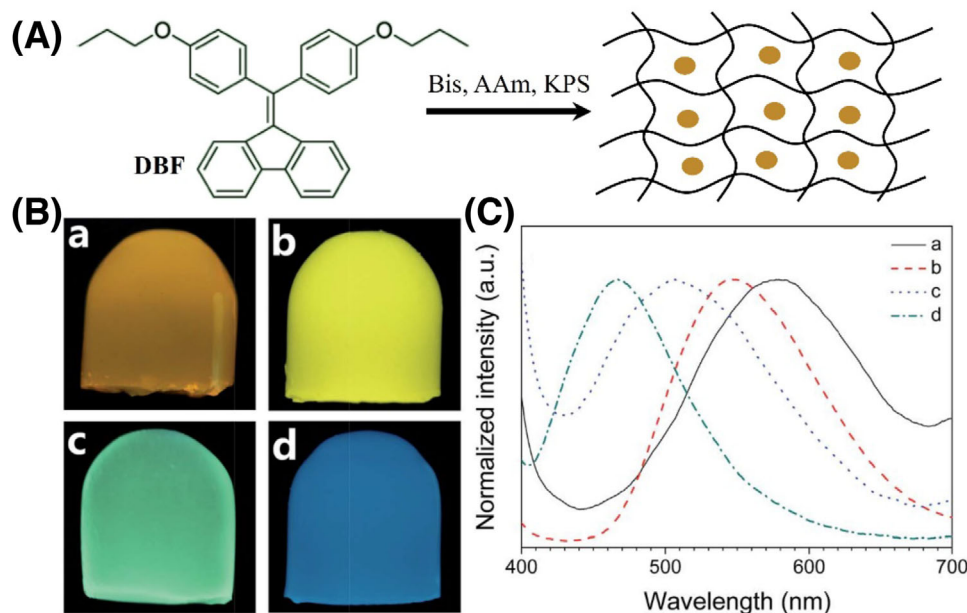
first reported organic AIEgen in 2001 by Prof. Tang,<sup>[21]</sup> great efforts have been globally devoted to developing new types of organic AIEgens with different skeletons, functions, and fluorescence colors,<sup>[22,23]</sup> including tetraphenylethene (TPE), substituted naphthalimide (NI),<sup>[24]</sup> and so forth. These impressive advances have laid a solid foundation for the construction of robust FPHs with versatile uses. Furthermore, the encapsulation of organic AIEgens by the hydrophilic crosslinked polymeric network is essential to improving the environmental friendliness and biocompatibility of AIE-active materials, which is especially important for many bio-related and soft robotic applications.<sup>[25]</sup>

Up to now, although the research on AIE-active FPHs is still in infancy, a number of elegant studies have been reported.<sup>[26–37]</sup> Nevertheless, there is no reported review to summarize the progress on these flourishing materials. Herein, we try to give a systematic overview on the construction and fluorescence properties of AIE-active FPHs. Since most reported FPHs are based on organic AIEgens, we thus classify FPHs primarily depending on the synthetic strategy, including physical doping, covalent bonding, and supramolecular polymerization of organic AIEgens into crosslinked polymer networks (Scheme 1). Subsequently, a brief introduction is provided for some important examples prepared from AIE-active inorganic–organic hybrid metal nanoclusters. Current challenges and future perspectives are also discussed.

## AGGREGATION-INDUCED EMISSIVE POLYMERIC HYDROGELS BASED ON ORGANIC AIEGENS

### Physical doping AIEgens into polymeric hydrogels

Generally, most of the reported organic AIEgens are hydrophobic and thus have a strong tendency to form the fluorescent aggregates with largely enhanced emission in hydrophilic matrix. Therefore, they are ideal building blocks for the construction of highly fluorescent polymeric hydrogels. To do this, the most straightforward strategy is directly blending one AIE molecule into the crosslinked polymer network. For example, Wang and coworkers presented a series of intelligent luminescent hydrogels with responsive fluorescence color change by physically incorporating a propeller-shaped di(4-propoxyphenyl)-dibenzofulvene (DBF) into chemically crosslinked poly(acrylamide) hydrogel (Figure 1A).<sup>[26,27]</sup> In this hydrophilic hydrogel matrix, hydrophobic DBF molecules tended to form brightly fluorescent aggregates. Importantly, the aggregation extent of the organic AIEgens was largely affected by introducing acetonitrile into the hydrogel matrix, because acetonitrile was a good solvent for DBF. As a consequence, the emission colors of the as-prepared hydrogels could be facily regulated to cover orange, yellow, green, and blue, depending on the



**FIGURE 1** (A) Chemical structure of DBF, as well as schematic illustration of the hydrogels. Bis, AAm, and KPS are bis-acrylamide, acrylamide, and potassium persulfate, respectively. (B) Photos of the hydrogel samples with different water contents (a: 90%, b: 70%, c: 60%, d: after being frozen in liquid  $N_2$  and thawed at room temperature), and (C) respective fluorescence spectra. Reproduced with permission: 2014, The Royal Society of Chemistry<sup>[26]</sup>

volume ratio of water/acetonitrile (Figure 1B,C). Following this study, they further found that the aggregation morphologies of DBF luminogens in hydrogels could be regulated by the freezing–thawing process. In these pioneering contributions, Wang et al. demonstrated the possibility to vary both fluorescence intensity and color of FPHs by controlling the aggregation extent of the embedded AIEgens in response to external stimuli.

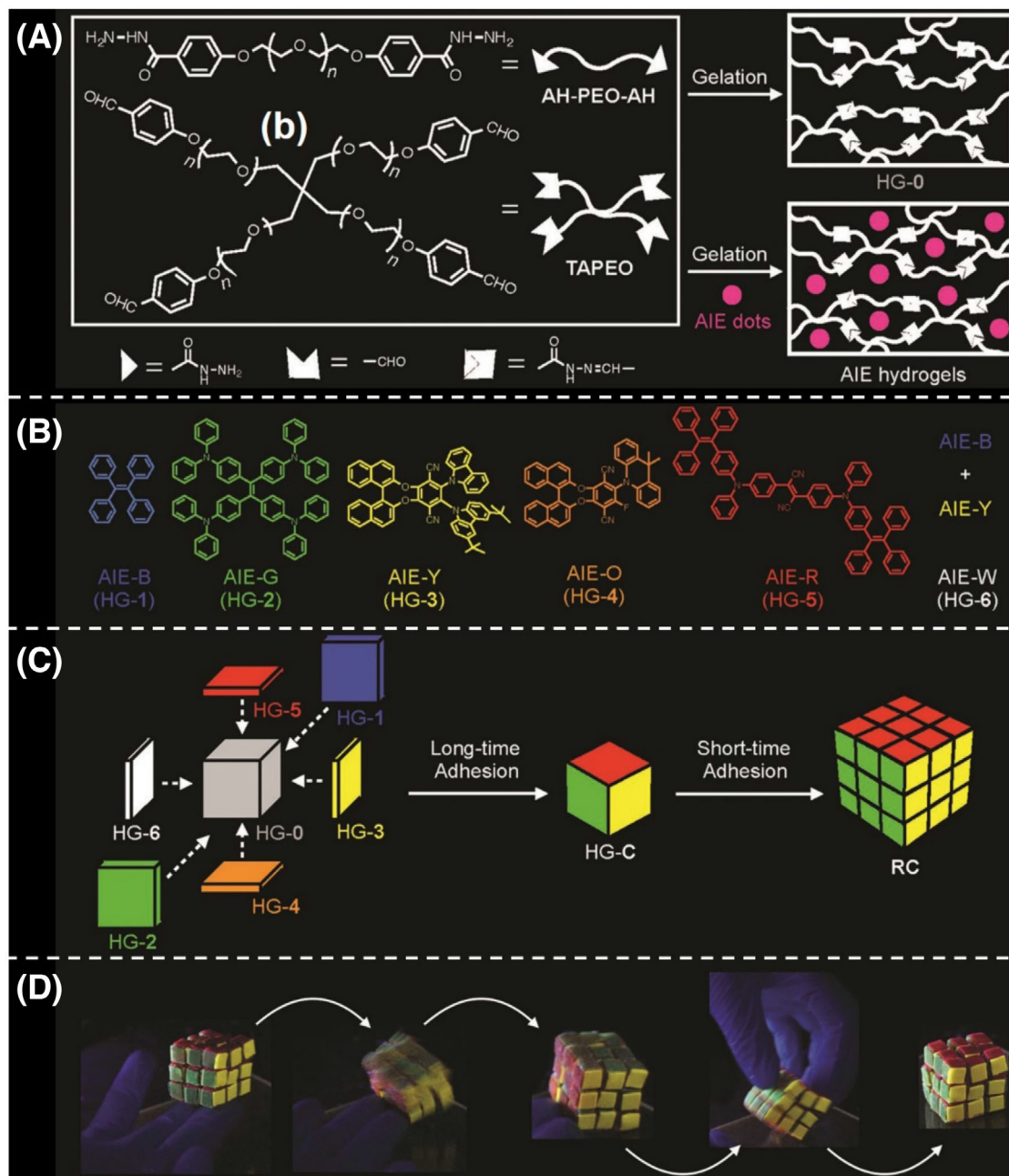
Besides, Ji and coworkers physically introduced several different-colored AIEgens into crosslinked polymeric hydrogels prepared from acylhydrazine-terminated polyethylene oxide (PEO) and tetra-aldehyde-terminated PEO (Figure 2A,B).<sup>[28]</sup> Owing to the dynamic and reversible nature of the formed acylhydrazone bonds, the obtained multicolor fluorescent hydrogel films could be easily bonded to one non-fluorescent hydrogel cube to form a functional macroscopic “Rubik’s Cube (RC)” (Figure 2C). Interestingly, this hydrogel analog can behave like a real RC, in which the adhered fluorescent hydrogel films can be easily rotated by hands to produce interchangeable multicolor fluorescent patterns (Figure 2D) that may find uses in selective colorimetric sensor arrays and information storage. By using similar AIEgens, they further fabricated muscle-like structured hydrogels that show the unprecedented AIEgen-guided selective self-healing behavior.<sup>[29]</sup> Very recently, they blended a pH-responsive AIEgen (tetra-(4-pyridylphenyl) ethylene, TPE-4Py) into the crosslinked poly(acrylamide/sodium 4-styrene sulfonate) network to develop a biomimetic fluorescent hydrogel actuator (Figure 3A).<sup>[30]</sup> In acidic conditions, the TPE-4Py molecules are protonated and thus capable of stable binding to the negatively charged benzene sulfonate groups along the polymer chain (Figure 3B). When the environment was changed to be neutral or alkaline, the hydrophobic TPE-4Py tends to form aggregates, leading to both emission color change and volume shrinkage of the active layer. As a result, pH-triggered synergistic emission color/shape change was observed for the specially designed three-armed bilayer hydrogel actuator (Figure 3C). In parallel, the

TPE-4Py molecule has also been physically introduced into poly(acrylic acid) hydrogel matrix to produce a smart FPH system with temperature-responsive fluorescence response, because the motion of the polymer segments,<sup>[31]</sup> as well as the ionic interaction between TPE-4Py and carboxyl groups, are known to be dependent on temperature change. Furthermore, Zhao and coworkers simultaneously introduced red light-emitting europium complexes as internal reference and pH-responsive blue fluorescent quaternary ammonium tetraphenylethylene derivative as indicator into one polymeric hydrogel matrix.<sup>[32]</sup> The as-prepared dual-emissive hydrogel displayed a linear fluorescence response between pH 6.5 and 7.6 with a resolution of 0.1 unit, which had been successfully used for the discrimination of normal/tumor tissue *in vivo*. All of these impressive recent advances not only greatly broadened the list of AIE-active FPHs, but also clearly demonstrated their huge application potential in many frontier fields such as information encoding/transformation, bio-inspired soft robotics, bio-sensing/medicinal diagnostic chips, and so forth.

## Covalent bonding AIEgens into polymeric hydrogels

Hydrophobic organic AIEgens have also been covalently grafted onto crosslinked polymer chains to produce FPHs. This covalent bonding strategy is helpful to avoid unexpected leakage of small-molecule AIEgens, which is possibly encountered by the FPHs prepared from the above-discussed physical incorporation strategy. To do this, organic AIEgens could be covalently anchored onto crosslinked polymer either as pendant/terminal groups or in the main polymer chain according to various demonstrated synthetic strategies that are described in the following sections.

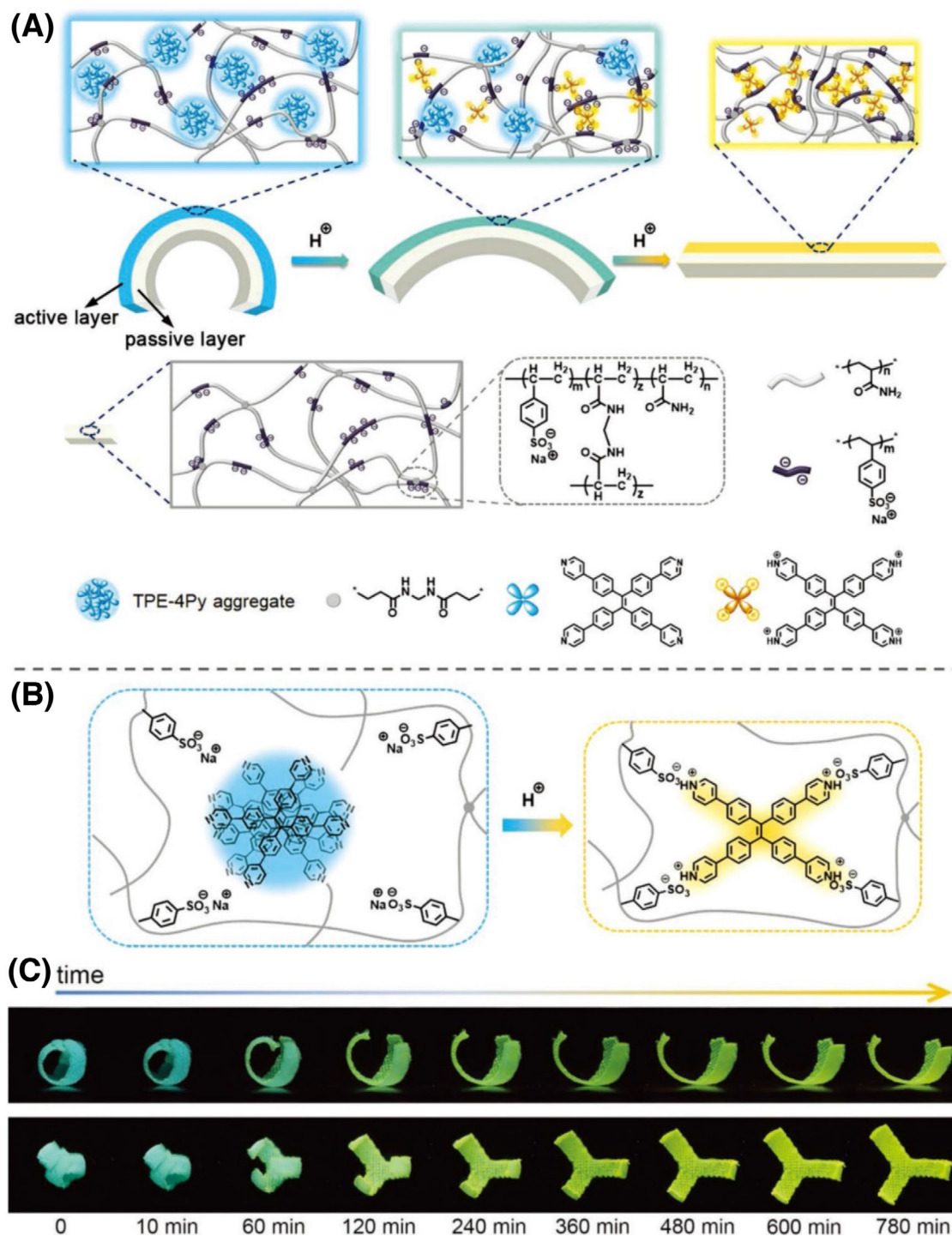
When the responsive AIEgen-containing vinyl monomers were radically copolymerized with hydrophilic comonomers and crosslinkers, the hydrophobic AIEgens would have



**FIGURE 2** (A) Illustration showing the preparation of different-colored fluorescent polymeric hydrogels by physical doping of various organic AIEgens into the acylhydrazone-bonded PEO hydrogels. (B) Chemical structures of these organic AIEgens. (C) Schemes illustrating the construction of Rubik's cube-like FPHs. (D) Images showing the procedure to produce changeable patterns by rotating the Rubik's cube-like FPHs both horizontally and vertically. Reproduced with permission: 2019, Wiley-VCH<sup>[28]</sup>

covalently connected onto the hydrophilic crosslinked polymer network as pendant groups, leading to intelligent FPHs with tunable fluorescence property. In a previous contribution,<sup>[33]</sup> we utilized *N,N*-dimethylethylenediamine to substitute the naphthalimide (NI) luminogen to give an AIE-active 4-(*N,N*-dimethylaminoethylene) amino-*N*-allyl-1,8-naphthalimide (DEAN) monomer with propeller-like conformation. The specially designed DEAN monomer was weakly fluorescent under neutral conditions, but emitted intense yellowish light under acid conditions via the protonation of the dimethyl amino groups to inhibit its photoinduced electron transfer (PET) with NI luminogen. As expected, the AIE-active FPH prepared by copolymerizing DEAN into chemically crosslinked poly(acrylamide) network also exhibited tunable emission response upon pH stimulation. Further

study revealed that the fluorescence intensity of DEAN can also be controlled by  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  but in different manners (Figure 4).<sup>[34]</sup> Specifically, both  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  can coordinate with the nitrogen atom of dimethylamino group and the nitrogen atom of naphthalimide ring, significantly reducing the PET process to enhance the fluorescence intensity. Since the  $\text{Al}^{3+}$ -DEAN complex ( $9.08 \times 10^4 \text{ kcal mol}^{-1}$ ) has higher total energy than the  $\text{Zn}^{2+}$ -DEAN complex ( $9.07 \times 10^4 \text{ kcal mol}^{-1}$ ), indicating that  $\text{Al}^{3+}$ -DEAN complex is much easier to be dissociated by the produced  $\text{NH}_3$ . They thus have different fluorescence intensity reduction kinetics under alkaline conditions (Figure 4G). As a consequence, the fluorescence of the AIEgen-grafted poly(acrylamide) hydrogel containing urease enzyme could be spatiotemporally regulated in urea solutions, because urease enzyme was able

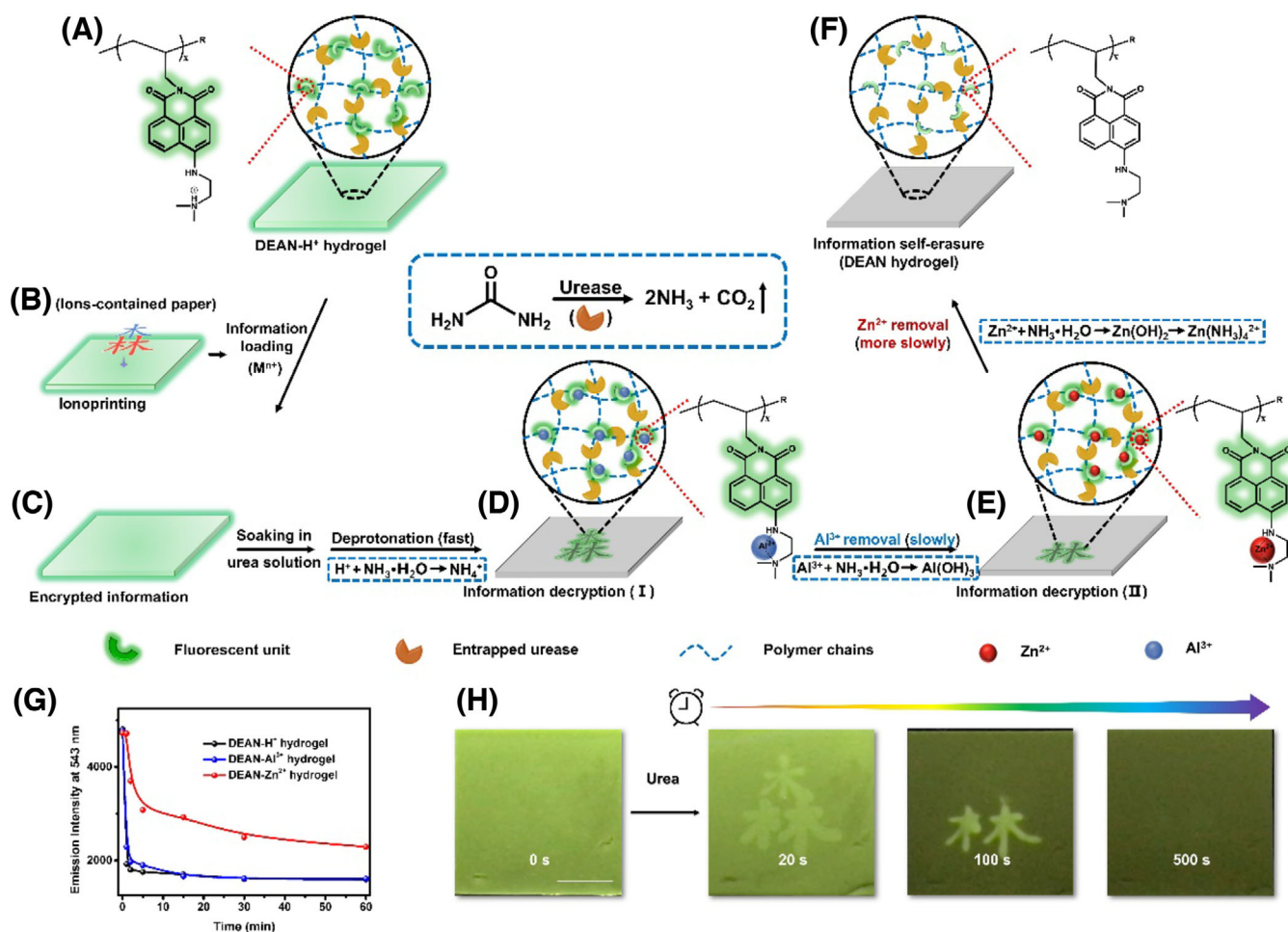


**FIGURE 3** (A) Schemes showing the synergistic shape and fluorescence color change of the TPE-4Py/PAS-based bilayer hydrogel actuator. The chemical structures of the hydrogel and TPE-4Py AIEgen have also been given. (B) The proposed mechanism for the pH-sensitive fluorescence color change. (C) Simultaneous fluorescence color change and complex shape deformation of the three-arm-shaped bilayer actuator. Reproduced with permission: 2020, Wiley-VCH<sup>[30]</sup>

to decompose urea into  $NH_3$ . Based on these findings, a snapchat-like information decryption system was realized for the first time, in which confidential information encoded on the hydrogel could be stepwise decrypted and further automatically erased in urea solution (Figure 4H).

Even if the AIEgens themselves are not sensitive to external stimuli, it is still possible to endow the obtained FPHs with tunable fluorescence behavior, because the aggregation extent of AIEgens can be facily regulated by the conformational change of polymer chains in response to certain external stimuli. Recently, we presented a typical system

by copolymerizing a phenoxy-substituted naphthalimide monomer (PhAN) into the thermo-responsive PNIPAM network.<sup>[35]</sup> It was weakly fluorescent at room temperature, but emitted intense blue light above volume phase transition temperature (about  $33^\circ C$ ) due to the shrinkage of naphthalimide-grafted PNIPAM polymer network and subsequently more compact NI aggregation. However, this FPH example was restricted to only two-state switching of fluorescence property (on-off emission response upon temperature change), limiting its potential use for on-demand information display or anticounterfeiting. To this end, another interesting

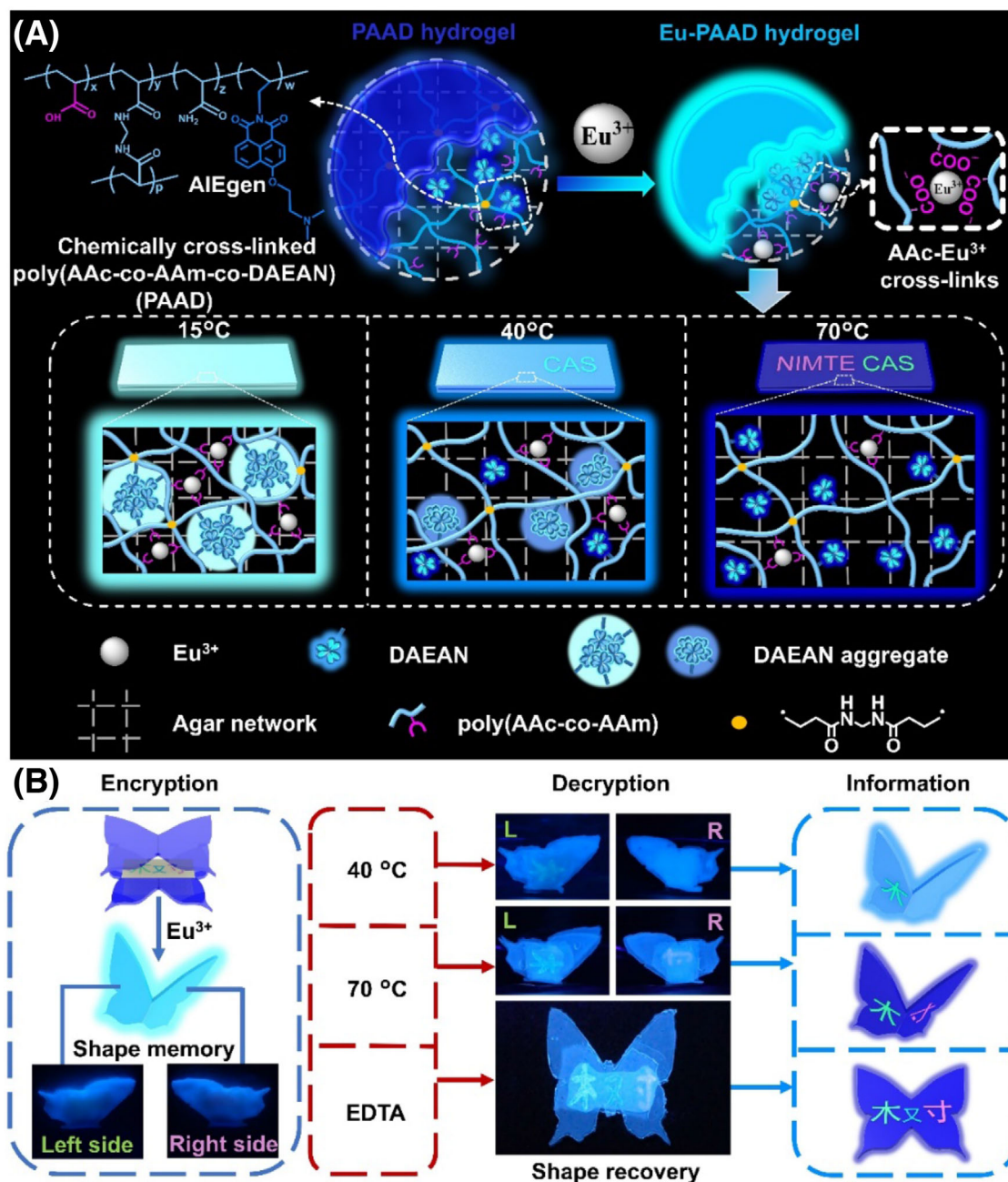


**FIGURE 4** (A) Schematic illustration showing the preparation of the naphthalimide luminogen-grafted FPH system for instantaneous information storage. (B) The process to encrypt information by locally ionoprinting the hydrogel with Zn<sup>2+</sup> as well as Al<sup>3+</sup> that can chelate naphthalimide moieties. (C–F) Stepwise decryption and self-erasure processes of the encoded information in urea solution through enzyme-catalyzed reaction to produce NH<sub>3</sub>, which can decompose the complexes. (G) Changes in the peak fluorescence intensities at 543 nm of DEAN-H<sup>+</sup>, DEAN-Zn<sup>2+</sup>, and DEAN-Al<sup>3+</sup> hydrogels as a function of immersing time in urea solution. (H) Photos showing the stepwise information decryption and self-erasure. Reproduced with permission: 2020, Wiley-VCH<sup>[34]</sup>

double-network FPH example was further developed.<sup>[36]</sup> As shown in Figure 5A, the system was prepared by radical polymerization of a dimethylaminoethoxy-substituted naphthalimide monomer (DAEAN) into the chemically crosslinked poly(acrylic acid-co-acrylamide) (poly(AAc-AAm)) network that is interpenetrated with a hydrogen-bonded agar network. Owing to the spontaneous aggregation of substituted naphthalimide AIEgens, the as-prepared hydrogel emitted bright blue light. Its emission intensity could be further enhanced by the formation of lanthanide coordinated polymer segments via AAc–Eu<sup>3+</sup> crosslinks that cause heavier AIEgen aggregation. Benefiting from thermo-induced stepwise dissociation of AAc–Eu<sup>3+</sup> crosslinks and AAc–AAm hydrogen bonds to regulate the crosslinked polymer chain conformation, the developed system was endowed with thermo-triggered multistate fluorescence-switching capacities. Additionally, the introduction of the dynamic and reversible AAc–Eu<sup>3+</sup> crosslinks enabled us to program the AIE-active FPH into various complex 3D structures by the combined shape memory and self-healing effects. On the basis of these appealing advantages, a potential application in the construction of 3D anticounterfeiting platforms for high-level information encryption and on-demand decryption was further demonstrated (Figure 5B). Besides temperature, other

external stimuli (e.g., solvent) that is capable of changing the crosslinked polymer chain conformation have also been used to affect the fluorescent property of FPHs, as is evidenced by the phenyldiaminotriazine-grafted poly(acrylamide-co-oligo(ethylene glycol) methyl ether methacrylate) hydrogel whose fluorescent behavior depended on the swelling degree.<sup>[37]</sup> All of these systems have demonstrated the potential of preparing stimuli-responsive FPHs by grafting AIEgens as pendant groups. Considering the fact that many different external stimuli (e.g., pH, salts, light, electricity) are known to affect smart polymer chain conformation,<sup>[38–41]</sup> more research efforts are expected to construct robust FPHs with multiresponsiveness and versatile uses.

Now that the conformation change of the crosslinked polymer chains is able to affect the fluorescent property of the grafted AIEgens, people are wondering whether it is possible to use highly sensitive fluorescence color/intensity change of AIEgens to visually trace the polymer gelation process. As detailed in the elegant work reported by Wang et al.,<sup>[42]</sup> the answer is yes. As shown in Figure 6A, they labeled chitosan with TPE luminogen as pendant group, which was briefly named as TPE-CS. For TPE-CS solution, no specific fluorescence patterns were found in the confocal laser scanning fluorescence microscope image (Figure 6C). As the thermal

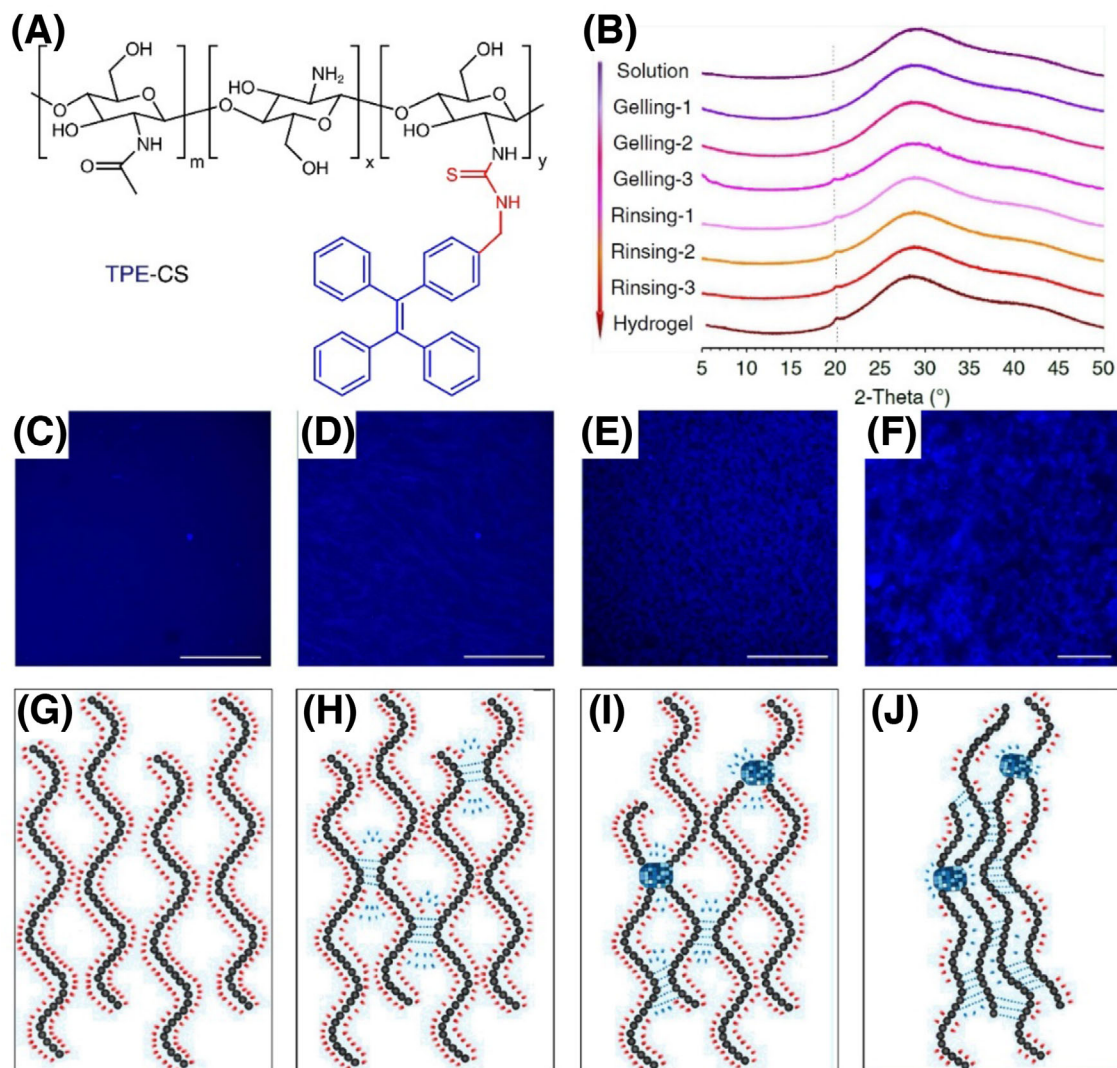


**FIGURE 5** (A) Illustration showing the chemical structure of the PAAD hydrogel grafted with AIE-active naphthalimide luminogen as the pendant group, as well as the proposed mechanism for its thermoresponsive multistate fluorescence response. (B) FPH-based 3D anticounterfeiting platform for on-demand decryption, which was prepared by folding 2D information carrier into 3D shape by hands and then immersed into  $\text{Eu}^{3+}$  solutions to fix such 3D hydrogel structure via shape memory process. Different information would appear at 40°C (“木”) and 70°C (“村”). The whole information (“树”) was decrypted when ethylenediaminetetra acetic acid disodium salt was used to break the  $\text{Eu}^{3+}$ -AAc crosslinks to induce shape recovery from 3D to 2D. Reproduced with permission: 2020, Wiley-VCH<sup>[36]</sup>

gelation proceeded, some bright areas gradually appeared and kept growing over time (Figure 6D–F). This visual observation, together with other pseudo in situ investigations (e.g., XRD investigation shown in Figure 6B), revealed the mechanism of gelation process, focusing on the formation of crosslinking points via hydrogen bonds and crystalline. This is the first time that people have utilized AIE fluorescent imaging for the visualization of entire gelation process of CS, which is beneficial to the fundamental understanding of gelation process, as well as the microstructure modulation of hydrogel materials.

Another general method to produce AIE-active FPHs is to covalently link organic AIEgens as the terminal ends of

crosslinked polymer chains. One impressive example was reported by Zhang et al.<sup>[43]</sup> The material was obtained by conjugating a salt-responsive peptide with the TPE luminogen. In the presence of NaCl, the monodisperse peptide oligomers self-assembled into brightly blue light-emitting polymeric hydrogel. However, the formation of this salt-responsive peptide hydrogel was limited to one-way process and not reversible. Therefore, they redesigned the system by changing the peptide sequence to TPE-MAX depicted in Figure 7A.<sup>[44]</sup> Because of its pH-responsive nature, this alternative peptide could self-assemble into crosslinked polymeric structures with intense fluorescence (Figure 7B) via intermolecular association of apolar residues in alkaline solutions



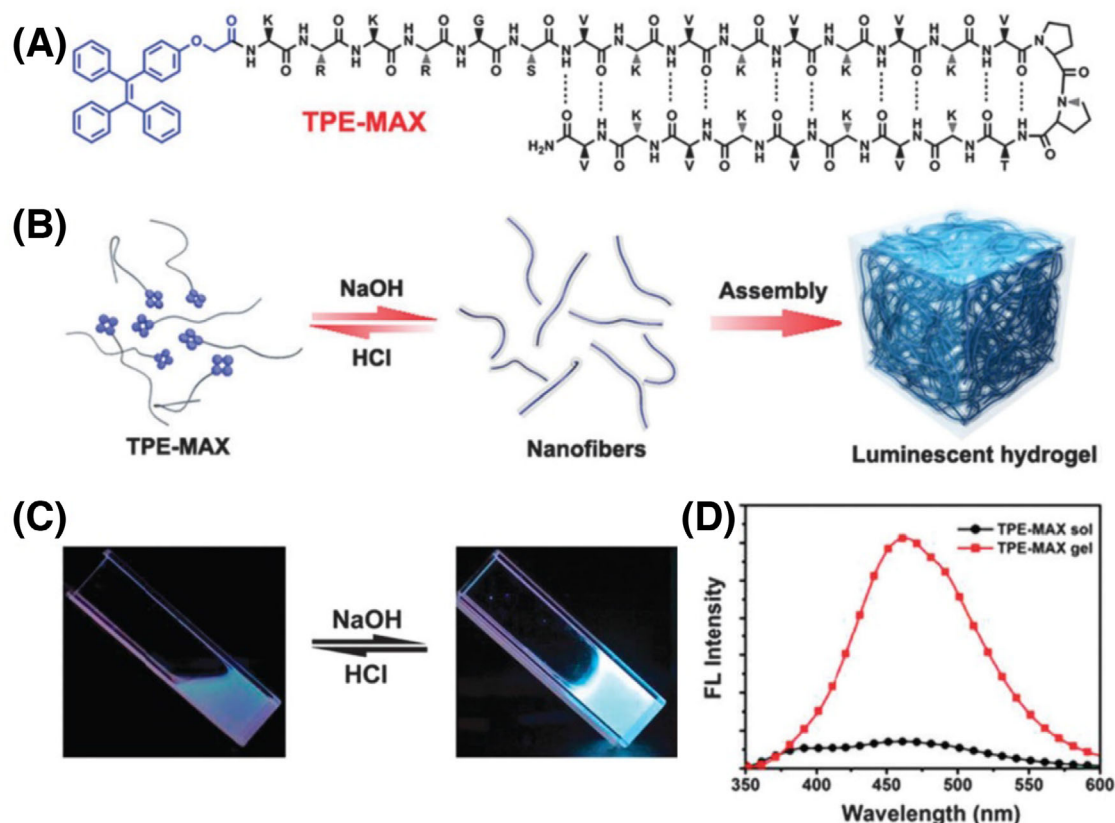
**FIGURE 6** (A) Chemical structure of the TPE-functionalized chitosan polymer, TPE-CS. (B) XRD patterns recorded during the gelation process of TPE-CS, illustrating the evolution of crystalline. (C–F) Confocal laser scanning fluorescence microscope images recorded during the gelation process from solution to hydrogel. Scale bar is 250  $\mu\text{m}$  for (C–E) and 25  $\mu\text{m}$  for (F). (G–J) Schematic illustration showing the formation of crosslinks during the gelation process. Reproduced with permission: 2016, Nature Publishing Group<sup>[42]</sup>

(pH 10.0), leading to the heavy aggregation of TPE moieties. When pH was adjusted to acid conditions (pH 6.0), the brightly blue light-emitting hydrogel redissociated into solution with weak emission (Figure 7C,D). This pH-sensitive sol–gel–sol transition could be cycled for several times. This smart FPH system was potentially suitable for serving as the luminous sensors in various biological processes, because many biological metabolic pathways and chemical reactions are associated with pH changes. In addition to postmodification, another important design is to employ AIEgen-containing initiators to initiate polymerization. Recently, Wang et al. and Hou et al. reported a series of AIE-active FPH systems by employing a TPE-containing RAFT reagent to induce the radical polymerization of diacetone acrylamide and *N,N*-dimethylacrylamide,<sup>[45,46]</sup> followed by the crosslinking reaction with diacylhydrazide. Due to the reversible nature of diacylhydrazide bonded interactions, these systems have multifunctions such as self-healing, responsive fluorescence, and good biocompatibility, holding great potential in bioscience and biotechnology.

To covalently graft AIEgens into polymeric hydrogels, another convenient method is to embed the AIEgens in the

polymer main chain. In this design, it is usually necessary to synthesize the modified AIEgens with two or more polymerization sites (e.g., -OH, -NH<sub>2</sub>). Their further reaction with comonomers containing bi- or multifunctional -COOH or -NCO groups will produce the targeted FPHs with unique alternating and multiblocked polymer chains. Especially, when the comonomers are hydrophilic, the obtained multiblocked amphiphilic macromolecules tend to self-assemble into AIE-active micelles in the hydrogel matrix. These micelles not only provide stable AIEgen nanoaggregates to ensure intense fluorescence, but also protect the AIEgens from exposure to hydrophilic issues, suggesting their good biocompatibility and thus huge bio-related uses, as is evidenced by the elegant work by Liow and coworkers.<sup>[25]</sup> They constructed a thermogelling copolymer consisting of hydrophobic TPE and poly(propylene glycol) segments, and hydrophilic poly(ethylene glycol) segment (Figure 8A). Since the restricted intramolecular rotation process of AIEgens were enhanced in the close-packed hydrogel, this AIE-active thermogel exhibited exceptionally high emission (Figure 8B). The hydrogel was also proved to be nontoxic. These appealing merits allowed the FPH to serve as an efficient





**FIGURE 7** (A) Chemical structure of the TPE-terminated peptide, TPE-MAX. (B) The proposed mechanism for its pH-sensitive gelation process. (C) Photos showing the pH-sensitive sol-to-gel transition process, as well as (D) the fluorescence spectra of the hydrogel and solution. Reproduced with permission: 2015, The Royal Society of Chemistry<sup>[44]</sup>

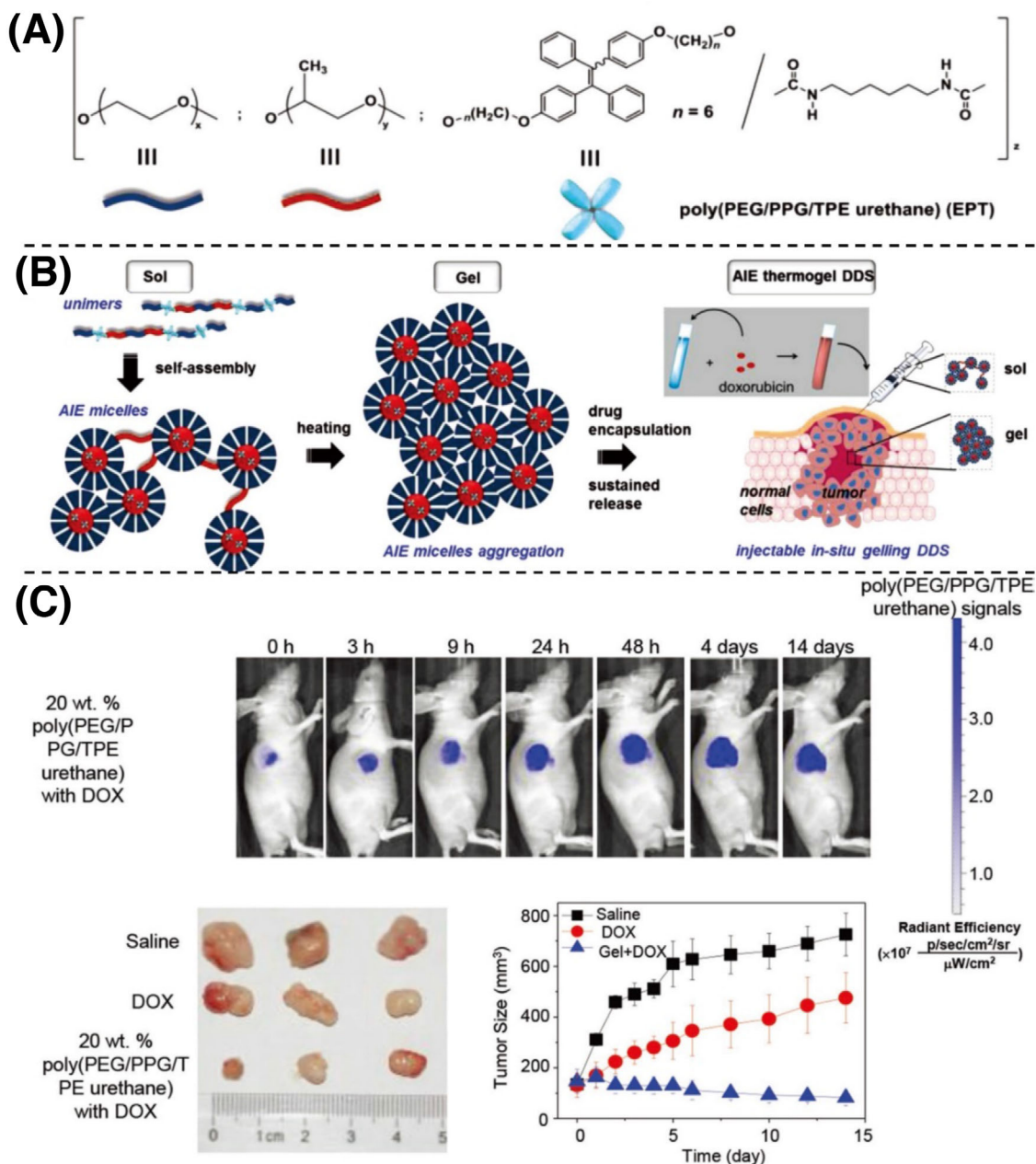
self-indicating system with intense emission for long-term and real-time *in vivo* drug-release monitoring (Figure 8C). However, despite this impressive advance, the development of AIE-active FPHs is still largely lagging, partially because of the tedious synthetic procedures. More efforts are thus suggested to exploring new and simple synthetic methods or the employment of well-organized supramolecular interactions in order to construct powerful FPHs.

### AIE-active FPHs via supramolecular polymerization

AIE-active FPHs can also be constructed by the spontaneous self-assembly process of supramolecular polymerization from low-molecular weight AIEgen-containing monomeric units and comonomeric molecules. Common driving forces for supramolecular polymerization include electrostatic interactions, host-guest interactions, hydrogen bonds, and so forth. Compared with chemically crosslinked polymeric hydrogel systems, FPHs prepared by supramolecular polymerization can be tailored regarding of their chemical structures, compositions, and sensitiveness to external stimuli owing to the highly dynamic and reversible nature of supramolecular interactions.<sup>[47–49]</sup> As a consequence, not only tunable fluorescence property but also widely adjustable mechanical strength (e.g., gel-to-sol transition) and desirable self-healing features will be realized, indicating their huge potential uses.

Electrostatic interactions are a typical kind of supramolecular interactions between oppositely charged ions (e.g.,

cations like quaternary ammonium units and anions like carboxylate or sulfonate groups). By modifying the organic AIEgens with opposite charges as supramolecular interaction sites, AIE-active supramolecular polymeric hydrogels could be prepared via electrostatic interaction-based supramolecular polymerization/crosslinking. Moreover, since the electrostatic interactions are known to be sensitive to temperature, competitive ions (especially biomolecules), or pH change,<sup>[48]</sup> these AIE-active supramolecular polymeric hydrogels are usually endowed with bioresponsive fluorescence/mechanical properties, suggesting their broad application prospect especially in biological fields. For example, Wang et al. presented a bioresponsive supramolecular fluorescent hydrogel via electrostatic interaction-based supramolecular crosslinking of poly(sodium *p*-styrenesulfonate) (1) and the tetraphenylethene derivative functionalized with two quaternary ammonium groups (2) (Figure 9A).<sup>[50]</sup> The obtained supramolecular hydrogel was stable and highly blue-light-emitting owing to the aggregation of TPE luminogens. When biomolecule such as ATP, which interacted with TPE-Am more strongly than PSS, was added, the supramolecular polymeric network was destroyed to decrease the AIEgen aggregation extent, triggering simultaneous gel-to-sol transition and fluorescence-intensity reduction. As expected, the supramolecular polymeric network could be rebuilt upon the addition of phosphatase ATPase that can decompose ATP, leading to both the hydrogel reformation and the fluorescence recovery. Low cytotoxicity of 1, 2, and the obtained hydrogel were further demonstrated (Figure 9B). On the basis of these advantages, its potential application for cell imaging has been explored (Figure 9C). Very recently, another

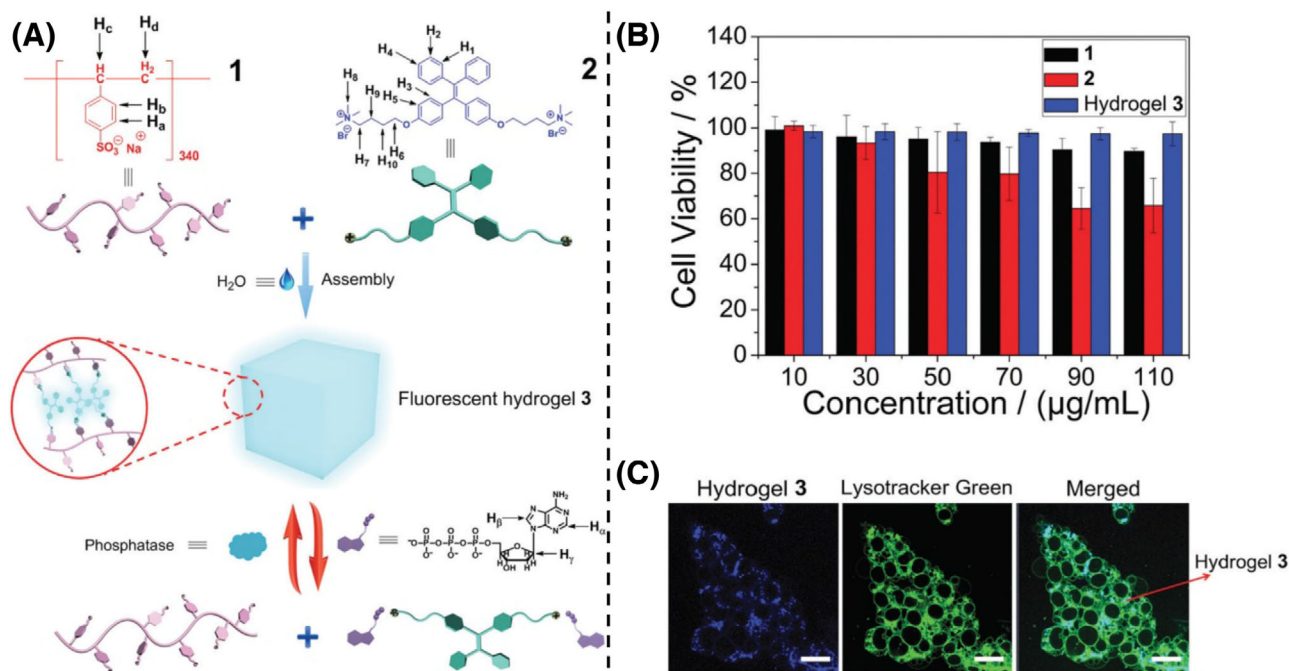


**FIGURE 8** (A) Chemical structure of poly(PEG/PPG/TPE urethane) containing TPE luminogen in the main polymer chain. (B) The proposed mechanism for the gelation process and the preparation of the local drug-delivery system. (C) In vivo noninvasive fluorescence imaging of nude mice bearing HepG2 tumor with postintra-tumoral injection of DOX-loaded thermogel for indicated time points, as well as the comparison of its tumor volume inhibition capacities with other methods. Reproduced with permission: 2017, Wiley-VCH<sup>[25]</sup>

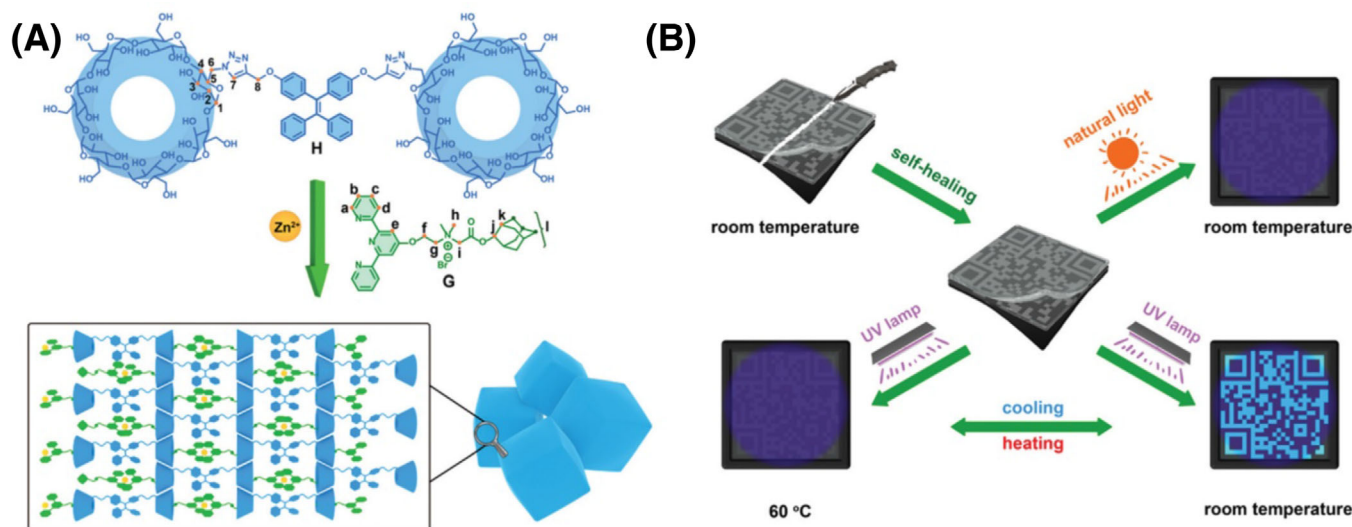
interesting supramolecular polymeric hydrogel was constructed via electrostatic interaction-based supramolecular polymerization/crosslinking between malonic acid and unique AIE-active aromatic thioether luminogen with four self-complementary guadiniumcarbonyl-pyrrole units.<sup>[51]</sup> Both the fluorescence intensity response and the gel-to-sol transition could be induced by various external stimuli, including heat, vortex,  $\text{Et}_3\text{N}$ , trifluoroacetic acid. These solid examples have demonstrated that electrostatic interaction is a promising approach to prepare AIE-active supramolecular hydrogels with tailored responsiveness and versatile uses.

Host-guest interaction is another important driving force for supramolecular polymerization and crosslinking. Owing to its dynamic and reversible nature, AIE-active supramolecular polymeric hydrogels based on host-guest interaction are usually not only responsive to multiple external stim-

uli, but also endowed with satisfying self-healing property that is essential for long-term service. One impressive example was recently reported by Li and coworkers (Figure 10),<sup>[52]</sup> which was prepared by the host-guest interaction between TPE-bridged bis-( $\beta$ -cyclodextrin) ( $\beta$ -CD) and terpyridine-containing adamantane molecules, followed by  $\text{Zn}^{2+}$ -terpyridine coordination interactions. The as-prepared blue-light-emitting hydrogel was proved to show multiresponsiveness to competitive ligands and temperature, and be capable of recovering the damaged area caused by external forces. These satisfying properties enabled the authors to process the supramolecular fluorescent hydrogel into protected quick response (QR) codes with improved durability and security. In parallel, Yao and coworkers utilized host-guest interaction between  $\alpha$ -CD and benzimidazolium-based guest molecule to report one AIE-active SPH system that



**FIGURE 9** (A) Schematic illustration showing the fabrication of AIE-active FPH via electrostatic interactions, as well as its bioresponsive gel-to-sol transition process. (B) Cytotoxicity of **1**, **2**, and hydrogel **3**, which were determined from standard MTT assays using the HEK293 cell line. (C) confocal laser scanning microscopy images of HEK293 cells incubated with hydrogel **3** (scale bar: 20 μm). Reproduced with permission: 2018, The Royal Society of Chemistry<sup>[50]</sup>

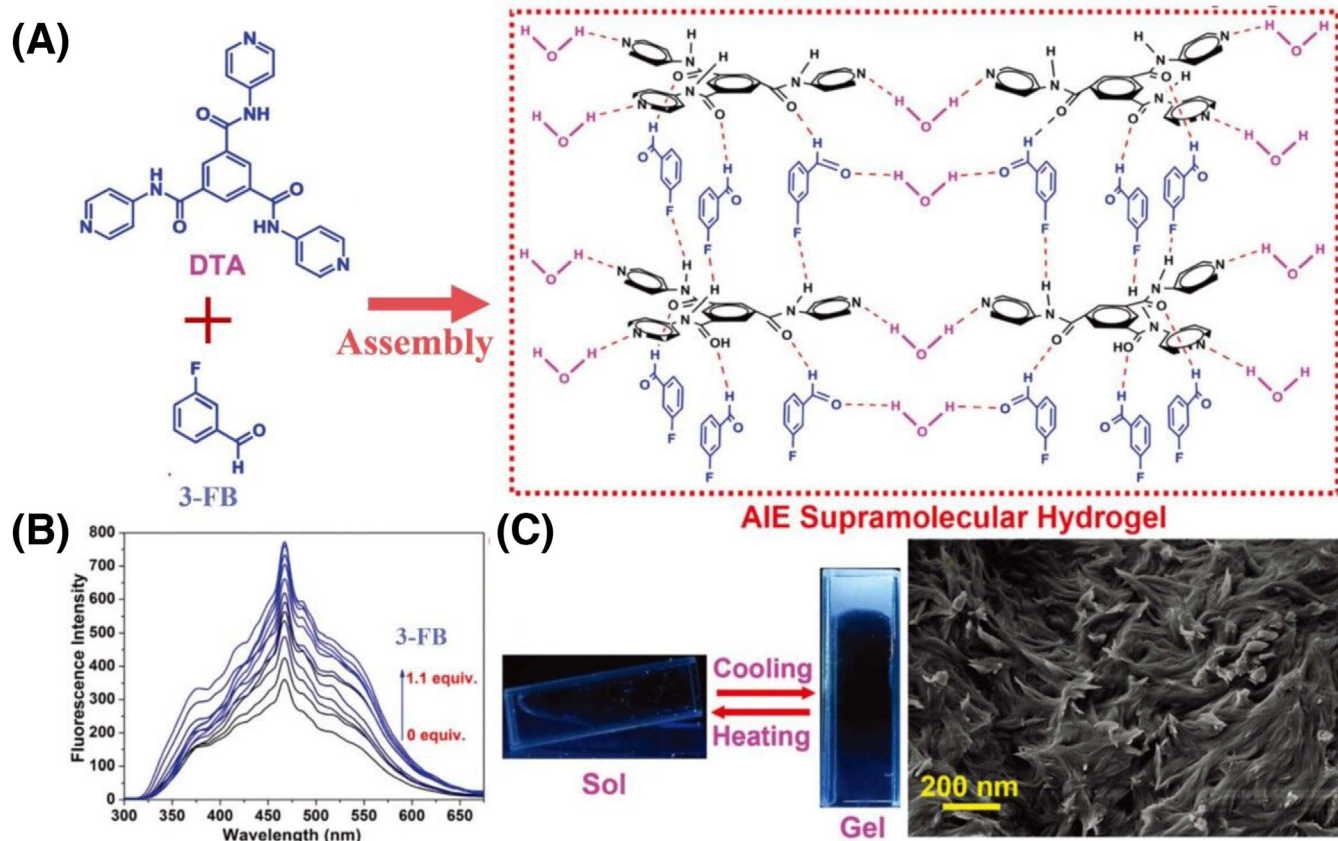


**FIGURE 10** (A) Schematic illustration showing the fabrication of AIE-active FPH via Host-guest interactions, as well as the cartoon showing the protected quick response (QR) codes with improved durability and security. Reproduced with permission: 2020, The Royal Society of Chemistry<sup>[52]</sup>

allowed selective recognition of negative-charged dyes.<sup>[53]</sup> Very recently, Wei et al. utilized the host-guest interaction of cyclodextrin and a cyanostilbene derivative to prepare one AIE-active FPH microreactor with both excellent recyclability and microscopic visualization,<sup>[54]</sup> which was expected to provide a new inspiration for heterogeneous catalysis. Besides cyclodextrin, other host molecules such as Pillar[5]arene has also been employed to construct AIE-active FPH. For example, Zhao et al. employed the host-guest assembly process of *p*-hydroxybenzoic acid-functionalized pillar[5]arene and tri-(pyridine-4-yl)-functionalized trimesic amide moieties to prepare a white-light-emitting hydrogel material suitable for ultrasensitive detection and separation of

Fe<sup>3+</sup>, Pb<sup>2+</sup>, and Cr<sup>3+</sup>.<sup>[55]</sup> All of these contributions not only have demonstrated the huge potential of host-guest interactions to fabricate powerful FPHs, but also moved AIE-active FPHs much closer to practical uses, including reliable long-term display or concealment of encoded information, and sensitive measurement of certain dyes or ions.

Hydrogen bond is also an important type of supramolecular interaction for the construction of AIE-active supramolecular polymeric hydrogels. Usually, one single hydrogen bond is too weak and not sufficient to stabilize supramolecular materials. Therefore, the design of monomeric units with multiple donor and acceptor sites is favorable for preparing supramolecular polymeric hydrogels. For example,



**FIGURE 11** (A) Schematic illustration showing the assembly of AIE-active FPH via hydrogen bonds. (B) Fluorescence spectra of DTA with increasing amount of 3-FB. (C) Photos showing the temperature-sensitive sol-to-gel transition process, as well as the SEM image of the freeze-dried FPH sample. Reproduced with permission: 2019, The Royal Society of Chemistry<sup>[56]</sup>

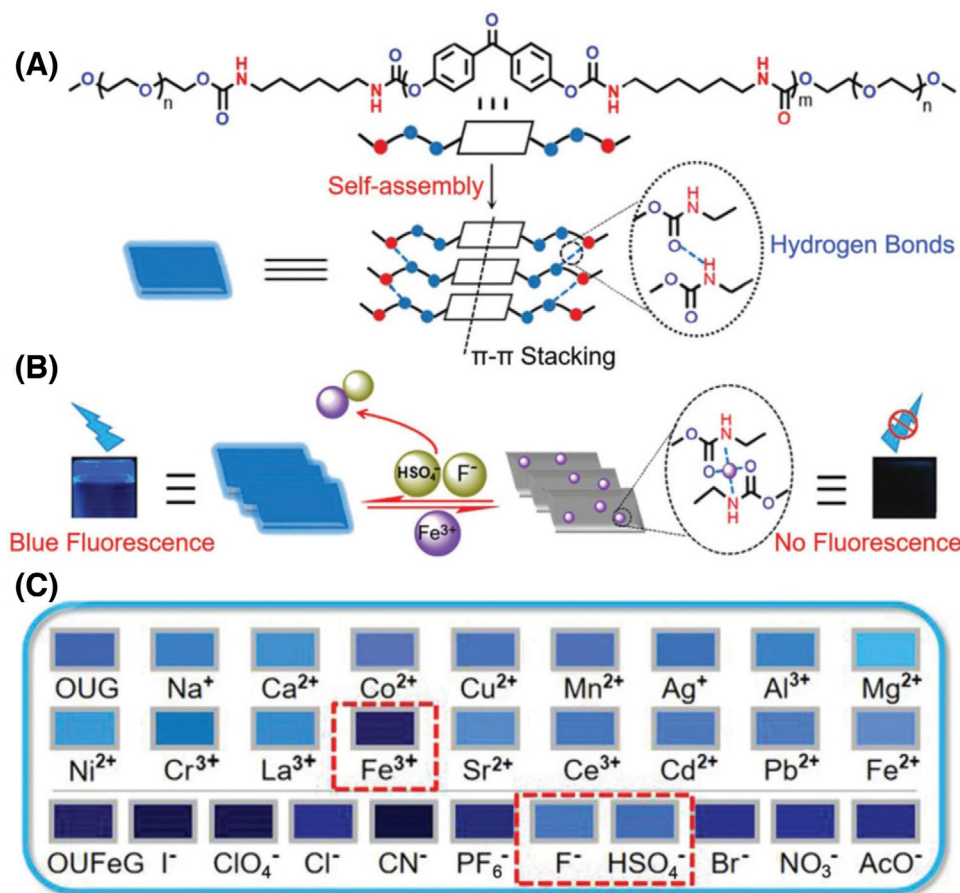
Lin designed and synthesized a host compound  $N^1, N^3, N^5$ -tri(pyridin-4-yl)benzene-1,3,5-tricarboxamide (DTA),<sup>[56]</sup> which could form high-density hydrogen bonds with the guest molecule 3-fluorobenzaldehyde (3-FB) (Figure 11A). This kind of multiple hydrogen-bonded supramolecular polymerization/crosslinking resulted in a supramolecular polymeric hydrogel system with aggregation-induced emission-enhancement property. Benefiting from the high sensitivity of fluorescence-based detection, the DTA host with numerous hydrogen bond donor sites was further used for the selective detection of 3-fluorobenzaldehyde with a detection limit of  $8.87 \times 10^{-9}$  M (Figure 11B). Because of the reversible formation and dissolution of hydrogen bonds upon temperature change, the desirable sol-to-gel transition accompanying with on-off fluorescence response was also demonstrated (Figure 11C).

In view of the relatively weak strength of one single noncovalent interaction, there has been a recent interest to synergize several types of weak interactions in order to develop AIE-active FPHs. For example, Feng and coworkers designed and synthesized an AIE-active oligourethane gelator that could self-assemble into supramolecular hydrogel system through the combination of hydrogen-bonding,  $\pi$ - $\pi$  stacking, and van der Waals interactions (Figure 12A).<sup>[57]</sup> Owing to the weak and dynamic nature of these supramolecular interactions, the fluorescence intensity of the self-assembled system could be selectively adjusted by  $\text{Fe}^{3+}$ ,  $\text{HSO}_4^-$ , and  $\text{F}^-$ , indicating its capacity for real-time detection of these ions (Figure 12B,C). Very recently, Sun et al. also took advantage of hydrogen-bonding,  $\pi$ - $\pi$  stacking, and van der Waals interactions to

present another AIE-active supramolecular hydrogel example with acid/base-triggered transparency/fluorescence response, and further demonstrated its potential use for smart window and secret display materials.<sup>[58]</sup> Besides, Talloj et al. utilized the self-assembly of tetraphenylethylene dipeptides via combined hydrogen-bonding interactions and hydrophobic interactions to fabricate a FPH example with excellent biocompatibility.<sup>[59]</sup> All of these elegant studies have clearly demonstrated the possibility to construct multifunctional FPHs via a combination of various supramolecular interactions.

## AIE-ACTIVE POLYMERIC HYDROGELS PREPARED FROM INORGANIC-ORGANIC HYBRID METAL NANOCLUSTERS

The AIE phenomenon, despite being firstly discovered in organic molecules with propeller-like conformation, has recently been expanded into luminescent metal nanoclusters (NCs), which are prepared either through reduction of metal cations in the presence of a variety of ligands or by coordination between metal cations and ligands. Because of their good photostability, biocompatibility, and ultrasmall size, luminescent NCs have recently been assembled into polymeric hydrogels by Goswami and coworkers.<sup>[60]</sup> They first synthesized negatively charged glutathione-decorated Au NCs, which were then crosslinked with positively charged chitosan solutions via electronic interactions. The as-prepared hydrogels exhibited intense emission owing to the inhibition of



**FIGURE 12** (A) Schematic illustration showing the chemical structure of AIE-active FPH via combined hydrogen bonding,  $\pi$ - $\pi$  stacking, and van der Waals interactions. (B) The proposed mechanism for selectively detecting  $\text{Fe}^{3+}$ ,  $\text{HSO}_4^-$ , and  $\text{F}^-$ . (C) Photos showing the fluorescence response of the FPH for various metal ions and anions. Reproduced with permission: 2020, The Royal Society of Chemistry<sup>[57]</sup>

nonradiative decay pathways of Au NCs. Remarkably, emission colors of the hydrogels could be regulated from green to red or orange by varying pH value. To gain more insight into the emission property of Au NCs-containing hydrogel, Liu et al. recently implemented a series of time-dependent and temperature-dependent photoluminescence spectra,<sup>[61]</sup> as well as morphological evolution monitoring, to systematically investigate the AIE-active hydrogel that was coassembled from thiobarbituric acid-modified Au NCs and  $\text{Zn}^{2+}$ . It was found that its emission derived from the synergistic contribution of the  $\pi$ - $\pi$  stacking of ligands, the ligand-to-metal charge transition, and the orderliness degree of aggregates. This work took a deep insight into the gelation process of Au NCs-containing hydrogel and provided some important points for the future design of polymeric hydrogels with tunable emission property. Besides Au NCs, silver nanoclusters (Ag NCs) have also attracted much attention because of their interesting optical properties. For example, some Ag NCs, despite being weakly luminescent in solutions, exhibited intense aggregation-induced emission. Additionally, such desirable fluorescence-to-phosphorescence switching behavior of Ag NCs has also been distinguished. One elegant example was very recently reported by Xie et al.<sup>[62]</sup> As illustrated in Figure 13, the water-soluble coordinated Ag NCs were prepared in alkali aqueous solutions of  $\text{AgNO}_3$  and thiosalicylic acid. Upon the addition of antisolvent such as ethanol, aqueous solutions of Ag NCs tended to self-assemble into highly ordered fibers, which simultaneously gelled to give crosslinked network with aggregation-enhanced photo-

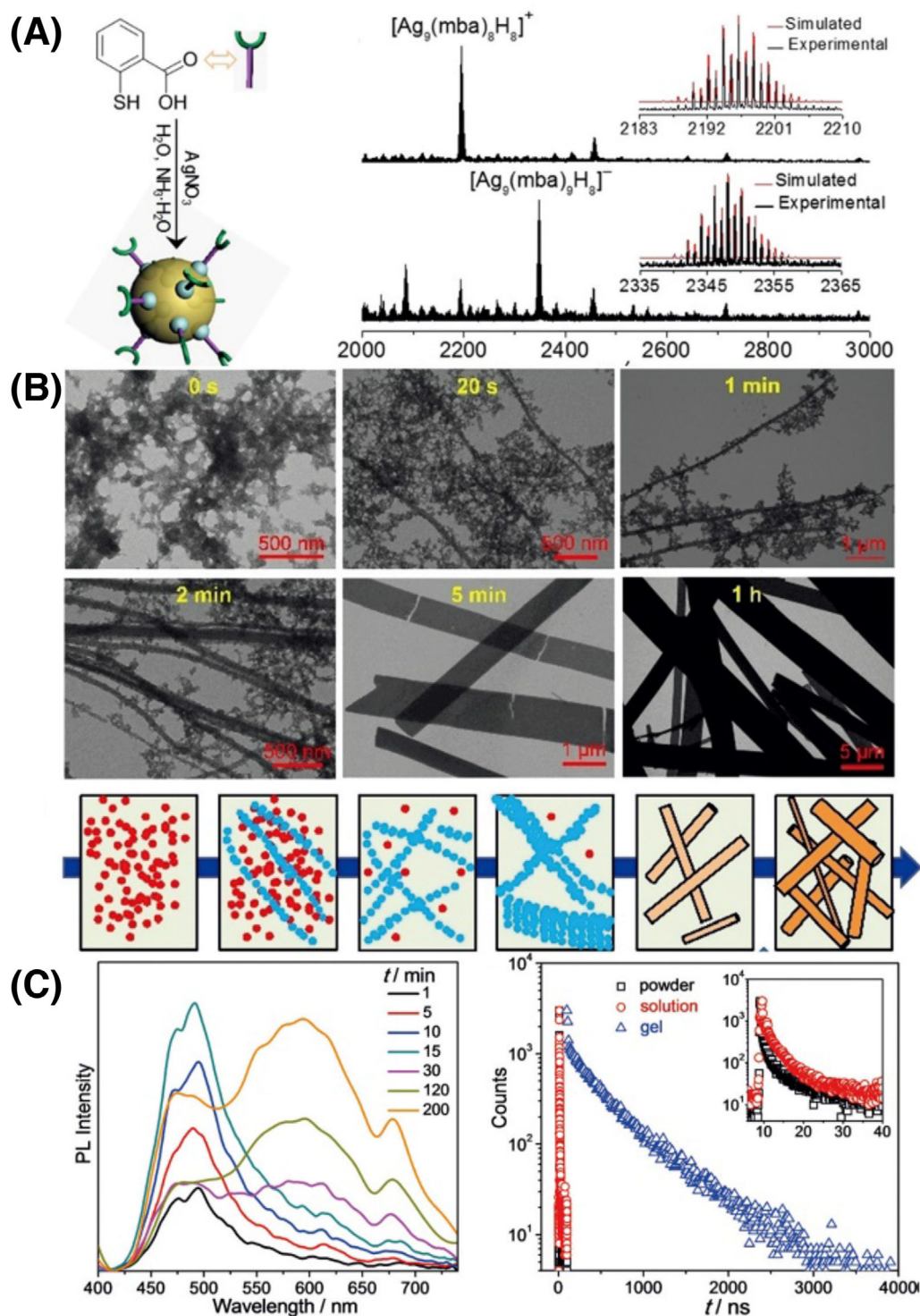
luminescence. At the same time, an interesting fluorescence-to-phosphorescence transition was induced by gelation. The results presented in these contributions will not only provide deep insight into the understanding on the assembled structure and luminescent performance of NCs, but also open up the possibility of utilizing nontypical AIE-active materials such as NCs to develop luminescent hydrogels.

## COMPARISON OF THE AIEGENS AND OTHER FLUOROPHORES IN POLYMERIC HYDROGELS

Besides these above-mentioned AIEgens, many kinds of natural or synthetic fluorophores have been employed as the building blocks for FPHs, primarily including normal organic fluorophores, fluorescent proteins, lanthanide complexes, and luminescent nanoparticles. The performance of these luminogens in polymeric hydrogels are briefly compared as follows.

### Organic fluorophores with AIE effect

As discussed above, organic AIEgens usually exhibit poor fluorescence at low concentration but tend to emit intense fluorescence in the aggregation state. This unique property provides a great opportunity to produce highly fluorescent polymeric hydrogels, because these hydrophobic AIEgens spontaneously form aggregates in the hydrophilic hydrogel



**FIGURE 13** (A) Synthetic procedure of Ag NCs, and the ESI-MS characterization as well as magnifications of both experimental and simulated isotopic distributions of the denoted peaks. (B) Evolution of the time-dependent self-assemblies as a function of time upon the addition of EtOH and the schematic illustration showing the gelation process. (C) Time-dependent optical properties of the gel after addition of EtOH and Emission curves recorded at different times. Reproduced with permission: 2020, Wiley-VCH<sup>[62]</sup>

matrix. Moreover, as their fluorescence intensities are dependent on the aggregation morphologies, it is much easier to regulate the emission intensity and even color of the AIE-active FPHs by controlling the polymer chain conformation in response to external stimuli. This is beneficial to the construction of smart FPHs with versatile uses, including the study of polymer chain conformation, optical sensing, bioimaging, and so forth. However, most of the organic AIEgens displayed quite broad fluorescence band that may be a problem in some cases. Moreover, most of the organic AIEgens, especially

those with long-wavelength emission, are not commercially available now, which make the AIE-active FPHs not accessible for many researchers.

### Normal organic fluorophores

Organic fluorescent dyes (e.g., pyrene, fluorescein, coumarin)<sup>[63,64]</sup> are the most common emitters whose emission intensity/color and responsiveness can be facilely

tuned by elaborate structure design. Especially, many of their important derivatives are commercially available now. Therefore, intense studies have been conducted to introduce them into the smart polymeric hydrogels for various applications, including optical sensing, bioimaging, encryption, and so forth. However, they may suffer from aggregation-caused quenching because of the formation of excimers and exciplexes, which potentially weakens their performance in polymeric hydrogels, especially when high-concentration fluorophores are required. Additionally, compared with AIEgens, their fluorescence intensities are less likely affected by the polymer chain conformation change, restricting the potential uses for polymer conformational studies.

## Fluorescent proteins

Many fluorescent proteins are natural molecules with good fluorescence stability and superior biocompatibility.<sup>[65]</sup> But they may suffer from the complex structure, which makes their emission colors/intensities not easily modulated on demands by facile structural modification. Therefore, the FPHs based on fluorescent proteins, despite very promising for bio-related uses, are still very few.

## Lanthanide complexes

Lanthanide complexes usually have sharp emission bands, high color purity, and fabulous photochemical stability.<sup>[66]</sup> Therefore, the FPHs based on lanthanide complexes are worth being studied. However, it is usually necessary to specially design a ligand that can absorb enough energy and effectively transfer energy to the central lanthanide ions through a resonance energy transfer (RET) process in order to produce highly fluorescent FPHs. Additionally, luminescence properties of some hydrogel systems are adversely affected by the hydration effect.<sup>[9]</sup>

## Luminescent nanoparticles

Luminescent nanoparticles are reported to have high photochemical stability, low cytotoxicity, and good chemical/physical stability.<sup>[67,68]</sup> To the best of our knowledge, their optical properties largely depend on the particle size, particle synthesis, and surface-modification process. And their photoluminescence mechanisms are still poorly understood. Therefore, the reported FPHs based on luminescent nanoparticles are still quite few.

## SUMMARY AND OUTLOOK

In this review, we have given a systematic summary of the recent studies on the design and fabrication of AIE-active FPHs. Generally, most of these reported FPHs were prepared by physical doping or covalent bonding of organic AIEgens into crosslinked polymeric networks. To produce materials with dynamic chemical structure and composites, another strategy for the construction of FPHs has been proposed by supramolecular polymerization from low-molecular weight

organic AIEgen-modified monomeric units and comonomeric molecules. Besides organic AIEgens, such inorganic–organic hybrid AIE-active materials as metal nanoclusters have also been employed as building blocks for FPHs. Benefiting from the spontaneously formed compact AIEgen aggregates that are tightly protected by the crosslinked hydrophilic polymeric chains, most of the reported FPHs are endowed with intense fluorescence, good biocompatibility, and environmental friendliness, suggesting many potential uses in the fields of biology, biomimetics, and so forth.

Despite these recent advances, AIE-active FPHs still belong to a quite young research area with a large number of possibilities. First of all, it is quite necessary to explore simple and especially easy-to-operate synthetic methods for both the AIEgen blocks and the FPHs. This is because many scientists and students from material science or biological backgrounds are interested in the study of AIE-active FPHs, but usually not familiar with the tedious and multistep organic synthesis procedures. Second, most of the reported FPHs were constructed from organic AIEgens such as TPE and substituted NI, whose emission bands primarily fall into the blue or green light region. More efforts are thus suggested to develop robust red-light-emitting FPHs, as well as systems with emission spectrum far more into the near-IR region, which are especially important for bio-related applications.<sup>[15]</sup> Furthermore, in terms of chemical structures, there have also been many newly developed AIE-active luminogens with excellent luminescent intensity and stability, including metal nanoclusters, organic clusters, and carbon dots.<sup>[69–72]</sup> The future introduction of these new AIE-active materials into hydrophilic polymeric hydrogels is expected to result in many as-yet-imagined performances and applications.

Besides tunable fluorescence color/intensity property, we suggest more attention be paid to the construction of multifunctional AIE-active FPHs, which can bring new opportunities for practical uses. For example, the integration of self-healing feature via reversible supramolecular interactions is helpful to ensure the long-term service of AIE-active FPHs. Shape memory FPHs are capable of being programmed into complex 3D hydrogel structures, indicating the development of 3D anticounterfeiting platforms with high-level information decryption capacities.<sup>[36]</sup> Smart AIE-active FPHs-based actuators with synergistic volume, shape, and fluorescence color change hold great potential for uses as biomimetic soft actuators/robots. Biocompatible AIE-active FPHs with customized biodegradability are highly desirable for drug-delivery monitoring, biosensing, and diagnosis. Other noteworthy functions include magnetism, electrical conductivity, and so forth.

In conclusion, AIE-active FPHs represent a new class of promising luminescent materials with numerous possibilities. The future booming of this new area requires combined and continuous efforts from people with various backgrounds. We hope this review is attractive to researchers, potentially arousing new interests and bringing new opportunities.

## ACKNOWLEDGMENTS

We thank National Natural Science Foundation of China (52073297, 21774138, 51773215), Key Research Program of Frontier Sciences, Chinese Academy of Sciences (QYZDB-SSW-SLH036), Youth Innovation Promotion Association of

Chinese Academy of Sciences (2019297), the Open Fund of Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology (2019B030301003).

## ORCID

Tao Chen  <https://orcid.org/0000-0001-9704-9545>

## REFERENCES

1. E. A. Widder, *Science* **2010**, *328*, 704.
2. X. Le, W. Lu, J. Zhang, T. Chen, *Adv Sci* **2019**, *6*, 1801584.
3. J. Hai, T. Li, J. Su, W. Liu, Y. Ju, B. Wang, Y. Hou, *Angew Chem Int Ed* **2018**, *57*, 6786.
4. D. Li, W. Hu, J. Wang, Q. Zhang, X. M. Cao, X. Ma, H. Tian, *Chem Sci* **2018**, *9*, 5709.
5. Z. Li, G. Wang, Y. Wang, H. Li, *Angew Chem Int Ed* **2018**, *57*, 2194.
6. W. Liu, W. Zhang, X. Yu, G. Zhang, Z. Su, *Polym Chem* **2016**, *7*, 5749.
7. D. Lu, M. Zhu, S. Wu, Q. Lian, W. Wang, D. Adlam, J. A. Hoyland, B. R. Saunders, *ACS Appl Mater Interfaces* **2020**, *30*, 1909359.
8. W. Lu, C. Ma, D. Zhang, X. Le, J. Zhang, Y. Huang, C. -F. Huang, T. Chen, *J Phys Chem C* **2018**, *122*, 9499.
9. S. Wei, W. Lu, X. Le, C. Ma, H. Lin, B. Wu, J. Zhang, P. Theato, T. Chen, *Angew Chem Int Ed* **2019**, *58*, 16243.
10. C. N. Zhu, T. Bai, H. Wang, W. Bai, J. Ling, J. Z. Sun, F. Huang, Z. L. Wu, Q. Zheng, *ACS Appl Mater Interfaces* **2018**, *10*, 39343.
11. Q. Zhu, K. Vliet, N. Holten-Andersen, A. Miserez, *Adv Funct Mater* **2019**, *29*, 1808191.
12. C. Ma, W. Lu, X. Yang, J. He, X. Le, L. Wang, J. Zhang, M. J. Serpe, Y. Huang, T. Chen, *Adv Funct Mater* **2018**, *28*, 1704568.
13. N. Mehwish, X. Dou, Y. Zhao, C. L. Feng, *Mater Horiz* **2019**, *6*, 14.
14. Y. Li, D. J. Young, X. J. Loh, *Mater Chem Front* **2019**, *3*, 1489.
15. S. Wei, Z. Li, W. Lu, H. Liu, J. Zhang, T. Chen, B. Z. Tang, *Angew Chem Int Ed* **2020**. <https://doi.org/10.1002/anie.202007506>
16. K. Benson, A. Ghimire, A. Pattammattel, C. V. Kumar, *Adv Funct Mater* **2017**, *27*, 1702955.
17. G. Liu, Y. -M. Zhang, X. Xu, L. Zhang, Y. Liu, *Adv Opt Mater* **2017**, *5*, 1700149.
18. Y. Zhang, X. Le, Y. Jian, W. Lu, J. Zhang, T. Chen, *Adv Funct Mater* **2019**, *29*, 1905514.
19. J. Li, J. Wang, H. Li, N. Song, D. Wang, B. Z. Tang, *Chem Soc Rev* **2020**, *49*, 1144.
20. J. Yang, M. M. Fang, Z. Li, *Aggregate* **2021**, *1*, 6.
21. J. Luo, Z. Xie, J. W. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem Commun* **2001**, 1740.
22. B. Li, T. He, X. Shen, D. Tang, S. Yin, *Polym Chem* **2019**, *10*, 796.
23. S. Xu, Y. Duan, B. Liu, *Adv Mater* **2020**, *32*, 1903530.
24. P. Gopikrishna, N. Meher, P. K. Iyer, *ACS Appl Mater Interfaces* **2018**, *10*, 12081.
25. S. S. Liow, Q. Dou, D. Kai, Z. Li, S. Sugiarto, C. Y. Yu, R. T. Kwok, X. Chen, Y. L. Wu, S. T. Ong, A. Kizhakeyil, N. K. Verma, B. Z. Tang, X. J. Loh, *Small* **2017**, *13*, 1603404.
26. H. Zheng, C. Li, C. He, Y. Q. Dong, Q. Liu, P. Qin, C. Zeng, H. Wang, *J Mater Chem C* **2014**, *2*, 5829.
27. Y. Lin, C. Li, G. Song, C. He, Y. Q. Dong, H. Wang, *J Mater Chem C* **2015**, *3*, 2677.
28. X. Ji, Z. Li, X. Liu, H. Q. Peng, F. Song, J. Qi, J. W. Y. Lam, L. Long, J. L. Sessler, B. Z. Tang, *Adv Mater* **2019**, *31*, 1902365.
29. X. Ji, Z. Li, Y. Hu, H. Xie, W. Wu, F. Song, H. Liu, J. Wang, M. Jiang, J. W. Y. Lam, B. Z. Tang, *ACS Chem* **2020**, 1146. <https://doi.org/10.31635/ccschem.020.202000302>
30. Z. Li, P. Liu, X. Ji, J. Gong, Y. Hu, W. Wu, X. Wang, H. Q. Peng, R. T. K. Kwok, J. W. Y. Lam, J. Lu, B. Z. Tang, *Adv Mater* **2020**, *32*, 1906493.
31. B. Li, Y. Zhang, B. Yan, D. Xiao, X. Zhou, J. Dong, Q. Zhou, *RSC Adv* **2020**, *10*, 7118.
32. Y. Zhao, C. Shi, X. Yang, B. Shen, Y. Sun, Y. Chen, X. Xu, H. Sun, K. Yu, B. Yang, Q. Lin, *ACS Nano* **2016**, *10*, 5856.
33. P. Li, D. Zhang, Y. Zhang, W. Lu, J. Zhang, W. Wang, Q. He, P. Théato, T. Chen, *ACS Macro Lett* **2019**, *8*, 937.
34. X. Le, H. Shang, H. Yan, J. Zhang, W. Lu, M. Liu, L. Wang, G. Lu, Q. Xue, T. Chen, *Angew Chem Int Ed* **2020**. <https://doi.org/10.1002/anie.202011645>
35. H. Liu, S. Wei, H. Qiu, B. Zhan, Q. Liu, W. Lu, J. Zhang, T. Ngai, T. Chen, *Macromol Rapid Commun* **2020**, *41*, 2000123.
36. H. Qiu, S. Wei, H. Liu, B. Zhan, H. Yan, W. Lu, J. Zhang, S. Wu, T. Chen, *Adv Intell Syst* **2020**, 2000239. <https://onlinelibrary.wiley.com/doi/full/10.1002/aisy.202000239>
37. J. M. Galindo, J. Leganés, J. Patiño, A. M. Rodríguez, M. A. Herrero, E. Díez-Barra, S. Merino, A. M. Sánchez-Migallón, E. Vázquez, *ACS Macro Lett* **2019**, *8*, 1391.
38. S. Grosjean, M. Wawryszyn, H. Mutlu, S. Brase, J. Lahann, P. Theato, *Adv Mater* **2019**, *31*, 1806334.
39. L. Hu, Y. Wan, Q. Zhang, M. J. Serpe, *Adv Funct Mater* **2019**, *30*, 1903471.
40. L. Hu, Q. Zhang, X. Li, M. J. Serpe, *Mater Horiz* **2019**, *6*, 1774.
41. P. Theato, B. S. Sumerlin, R. K. O'Reilly, T. H. Epp, *Chem Soc Rev* **2013**, *42*, 7055.
42. Z. Wang, J. Nie, W. Qin, Q. Hu, B. Z. Tang, *Nat Commun* **2016**, *7*, 12033.
43. C. Zhang, C. Liu, X. Xue, X. Zhang, S. Huo, Y. Jiang, W. Q. Chen, G. Zou, X. J. Liang, *ACS Appl Mater Interfaces* **2014**, *6*, 757.
44. C. Zhang, Y. Li, X. Xue, P. Chu, C. Liu, K. Yang, Y. Jiang, W. Q. Chen, G. Zou, X. J. Liang, *Chem Commun* **2015**, 51, 4168.
45. X. Wang, K. Xu, H. Yao, L. Chang, Y. Wang, W. Li, Y. Zhao, J. Qin, *Polym Chem* **2018**, *9*, 5002.
46. F. Hou, B. Xi, X. Wang, Y. Yang, H. Zhao, W. Li, J. Qin, Y. He, *Colloids Surf B* **2019**, *183*, 110441.
47. W. Lu, X. Le, J. Zhang, Y. Huang, T. Chen, *Chem Soc Rev* **2017**, *46*, 1284.
48. H. Wang, X. Ji, Z. Li, F. Huang, *Adv Mater* **2017**, *29*, 1606117.
49. X. Y. Lou, Y. W. Yang, *Aggregate* **2020**, *1*, 19.
50. H. Wang, X. Ji, Y. Li, Z. Li, G. Tang, F. Huang, *J Mater Chem B* **2018**, *6*, 2728.
51. D. Aschmann, S. Riebe, T. Neumann, D. Killa, J. -E. Ostwaldt, C. Wölper, C. Schmuck, J. Voskuhl, *Soft Matter* **2019**, *15*, 7117.
52. B. Li, C. Lin, C. Lu, J. Zhang, T. He, H. Qiu, S. Yin, *Mater Chem Front* **2020**, *4*, 869.
53. H. Yao, J. Wang, Y. Q. Fan, Q. Zhou, X. W. Guan, X. T. Kan, Y. M. Zhang, Q. Lin, T. B. Wei, *Dyes Pigm* **2019**, *167*, 16.
54. P. Wei, Z. Li, J. -X. Zhang, Z. Zhao, H. Xing, Y. Tu, J. Gong, T. S. Cheung, S. Hu, H. H. Y. Sung, I. D. Williams, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem Mater* **2019**, *31*, 1092.
55. Q. Zhao, G. -F. Gong, H. -L. Yang, Q. -P. Zhang, H. Yao, Y. -M. Zhang, Q. Lin, W. -J. Qu, T. -B. Wei, *Polym Chem* **2020**, *11*, 5455.
56. Y. Q. Fan, Q. Huang, Y. -M. Zhang, J. Wang, X. W. Guan, Y. Y. Chen, H. Yao, T. B. Wei, Q. Lin, *Polym Chem* **2019**, *10*, 6489.
57. Y. Feng, N. Jiang, D. Zhu, Z. Su, M. R. Bryce, *J Mater Chem C* **2020**, *8*, 11540.
58. X. W. Sun, Z. H. Wang, Y. J. Li, H. L. Yang, G. F. Gong, Y. M. Zhang, H. Yao, T. B. Wei, Q. Lin, *Soft Matter* **2020**, *16*, 5734.
59. S. K. Talloj, M. Mohammed, H. C. Lin, *J Mater Chem B* **2020**, *8*, 7483.
60. N. Goswami, F. Lin, Y. Liu, D. T. Leong, J. Xie, *Chem Mater* **2016**, *28*, 4009.
61. J. Liu, J. Feng, Y. Yu, L. Xu, Q. Liu, H. Zhang, J. Shen, W. Qi, *J Phys Chem C* **2020**, *124*, 23844.
62. Z. Xie, P. Sun, Z. Wang, H. Li, L. Yu, D. Sun, M. Chen, Y. Bi, X. Xin, J. Hao, *Angew Chem Int Ed* **2020**, *59*, 9922.
63. S. Uchiyama, C. Gota, T. Tsuji, N. Inada, *Chem Commun* **2017**, 53, 10976.
64. A. J. P. Teunissen, C. Perez-Medina, A. Meijerink, W. J. M. Mulder, *Chem Soc Rev* **2018**, *47*, 7027.
65. M. D. Weber, L. Niklaus, M. Proschel, P. B. Coto, U. Sonnewald, R. D. Costa, *Adv Mater* **2015**, *27*, 5493.
66. Y. Hasegawa, Y. Kitagawa, *J Mater Chem C* **2019**, *7*, 7494.
67. S. Bhattacharya, R. S. Phatake, S. Nabha Barnea, N. Zerby, J. J. Zhu, R. Shikler, N. G. Lemcoff, R. Jelinek, *ACS Nano* **2019**, *13*, 7396.
68. U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, T. Nann, *Nat Methods* **2008**, *5*, 763.
69. H. Zhang, Z. Zhao, A. T. Turley, L. Wang, P. R. McGonigal, Y. Tu, Y. Li, Z. Wang, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Adv Mater* **2020**, *32*, 2001457.
70. L. C. Mao, X. Y. Zhang, Y. Wei, *Chin J Polym Sci* **2019**, *37*, 340.
71. H. Yang, Y. Liu, Z. Guo, B. Lei, J. Zhuang, X. Zhang, Z. Liu, C. Hu, *Nat Commun* **2019**, *10*, 1789.
72. Z. Liu, X. Dai, Y. Sun, Y. Liu, *Aggregate* **2020**, *1*, 31.



## AUTHOR BIOGRAPHIES



**Dr. Wei Lu** received his Ph.D. degree in polymer chemistry and physics from Zhejiang University in China (2014). Soon afterwards he joined Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. He was promoted to Associate Professor in 2017 and Professor in 2020. His current research is focused on the fabrication of smart fluorescent polymeric materials for applications in chemical sensing and biomimetic skins/actuators.



**Shuxin Wei** received her M.S. degree from Tianjin University, China in 2018. Currently, she is a Ph.D. student in the Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, under the supervision of Prof. Tao Chen. Her research interests focus on the fluorescent

polymeric hydrogels with their applications as actuators and sensors.



**Prof. Tao Chen** received his Ph.D. in polymer chemistry and physics from Zhejiang University in 2006. After his postdoctoral training at the University of Warwick, he joined Duke University as a research scientist. He then moved back to Europe as an Alexander von Humboldt Research Fellow at Technische Universität Dresden, Germany. Since 2012, he is a full-time professor at Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. His research interests include smart polymeric materials and their hybrid systems with applications as actuators, shape memory polymers, and chemical sensing.

**How to cite this article:** Lu W, Wei S, Shi H, Le X, Yin G, Chen T. Progress in aggregation-induced emission-active fluorescent polymeric hydrogels. *Aggregate*. 2021;2:e37. <https://doi.org/10.1002/agt2.37>