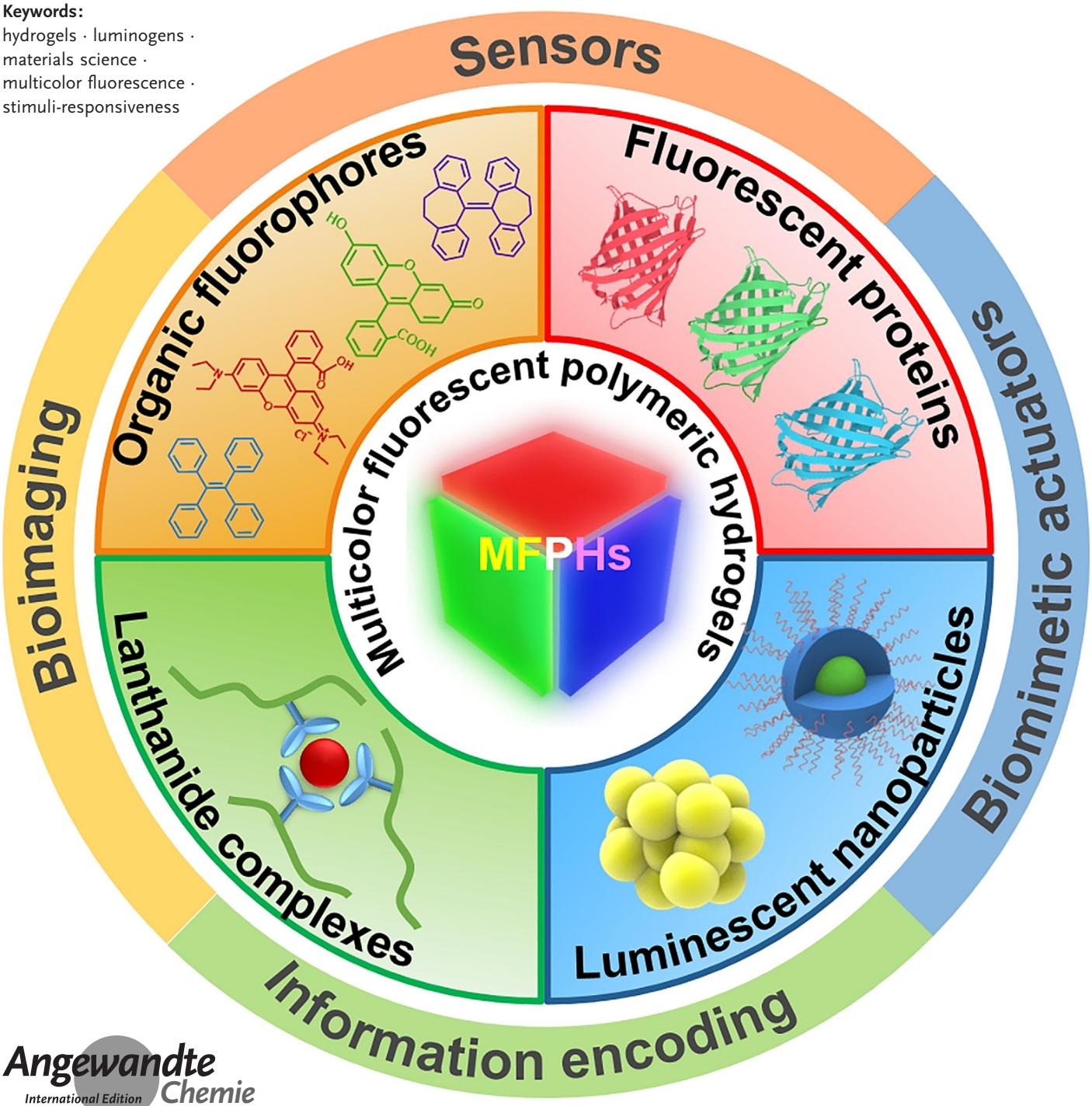
How to cite: *Angew. Chem. Int. Ed.* **2021**, *60*, 8608–8624
International Edition: doi.org/10.1002/anie.202007506
German Edition: doi.org/10.1002/ange.202007506

Multicolor Fluorescence

Multicolor Fluorescent Polymeric Hydrogels

Shuxin Wei[+], Zhao Li[+], Wei Lu, Hao Liu, Jiawei Zhang, Tao Chen,* and Ben Zhong Tang**

Keywords:
hydrogels · luminogens · materials science · multicolor fluorescence · stimuli-responsiveness



Multicolor fluorescent polymeric hydrogels (MFPHs) are three-dimensionally crosslinked hydrophilic polymer networks with tunable emission color. Different from the classic fluorescent materials that are used primarily in dry solid states or solutions, MFPHs exist as highly water-swollen quasi-solids. They thus present many promising properties of both solids and solution, including tissue-like mechanical properties, an intrinsic soft and wet nature, fabulous biocompatibility, along with a responsive volume, shape, and fluorescence color change. These advantageous properties hold great potential in many applications such as sensing, bioimaging, information encoding, encryption, biomimetic actuators, and soft robotics. This Review gives an in-depth overview of recent progress in the field of MFPHs, with a particular focus on the diverse construction methods and important demonstrated applications. Current challenges and future perspectives on MFPHs are also discussed.

From the Contents

1. Introduction

Fluorescent polymeric hydrogels (FPHs), rising stars of luminescent materials, are three-dimensionally crosslinked hydrophilic polymer networks with tunable luminous features.[1] In contrast to the classic fluorescent materials, which are used primarily as dry solids or in solution, FPHs exist as highly water-swollen quasi-solids and thus present many promising properties of both the solid and solution states, thus suggesting huge potential in a myriad of applications.[1,2] For example, their crosslinked 3D hydrophilic networks could significantly facilitate substance exchange with a surrounding aqueous environment to induce a remarkable fluorescence response, thus making them particularly useful for luminescent sensing, displays, information encryption, etc.[3] The tissue-like soft and wet nature of FPHs often results in minimized nonspecific interaction with cells, which highlights their potential use for bioimaging and diagnosis.[4] If the crosslinked polymer networks are endowed with functional groups, intelligent FPHs will be produced that are capable of undergoing stimuli-responsive volume, shape, and fluorescence changes, which can further expand their applications to biomimetic actuators or even soft robotics.[5] In this context, a large number of FPHs have been designed and prepared over the past decade by introducing organic fluorogens,[6] lanthanide complexes,[7] or luminescent nanoparticles[8] into the hydrogel matrix. These impressive advances have greatly enriched the types of FPHs and laid a solid foundation for further practical applications.

However, despite much progress, most of these reported FPHs have only one light-emitting center and exhibit an "on-off" fluorescence intensity switching behavior in response to external stimuli, but not the more preferable change in the fluorescence color, thus limiting their versatile applications. To this end, much recent research has focused on incorporating two or more luminogens into one hydrogel matrix to produce robust multicolor fluorescent polymetric hydrogels (MFPHs). As a consequence of the possible controlled overlapping of the fluorescence spectra of different luminogens, MFPHs can be endowed with a simultaneous change in the emission intensity and the color. Furthermore, since many luminogens are sensitive to different triggers, more than one stimulus can be used to induce a change in the fluorescence intensity and color, which may lead to multiresponsive MFPHs with versatile uses. Moreover, the preferred white-light-emitting polymeric hydrogels might also be fabricated by introducing red-, green-, and blue-light-

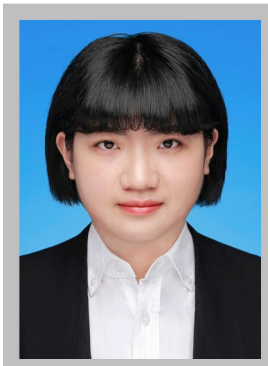
[*] S. Wei,[+] Prof. W. Lu, H. Liu, Prof. J. Zhang, Prof. T. Chen
Key Laboratory of Marine Materials and Related Technologies
Zhejiang Key Laboratory of Marine Materials and Protective Technologies
Ningbo Institute of Materials Technology and Engineering
Chinese Academy of Sciences, Ningbo 315201 (China)
and
School of Chemical Sciences
University of Chinese Academy of Sciences
19A Yuquan Road, Beijing 100049 (China)
E-mail: luwei@nimte.ac.cn
tao.chen@nimte.ac.cn
Dr. Z. Li[+]
Institute of Engineering Medicine
Beijing Institute of Technology
5 South Zhongguancun Street
Haidian District, Beijing 100081 (China)
Dr. Z. Li,[+] Prof. B. Z. Tang
Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, and Institute for Advanced Study
The Hong Kong University of Science and Technology (HKUST)
Clear Water Bay, Kowloon, Hong Kong (China)
E-mail: tangbenz@ust.hk
Prof. B. Z. Tang
Center for Aggregation-Induced Emission
SCUT-HKUST Joint Research Institutes
State Key Laboratory of Luminescent Materials and Devices
South China University of Technology
Guangzhou 510640 (China)
Prof. W. Lu
Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates (South China University of Technology)
Guangzhou 510640 (China)
[+] These authors contributed equally to this work.
The ORCID identification number for one of the authors of this article can be found under: https://doi.org/10.1002/anie.202007506.

emitting fluorogens into one single polymeric hydrogel system.[9]

Currently, although the research on MFPHs is still in its infancy, numerous excellent studies have been conducted in this field. However, there is still no reported review that introduces MFPHs. Herein, we try to provide an in-depth overview that summarizes the recent progress in MFPHs, with a particular focus on the diverse construction methods and important demonstrated applications. A perspective discussion on future opportunities and challenges in this exciting research area will also be given. With this Review, we hope to spark new ideas, motivate new efforts, and attract more like-minded researchers in this emerging wonderful world of MFPHs. It should be noted that this Review deals with only multicolor fluorescent hydrogels prepared by the physical or chemical crosslinking of hydrophilic synthetic or natural polymers. Readers interested in multicolor fluorescent organogels or hydrogels primarily assembled from small molecules are referred to other excellent reviews.[1,2a,b]

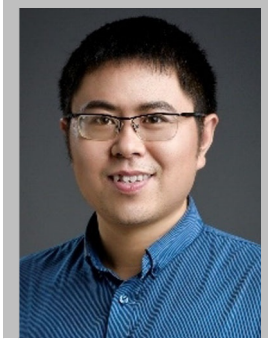
2. Design and Construction of MFPHs

MFPHs exist in nature, with many marine mollusks known to exist in a gel state and display dynamic luminescent behavior for camouflage, mutual communication, or even mating and reproduction purposes.[10] These interesting natural MFPHs are usually derived from a mixture of blue, green, and red fluorescent proteins or natural fluorogens. Similarly, the design of artificial MFPHs typically involves the simultaneous incorporation of two or more different fluorogens into the same polymeric hydrogel system. For some specially designed fluorogens with a tunable fluorescence color response, it is also possible to obtain single-fluorogen-based smart MFPHs in response to external stimuli. To date, many types of natural or synthetic fluorogens have been employed as building blocks for MFPHs, and these can be divided into fluorescent proteins, organic fluorophores, lanthanide complexes, and luminescent nanoparticles based on the types of fluorescent groups (Figure 1).



Shuxin Wei received her MS from Tianjin University, China, in 2018. Currently, she is a PhD student at the Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, under the supervision of Prof. Tao Chen. Her research interests focus on fluorescent polymeric hydrogels and their applications as actuators and sensors.

Zhao Li received his PhD from Shanghai Jiao Tong University (SJTU) under the supervision of Prof. Xinling Wang. He was then a postdoctoral fellow at the Hong Kong University of Science and Technology (HKUST) under the supervision of Prof. Ben Zhong Tang. He is currently an assistant professor at Beijing Institute of Technology (BIT). His research focuses on the development of luminescent soft materials.



Wei Lu received his PhD in polymer chemistry and physics from Zhejiang University in China (2014). He then 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 luminescent polymeric materials for applications in chemical sensing and biomimetic actuators.

Tao Chen received his PhD in polymer chemistry and physics from Zhejiang University in 2006. After postdoctoral training at the University of Warwick, he joined Duke University as a research scientist. After an Alexander von Humboldt Research Fellowship at Technische Universität Dresden, Germany, in 2012 he became full-time professor at Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences. His research includes smart polymeric materials and their hybrid systems with applications as actuators, shape memory polymers, and chemical sensing.

Ben Zhong Tang received his bachelor degree (1982) from the South China University of Technology (SCUT) and PhD (1988) from Kyoto University, before carrying out postdoctoral research at the University of Toronto (1989–1994). He then joined The Hong Kong University of Science and Technology (HKUST) and was promoted to Chair Professor in 2008 and Stephen K. C. Cheong Professor of Science in 2013. He was elected to the Chinese Academy of Sciences in 2009 and the Royal Society of Chemistry in 2013. His research includes the study of new advanced materials, luminescent processes, and polymerization reactions.

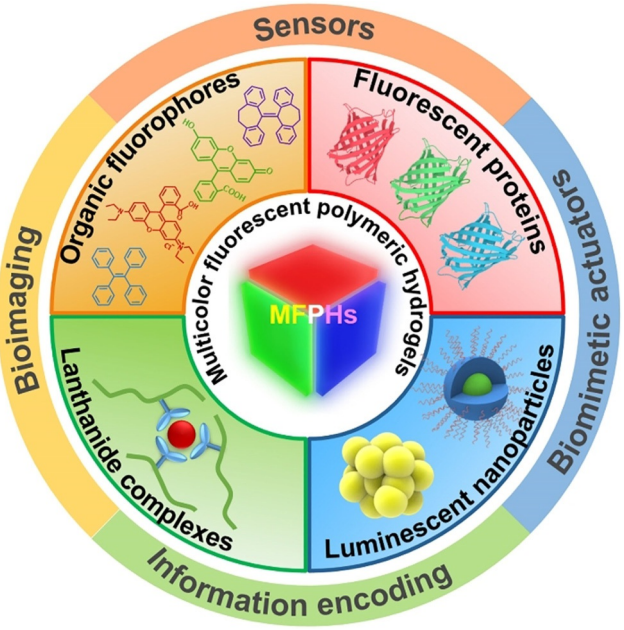


Figure 1. Overview of the construction strategies and promising applications of multicolor fluorescent polymeric hydrogels (MFPHs) based on different luminogens (e.g. fluorescent proteins, organic fluorophores, lanthanide complexes, and luminescent nanoparticles).

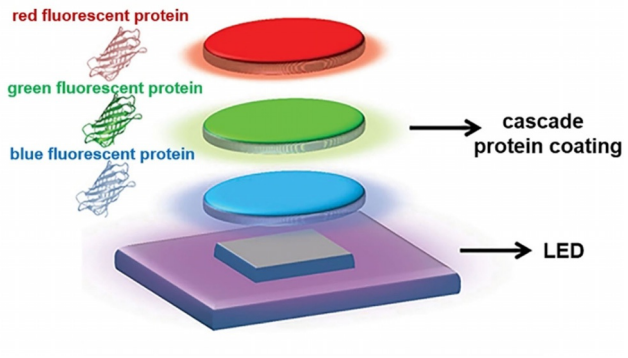


Figure 2. Schematic illustration showing MFPH-based coatings for bio-HLEDs, which consist of aqueous solutions of blue (mTagBFP), green (eGFP), and red (mCherry) fluorescent proteins together with trimethylolpropane ethoxylate and poly(ethylene oxide). Reproduced from Ref. [11] with permission. Copyright 2015 Wiley-VCH.

2.1. Fluorescent Proteins

Fluorescent proteins are typically natural fluorophores and are widely found in Euprymna scolopes, ctenophores, glow worms, and many other wonderful creatures. Their emission usually derives from inherent aromatic amino acids (e.g. tryptophan phenylalanine, and tyrosine). Many different kinds of fluorescent proteins, including green, red, blue, yellow, and cyan types, have been recognized since they were first discovered in the mid-20th Century. As a result of their high fluorescence stability, a wide range of possible fluorescence colors, and superior biocompatibility, fluorescent proteins are excellent building blocks for MFPHs. For example, Costa and co-workers demonstrated a novel approach to prepare white-light-emitting hydrogel materials using blue (mTagBFP), green (eGFP), and red (mCherry) fluorescent proteins (Figure 2).[11] The MFPHs consist of aqueous solutions of these fluorescent proteins together with trimethylolpropane ethoxylate and poly(ethylene oxide), which act as a gelation agent. The fluorescent protein-based hydrogels are endowed with excellent luminescence color quality and stability (a loss of luminous efficiency of less than 10% over 100 h), as well as a perfect coverage of the whole visible spectrum. These advantages make them capable of serving as coatings for bio-HLEDs. This design may provide a new path to exploit fluorescent protein based MFPHs in optoelectronic applications. Furthermore, fluorescent protein based MPFHs have also been constructed through the covalent crosslinking of proteins and glutaraldehyde. Such MPFHs exhibit strong autofluorescence for in vivo non-invasive tracking and visualization.[12] Nevertheless, despite many extraordinary features, many kinds of fluorescent proteins are well-defined and structurally complicated biomacromolecules or assemblies. It is thus difficult to modulate their emission colors and intensities on demand by facile structural modification. This can partially explain why multicolor fluorescent polymeric hydrogel systems containing fluorescent proteins are very limited compared to MPFHs based on artificial fluorophores, which are introduced in the next section.

2.2. Organic Fluorophores

Organic fluorescent dyes are excellent candidates for the design and construction of MFPHs because of their finely tuned emission intensity, color, and responsiveness through elaborate structure design. In particular, conventional organic dyes are some of the most widely studied photoluminescent materials of the past half century.[13] As shown in Figure 3 A,

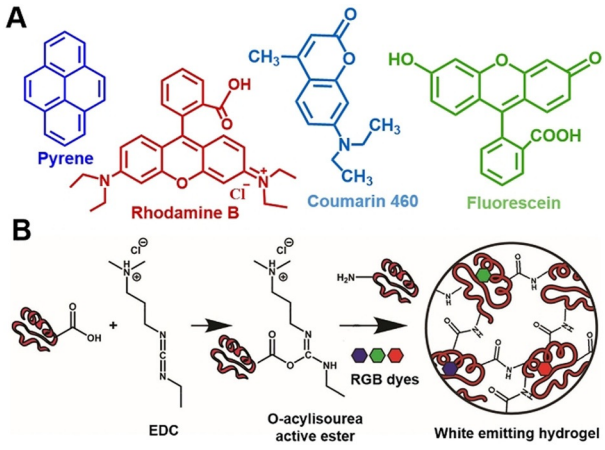


Figure 3. A) The chemical structures of some typical organic fluorogens such as pyrene, rhodamine B, coumarin 460, and fluorescein, which have planar aromatic cores and conjugated disc-like structures. B) Fabrication route for BSA-based fluorescent hydrogels containing RGB tricolor dyes. Reproduced from Ref. [9d] with permission. Copyright 2017 Wiley-VCH.

the majority of classic organic fluorogens such as pyrene, rhodamine B, coumarin 460, and fluorescein usually have planar aromatic cores and conjugated disc-like structures. The straightforward strategy to build MFPHs involves the introduction of a single fluorophore with stimuli-responsive color-changing properties into the hydrogel matrix.[14] For example, Li and co-workers recently developed multi-stimuli-responsive MPFHs, which are fabricated by embedding a protonation-sensitive fluorophore, 4,4′-{(1*E*,1′*E*)-[2-(3-aminopropoxy)pyrimidine-4,6-diyl]bis(ethene-2,1-diyl)}-bis(*N*,*N*-diethylaniline) (PPBEN), into a thermosensitive Pluronic F127 hydrogel matrix.[14d] The fluorescent color of the hydrogel can be adjusted by the pH value, with PPBEN emitting blue light in acidic solutions but emitting yellow light in aprotic solutions. Interestingly, owing to the thermally responsive hydrophobic property of the internal microstructure of the Pluronic F127 hydrogel, the ratio of protonated and deprotonated PPBEN could be facilely modulated by changing the temperature, thereby resulting in a multicolor emission response of the hydrogels from blue to yellow and even the more preferable white color as a function of temperature and [H^+]. Furthermore, by placing MPFHs onto a conductive indium tin oxide (ITO) glass substrate, which can convert electrical energy into heat, an electrically controlled multicolor light-emitting hydrogel-based LED can be achieved, which gives a new opportunity for preparing smart and tunable hydrogel-based luminescent devices. Furthermore, many other sensitive organic dyes and their derivatives have also been successfully used for the design of MPFHs, including *N*-(3-(benzo[*d*]thiazol-2-yl)-4-(*tert*-butyldiphenylsilyloxy)phenyl) acetamide (BTBPA),[14a] 8-hydroxypyrene-1-carbaldehyde (HPC),[14b] and 4′-(*N*-vinylbenzyl-4-pyridinyl)-2,2′:6′,2″-terpyridine perchlorate (VPTP).[14c]

In addition, the combination of two or more fluorophores with distinct emission colors is another important way to build MPFHs.[15] For example, Maynard and co-workers have fabricated checkerboard-patterned MFPHs consisting of thermoresponsive polymers functionalized with RhodG (Rhodamine Green carboxylic acid, succinimidyl ester, hydrochloride) and Lissamine Red (Lissamine rhodamine B sulfonyl chloride), which have different lower critical solution temperatures (LCST).[15a] At 37 °C, the Lissamine Red grafted polymeric hydrogel sections with the lower LCST will shrink and result in self-quenching of this red-light-emitting fluorophore. A temperature increase up to 45 °C results in the RhodG-grafted polymeric hydrogel sections with the higher LCST also undergoing a quenching of the green-light emission. In this way, smart checkerboard-patterned MFPHs have been demonstrated through control of the environment temperature.

This method can be extended to fabricate multicolor fluorescent hydrogels with three primary colors (red, green, and blue) that have diverse luminescence characteristics.[9a,d,16] Kumar and co-workers have demonstrated a multifunctional protein-based multifluorescent hydrogel by physical blending of blue (coumarin 460), green (fluorescein), and red (5(6)-carboxy-X-rhodamine) light-emitting fluorogens.[9d] In this system, a crosslinked bovine serum albumin (BSA) hydrogel is employed as the host and can provide scattered but dense binding sites to bind these three small organic dyes (Figure 3B). By modulating the blending ratio of the RGB tricolor dyes, it is possible to facilely produce the hydrogel systems with various colors and even white light. This is the first example of a multifunctional, proteinaceous white emitter, which may serve as a robust platform for further biomaterial-based sensing and lighting applications.

Despite being versatile building blocks for MFPHs, most of these classic organic dyes are primarily hydrophobic planar molecules, which usually have a strong tendency to form dense face-to-face packing in the highly hydrophilic polymeric hydrogel matrix. As a consequence, unfavorable aggregation-caused quenching (ACQ) might be observed. To this end, there has been an increasing research interest to develop aggregation-induced emissive (AIE) polymeric hydrogels, in which enhanced emission can be achieved by the aggregation of hydrophobic AIEgens in the quasi-solid hydrogels. For example, we reported "Rubik's cube (RC)" structured hydrogels bearing six different AIE colored faces.[17] As shown in Figure 4A, six AIEgen-based hydrogel films were produced by mixing various AIEgens with different emission colors into the hydrogel matrix consisting of acylhydrazine-terminated PEO and tetraaldehyde-terminated PEO. The dynamic covalent bond of acylhydrazone enables the six colorful hydrogel films to adhere to a non-emissive hydrogel cube to form a basic unit of an RC-like array. Interestingly, the RC-like MFPHs films can be rotated both horizontally and vertically to produce many colorful patterns, just like a real RC (Figure 4B). By using similar preparation approaches, several elegant AIEgen-based hydrogels have also been recently reported that show properties reminiscent of a bioinspired simultaneous change[18] or trackable photodimerization processes.[19] Very recently, attempts have also been conducted by Vazquez et al. to combine both AIE and ACQ fluorophores into one single hydrogel matrix.[9c] The host hydrogel, which is formed from physically crosslinked phenyldiaminotriazine through strong hydrogen-bonding interactions, shows aggregation-induced blue-light emission. Multicolor fluorescent and even white-light-emitting hydrogels were further fabricated by the incorporation of two ACQ molecules—fluorescein and rhodamine 101, with green and red emission colors, respectively. These examples have demonstrated the huge potential of preparing AIEgen-based, highly emissive MFPHs. Given the fact that a large number of functional AIEgens have been studied over the past two decades, more research efforts are expected to develop new types of MFPHs with improved functions and promising uses.

2.3. Lanthanide Complexes

Lanthanide complexes are another important type of fluorescent material with unique metal-controlled photoluminescence. They are usually characterized by high luminescence quantum yields, sharp emission bands, high color purity, and fabulous photochemical stability. However, the luminescence of lanthanide ions with millisecond lifetimes is easily quenched in aqueous solutions, mainly by nonradiative

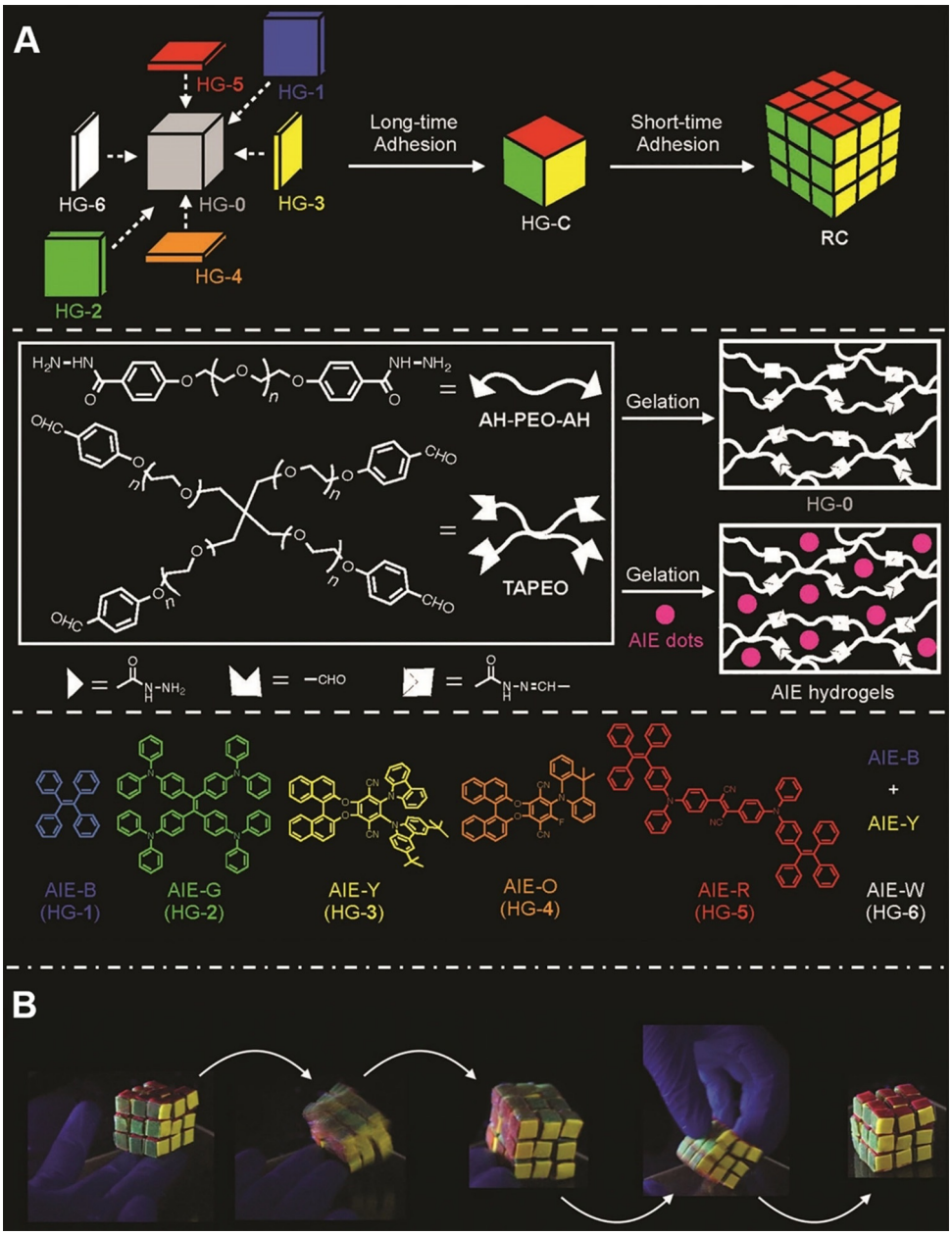


Figure 4. A) Schematic illustration showing the fabrication of Rubik's cube-like AIE hydrogels, which were prepared by adhering six colored hydrogel films onto a non-emitting hydrogel cube through dynamic covalent bonds with the acylhydrazone. The chemical structures of the polymeric hydrogels and AIEgens involved are also shown. B) Images showing that many colorful patterns could be fabricated by rotating the RC-like MFPHs both horizontally and vertically, just like a real RC. Reproduced from Ref. [17] with permission. Copyright 2019 Wiley-VCH.

decay processes involving high-energy vibrations, particularly O-H.[20] An effective method to overcome this obstacle is to introduce lanthanide ions into crosslinked hydrogel systems, whereby the hydration effect can be significantly reduced to increase the fluorescence intensity.[20a] Over the past decades, a number of MFPHs have been reported by crosslinking natural or synthetic polymers (e.g. alginate and sodium polyacrylate) with some typical lanthanide ions, especially Eu^{3+} and Tb^{3+}, which exhibit characteristic red- and green-light emission, respectively.[21]

Nevertheless, since alginate and sodium polyacrylate contain no conjugated molecular moieties and thus have comparatively low molar absorption coefficients, most of the above-mentioned MFPHs only exhibit weak to moderate emission intensities. The most convenient way to produce highly fluorescent lanthanide complexes is to employ ligands that can absorb enough energy and effectively transfer energy to lanthanide ions through a resonance energy transfer (RET) process (so-called antenna effect; see Figure 5A). In general, suitable "antenna" ligands should: 1) have chelating groups that can coordinate with lanthanide ions to form stable complexes; 2) have a relatively large absorption capacity of the excitation light; 3) possess an appropriate triplet-state energy that is close to, but not too close to, the energy of the excited states of the lanthanide ions to produce effective energy transfer between the donor and acceptor; and 4) have an intersystem crossing (ISC) quantum yield near unity.[20b,22] Therefore, a great number of lanthanide-coordinated MFPHs have been constructed from functionalized polymers with special chelating groups such as pyridinecarboxylic acid,[23] pyridinedicarboxylic acid,[24] bipyridine,[2c] and others[25] to enhance the "antenna effect". For example, Li et al. have reported a lanthanide-coordinated supramolecular multicolor fluorescent hydrogel starting from α-cyclodextrins (α-CDs) functionalized with 2,6-pyridinedicarboxylic acid (PDA).[24b] As shown in Figure 5B, the PDA moieties can form a 3:1 complex with Eu^{3+} or Tb^{3+}, while the α-CD moieties can self-assemble with azobenzene modified by a guanidinium group through host–guest interactions. Further addition of negatively charged sodium polyacrylate exfoliated laponite nanosheets (SPLNs) gives the hybrid hydrogels through electrostatic interactions. The obtained Eu^{3+}- or Tb^{3+}-coordinated supramolecular hydrogels display bright

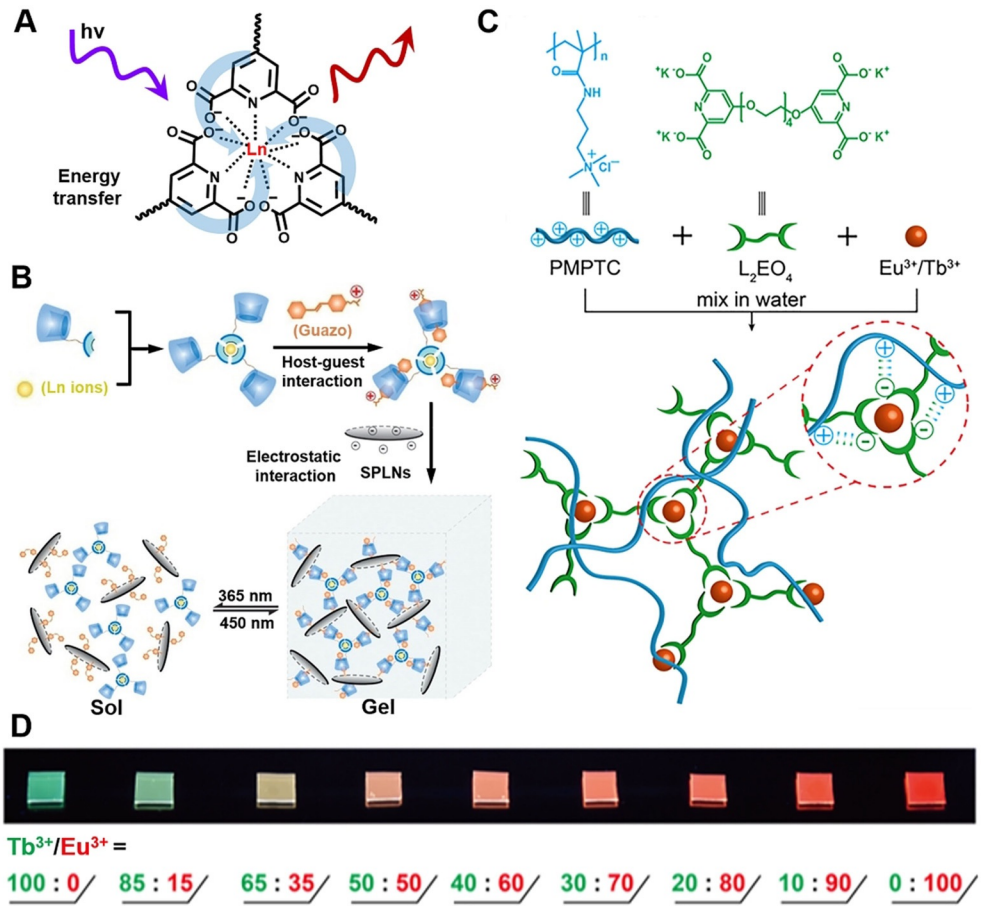


Figure 5. A) The energy-transfer process from the chelating ligand (e.g. pyridinedicarboxylic moiety) to the Ln ions in the fluorescent lanthanide complexes. B) The preparation of the supramolecular MFPH example through the hierarchical self-assembly of lanthanide ions, α-CDs functionalized with 2,6-pyridinedicarboxylic acid, azobenzene modified by a guanidinium group, and sodium polyacrylate exfoliated laponite nanosheets through metal–ligand coordination, host–gust recognition, and electrostatic interaction, respectively. Reproduced from Ref. [24b] with permission. Copyright 2018 Wiley-VCH. C) Schematic representation of a supramolecular MFPH, which was prepared by electrostatic interactions between the anionic lanthanide coordination polymers and cationic PMPTC. D) Photographs of the as-prepared hydrogel samples with various ratios of Tb^{3+} to Eu^{3+} ions taken under irradiation with 254 nm UV light. Reproduced from Ref. [24c] with permission. Copyright 2019 American Chemical Society.

red or green emissions, respectively. By applying a similar strategy, Wang et al. recently reported supramolecular polyelectrolyte complex hydrogels that were formed through electrostatic interactions between the anionic lanthanide coordination polymers and the cationic poly(3-(methacryloylamino)propyltrimethylammonium chloride) (PMPTC).[24c] As shown in Figure 5C, the fluorescent lanthanide-coordinated polymers were prepared from the bis-ligand L_2EO_4, which bears two dipicolinic acid (DPA) moieties and thus can coordinate with Eu^{3+} or Tb^{3+} in a molar ratio of 3:2. By varying the molar ratio of the Eu^{3+} and Tb^{3+} ions, the emission colors of the hydrogels can be effectively tuned to red, green, or a mixed color (Figure 5D). As a result of the dynamic coordination of lanthanide ions and electrostatic interactions, this unique type of MFPHs is also capable of being cold-welded and reshaped, thus suggesting its versatile applications. These reported hydrogels based on lanthanide complexes have greatly enriched the number of fluorescent components (Figure 6B),[27,28b] which make QDs attractive building blocks for MFPHs. The most convenient synthesis is to directly blend QDs into a hydrogel matrix to construct MPFHs.[29] However, the direct doping method might lead to an uneven distribution of QDs in the hydrogel systems. Therefore, the strategy of in situ entrapment or growth has recently been developed. For example, Banerjee and co-workers have prepared interesting MFPHs by adding Na_2S into supramolecular Cd^{2+}-coordinated metallohydrogels to produce in situ CdS nanocrystals.[30] The resulting QD-based hydrogels have a time-dependent fluorescence color change from blue to orange as a result of the continuous increase in the size of these QDs (Figure 6C). An alternative approach is to integrate the functionalized QDs into MFPHs through self-assembly. For example, Kelley and co-workers have demonstrated a multicolor DNA hydrogel, which was fabricated by the self-assembly of DNA-templated CdTe QDs with various emission colors into the DNA hydrogel network (Fig-

hydrogels, and pave the way for the development of multifunctional MFPHs with a plethora of future applications.

2.4. Luminescent Nanoparticles

Luminescent nanoparticles are newly developed but quite promising light-emitting materials that have a variety of advantages, including tunable emission color/intensity and low cytotoxicity as well as chemical and physical stability.[26] Most of them are artificially synthesized with diameters in one dimension of less than 100 nm. Typical examples include quantum dots (QDs), carbon dots (CDs), fluorescent dye doped silica nanoparticles (DSNPs), and metal nanoclusters (NCs).[27]

QDs are semiconductor nanomaterials with dimensions of about 1–10 nm and typically have core/shell (e.g. CdSe/ZnS) or core-only (e.g. CdS) structures functionalized with various coatings (Figure 6A).[27,28] They have the impressive ability to display fluorescence across all colors of the rainbow through modulation of the nanocrystal size and the

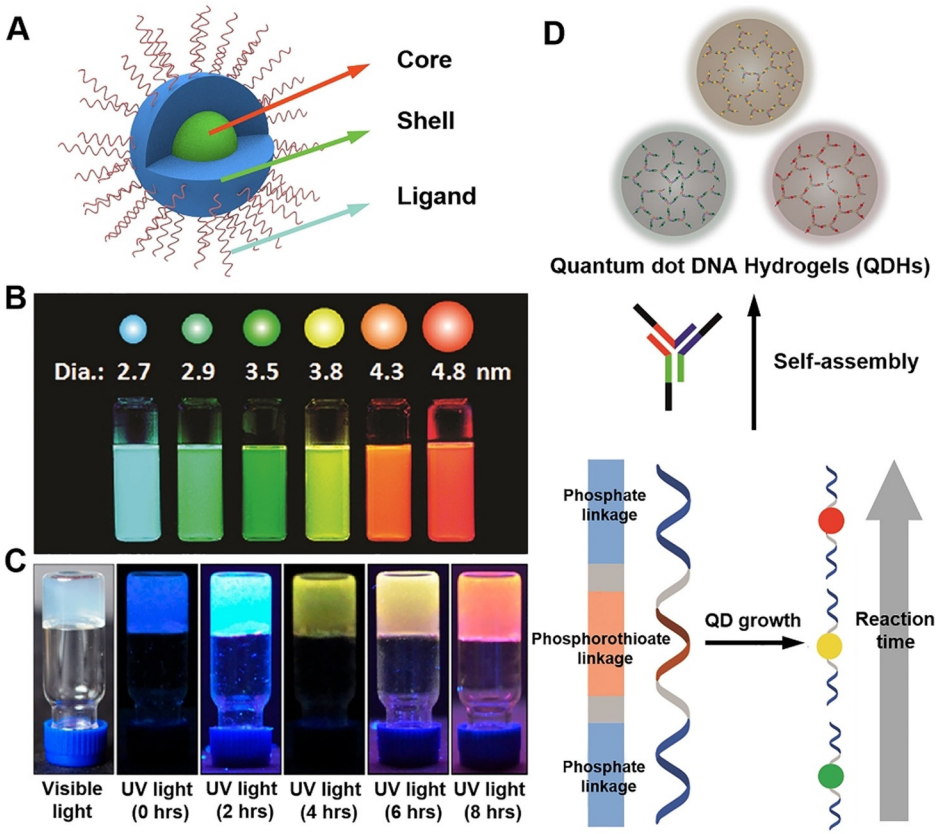


Figure 6. A) The typical core/shell structure of quantum dots (QDs) consisting of two or more kinds of semiconductor elements. B) Photographs showing the stunning rainbow colors of QDs with size-dependent fluorescence under irradiation with 365 nm UV light. Reproduced from Ref. [28b] with permission. Copyright 2011 American Chemical Society. C) Photographs showing the time-dependent change in the emission color of the QD-based MFPHs. With a gradual increase in the size of the QD crystal, a blue-to-yellow-to-orange color change of the MFPH sample was observed over time. Reproduced from Ref. [30] with permission. Copyright 2018 American Chemical Society. D) Schematic illustration showing the fabrication of QD-based DNA hydrogels by self-assembly of DNA-templated CdTe QDs with various emission colors into the DNA hydrogel network. Reproduced from Ref. [31] with permission. Copyright 2017 Nature Publishing Group.

ure 6D).[31] Importantly, the QD-based DNA hydrogels were proved to have low cytotoxicity and to be quite stable over a range of physiologically relevant temperatures and pH values, thereby showing their huge potential in multiplexed imaging studies and synergistic biomedical functionality.

Besides QDs, metal nanoclusters (NCs) are another important type of luminescent nanoparticles, which generally consist of several to tens of atoms (e.g. Au, Ag, Pt) and have a size similar to that of the Fermi wavelength of electrons.[32] As a consequence of their tunable emission color, high photostability, and good biocompatibility, metal NCs have become promising candidates for the design of MFPHs. For example, Xie, Liu, and co-workers proposed a unique "spatial confinement" strategy to prepare in situ glutathione (GSH) decorated Au NCs in chitosan solutions.[33] Luminescent nanogels were quickly formed by the electrostatic attraction between the positively charged chitosan polymer and the negatively charged carboxylic groups of the GSH ligands. The emission color of the nanogels could be changed to green, red, or orange by varying the ratio of gold and thiolate ligands or the pH value of the nanogel. It is worth noting that nonradiative decay pathways of Au NCs have been largely inhibited by their strong electrostatic interaction with chitosan, which leads to significantly enhanced emission of the nanogel. The method could be extended to prepare other types of metal NC based MFPHs, which may find wide potential applications.

2.5. Comparison of Different Luminogens

To date, various types of luminogens (fluorescent protein, organic fluorophores, lanthanide complexes, and luminescent nanoparticles) have been employed to construct MFPHs for various uses. Indeed, each type of luminogen has its own benefits and disadvantages, which will be briefly summarized as follows:

- Fluorescent proteins: good fluorescence stability; superior biocompatibility; intrinsic fluorescence; suitable for bioimaging; complex structure; emission colors and intensities are not easily modulated on demand by facile structural modification.
- Organic fluorophores: finely tuned emission intensity, color and responsiveness by elaborate structure design; easily available from commercial sources; prone to photobleaching, but sufficient for many applications.
- Lanthanide complexes: sharp emission bands; fabulous photochemical stability; high color purity; dynamic coordination; multiple emission lines.
- Luminescent nanoparticles: size-dependent fluorescence; high photochemical stability; low cytotoxicity; chemical and physical stability; complex structure; optical properties largely depend on particle synthesis and surface modification.

3. Promising Applications of MFPHs

MFPHs are the marriage of multicolor fluorescent materials and polymeric hydrogels. The synergistic integration of their properties means that many functionalities and applications of classic multicolor fluorescent materials are also generally applicable to MFPHs, including optical sensors,

bioimaging, information encoding, and encryption. Furthermore, the intrinsic features of the hydrophilic polymeric hydrogels have recently enabled some interesting uses of MFPHs (e.g. bioinspired color-changing actuators). The demonstrated applications of MFPHs will be introduced and discussed in this section.

3.1. Sensors

Multicolor luminescent materials with an analyte-specific emission color/intensity response have been widely used for sensing uses because of the high sensitivity and technical simplicity of fluorescence-based approaches. The classic fluorescent chemosensors primarily work in solutions or as solid films. From the viewpoint of practical in-field use, solid-state fluorescent sensory films are usually more attractive because of their portability, operational simplicity, and good stability. Nevertheless, one big challenge facing polymeric film sensors is the restricted sensitivity and relatively long equilibrium response time because of the hindered diffusion of analyte solutions inside the dense solid films.[34] Fortunately, the recently developed MFPH-based sensors hold great potential to address this difficult problem, because the highly hydrophilic 3D polymeric network consisting of thin sensing MFPHs films can facilitate ultrafast substance exchange with surrounding aqueous solutions of analytes. For example, Yang and co-workers reported an ultrafast hydrogel sensor for F^- by burying a hydrophobic small-molecule probe, BTBPA (*N*-(3-(benzo[*d*]thiazol-2-yl)-4-(*tert*-butyldiphenylsilyloxy)phenyl) acetamide), into a hydrophilic crosslinked polymer matrix.[14a] The sensing mechanism is based on the F^--triggered chemical reaction of BTBPA to induce a visible "blue-green" color change in the emission. The method proved not only selective and sensitive, but also highly rapid, and can report the F^- concentration of drinking water solutions within only 15 s. Besides physical mixtures, another effective strategy to develop MFPH-based sensors is by chemically grafting sensing molecules into a hydrogel matrix. As shown in Figure 7 A, the Liu group synthesized multicolor-fluorescent microgels containing a fluorescence resonance energy transfer (FRET) pair (NBDAE and RhBEA) and glucose-binding moieties (*N*-acryloyl-3-aminophenylboronic acid, APBA).[15d] Exposure to glucose solutions at appropriate pH values and temperatures regulates the microgel volume, thereby resulting in a tunable FRET efficiency and thus clear variations in the emission color (Figure 7 B–D). By using similar methods, powerful MFPH-based sensors for Zn^{2+} ions, pH value, and histamine have been successfully fabricated.[15b,35]

Additionally, there has been increasing research interest in mechanochromic hydrogels, which have a wide potential for strain sensing, indicating materials failure, and human/machine interacting applications. Recently, Miserez and co-workers reported a new concept to fabricate bilayer-structured mechanochromic MFPHs.[36] The top hydrogel layer was prepared from blue-light-emitting CDs, while the bottom hydrogel layer was based on red- or green-light-emitting Eu-terpyridine or Tb-terpyridine complexes, respectively (Figure 8 A). These two layers were linked through covalent bonding to prevent delamination under a large strain. Upon stretching, the bilayer hydrogel showed a force-induced

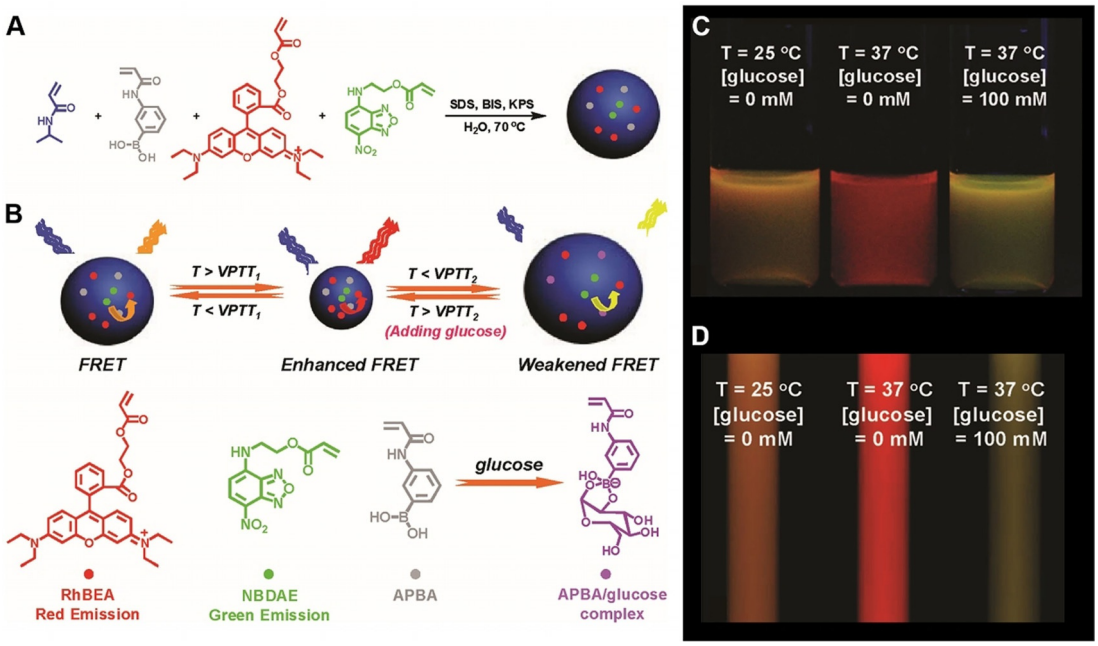


Figure 7. A) Schematic diagram of the fabrication of a multicolor fluorescent microgel sensor by the free-radical emulsion copolymerization technique. B) The color modulation mechanisms of microgels as a result of temperature variations and the addition of glucose. Images showing the change in the emission color of the microgel sensor in response to temperature and glucose taken: C) under a UV lamp and D) under an inverted fluorescence microscope equipped with a temperature-regulated incubator. Reproduced from Ref. [15d] with permission. Copyright 2011 American Chemical Society.

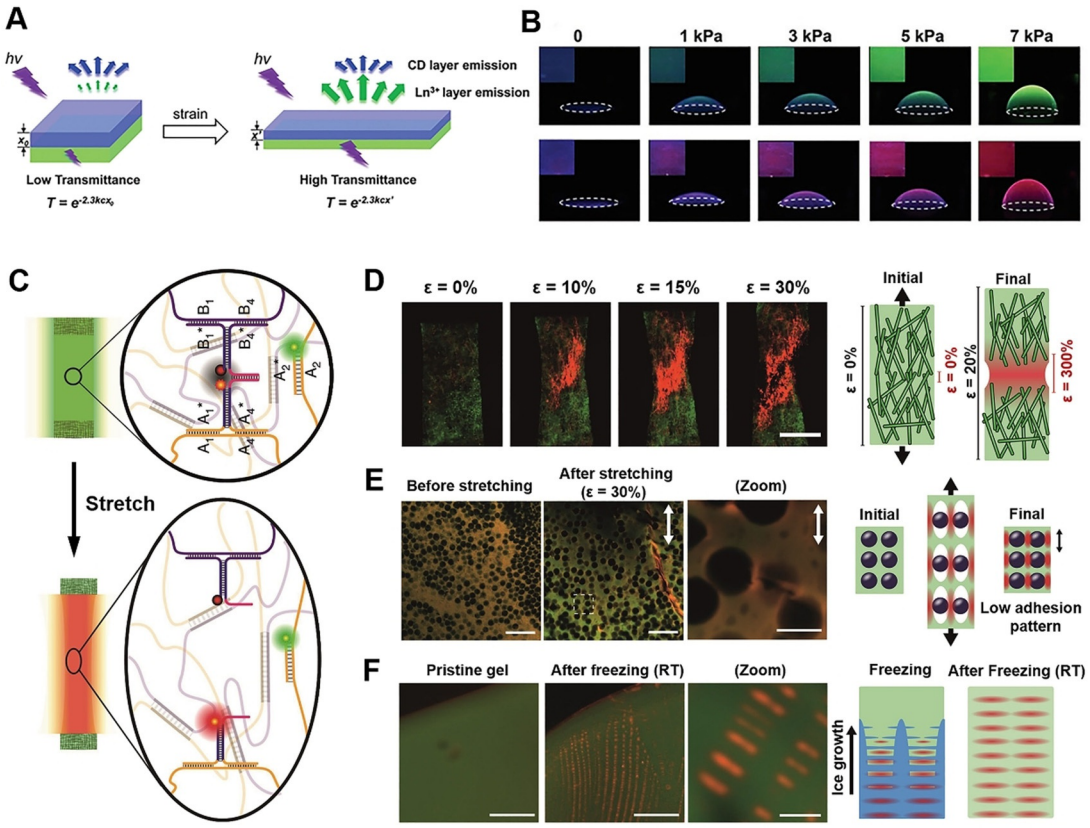


Figure 8. A) The structure and color-changing mechanism of bilayer mechanochromic MFPHs, in which the top hydrogel layer was prepared from blue-light-emitting CDs, while the bottom hydrogel layer was based on red- or green-light-emitting Eu-terpyridine or Tb-terpyridine complexes, respectively. B) Images showing the vivid change in the emission color under different bulging pneumatic pressures. Reproduced from Ref. [36] with permission. Copyright 2018 Wiley-VCH. C) Schematic demonstration showing the force-triggered color change mechanism of the mechanofluorescent 3D all-DNA MFPHs consisting of a FRET-type DNA tension probe and a green-light-emitting reference dye. D–F) Photographs and illustrations of its use for investigating the completeness and strain distribution of complex structures. Reproduced from Ref. [15e] with permission. Copyright 2019 Nature Publishing Group.

emission color response, because the top hydrogel layer was elongated and became thinner, thereby causing an increasing transmittance of emission light from the bottom hydrogel layer. More interesting colorimetric pressure sensors were further demonstrated. As can be seen in Figure 8B, a blue-to-cyan-to-green (Tb^{3+}-doped hydrogel as bottom layer) and a blue-to-violet-to-red (Eu^{3+}-doped hydrogel as bottom layer) change in the emission color was observed under different bulging pneumatic pressures. Additionally, Walther and co-workers reported mechanofluorescent 3D all-DNA hydrogels consisting of a FRET-type DNA tension probe and a green-light-emitting reference dye without mechanosensitivity.[15e] The FRET probe was composed of rationally designed DNA material functionalized with a red-light-emitting fluorogen and a quencher. When the sacrificial duplex of the DNA hydrogel was fractured by external forces, the FRET effect between the red-light-emitting fluorogen and the quencher is decreased and induces a green to red change of the emission color of the hydrogels (Figure 8C). Undoubtedly, such a MFPH-based mechanosensor has promising applications to monitor and investigate the completeness and strain distribution of complex structures (Figure 8D–F). In general, although mechanosensing systems are ubiquitous in nature and responsive to many functions of cells/organs, their artificial counterparts still remain underdeveloped. MFPHs could be a promising alternative for man-made mechanosensing systems because of their soft, wet, and especially tissue-like mechanical properties. More research is expected in this field.

3.2. Bioimaging

Since many MFPHs have good biocompatibility and tunable emission properties, it is highly anticipated that they may serve as platforms for in vitro cell imaging and sensing as well as in vivo detecting and tracking.[12,14b,15c,31,37] In this regard, many impressive advances have been achieved. For example, Wolfbeis and co-workers reported the first ratiometric fluorescent nanogel consisting of a pH indicator and FRET fluorescent pairs for multichannel fluorescence sensing and imaging of intracellular pH values.[15c] By using functionalized pyrene derivatives whose protonation and deprotonation states emit green and red light, respectively, Yang and co-workers have prepared another nanogel-based fluorescent probe for use as an imaging indicator for detecting pH values

in cytosol (Figure 9A).[14b] The green channel of fibroblast cells with the intracellular fluorescent probes undergoes a clear fluorescence decrease, while the emission intensity of the red channel gradually increases as the intracellular pH value is changed from acid to alkaline (Figure 9B). This labeling technique, which shows clearly different fluorescence colors for tumor and normal tissues, is critical to help surgeons distinguish tumor issues with improved precision in surgical operations.

In the area of in vivo detecting and tracking, Xu and co-workers have developed an injectable and biocompatible MFPH-based imaging probe (Figure 9C).[37a] Although no traditional organic dyes are used, the system still emits strong fluorescence under irradiation with UV light. This hydrogel probe was further demonstrated to have tunable degradation and mechanical properties, as well as the ability to gel in situ after injection. The combination of these promising properties enabled the in vivo degradation profiles of injected hydrogel implants to be successfully investigated by real-time but non-invasive fluorescence intensity monitoring (Figure 9D). Furthermore, Lin and co-workers demonstrated a powerful dual-emissive hydrogel particle with a core/shell structure for in vitro and in vivo photoluminescence imaging.[37b] Its hydrophobic core consists of red-light-emitting europium complexes and PNIPAM-*co*-PS, while its hydrophilic shell is composed of pH-sensitive blue-light-emitting quaternary ammonium tetraphenylethylene derivatives (d-TPE) and PNIPAM-*co*-PAA. Thus, the hydrogel probe as a whole is endowed with a pH-sensitive emission color response. Although AIE molecules usually have a wide emission spectrum, the introduction of the lanthanide complex with a narrow emission band in the hydrogel system successfully achieved a high-contrast and sensitive MFPH-based probe, which can be used for the discrimination of normal/tumor tissue in vivo. All of these successful attempts together have provided solid evidence for the huge potential applications of MFPHs in both in vitro and in vivo imaging techniques. Nevertheless, most of the currently developed MFPHs show down-conversion luminescence and are usually excited by UV light, which has an adverse effect on biological tissues. Future research efforts should target the fabrication of MFPHs with up-conversion luminescence that can be excited by near-infrared light.

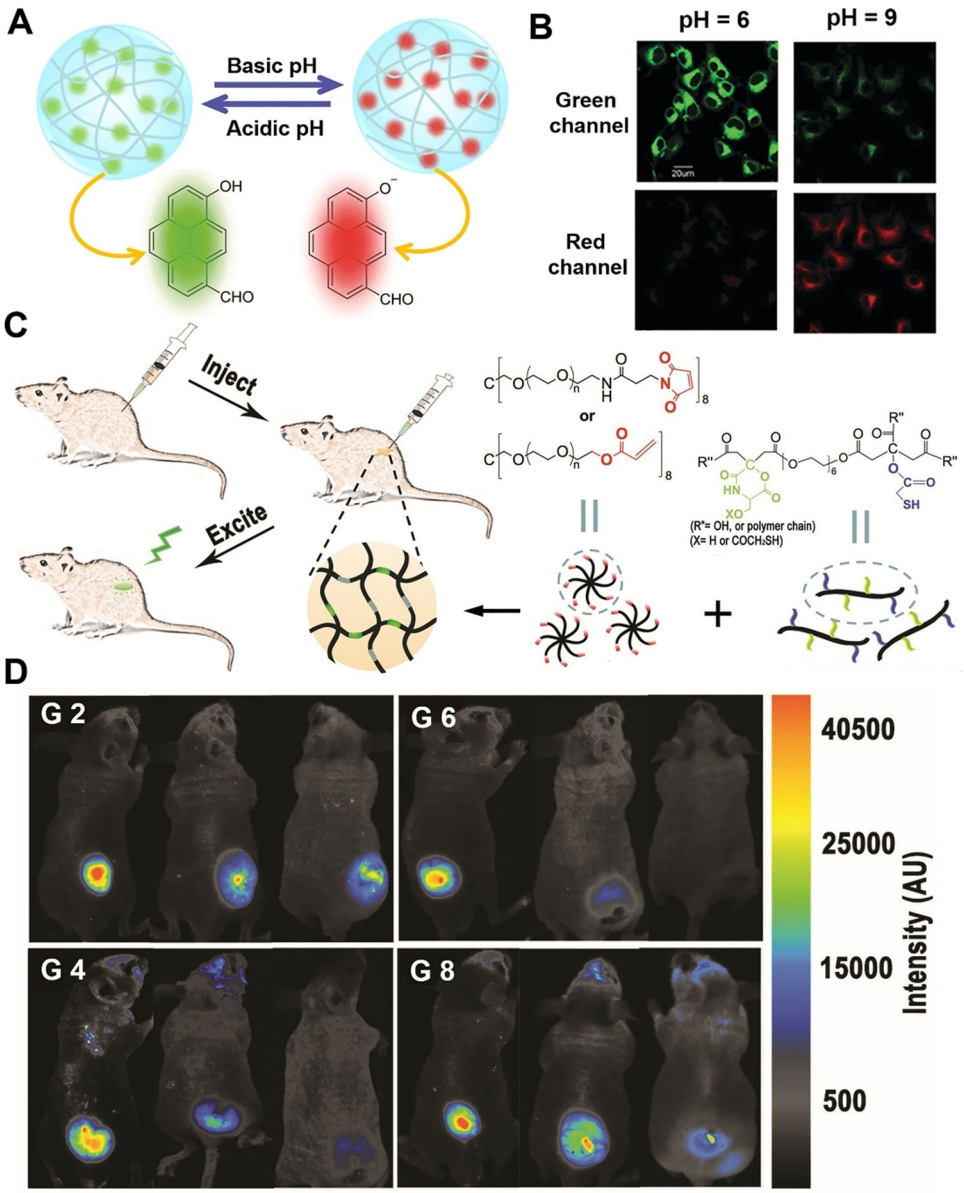


Figure 9. A) Schematic illustration of the pH-sensitive color change mechanism of a multicolor fluorescent nanogel containing a pyrene derivative. B) Confocal microscopy images of fibroblast cells imaged by intracellular fluorescent probes at pH 6 and pH 9 in green and red channels. Reproduced from Ref. [14b] with permission. Copyright 2014 The Royal Society of Chemistry. C) Illustration showing the synthesis of the fluorescent hydrogels for in vivo bioimaging and tracking use by the reaction of multivalent thiol-functionalized polymers and multiarm PEG acrylates or maleimides. D) Fluorescent images of nude mice injected with hydrogel-based fluorescent scaffolds on day 1, 2, and 3 (left to right). G2, G4, G6, and G8 are the hydrogel samples with different crosslinking agents and external conditions. Reproduced from Ref. [37a] with permission. Copyright 2018 Wiley-VCH.

3.3. Information Encoding or Encryption

Stimuli-responsive fluorescent materials are widely studied for applications such as information encoding and encryption, because of their facile design, easy handling, and high-throughput advantages. Compared with traditional monochromatic materials, multicolor fluorescent materials exhibit an on-demand change in the emission color and can thus contribute to more complex data encryption.[14c,15a,16,38] Furthermore, multicolor fluorescent polymeric hydrogels may also provide some extra potential uses, such as wearable materials, because of the soft materials involved. For example, Huang, Sessler, and co-workers have constructed a series of hydrogel building blocks of different emission colors by

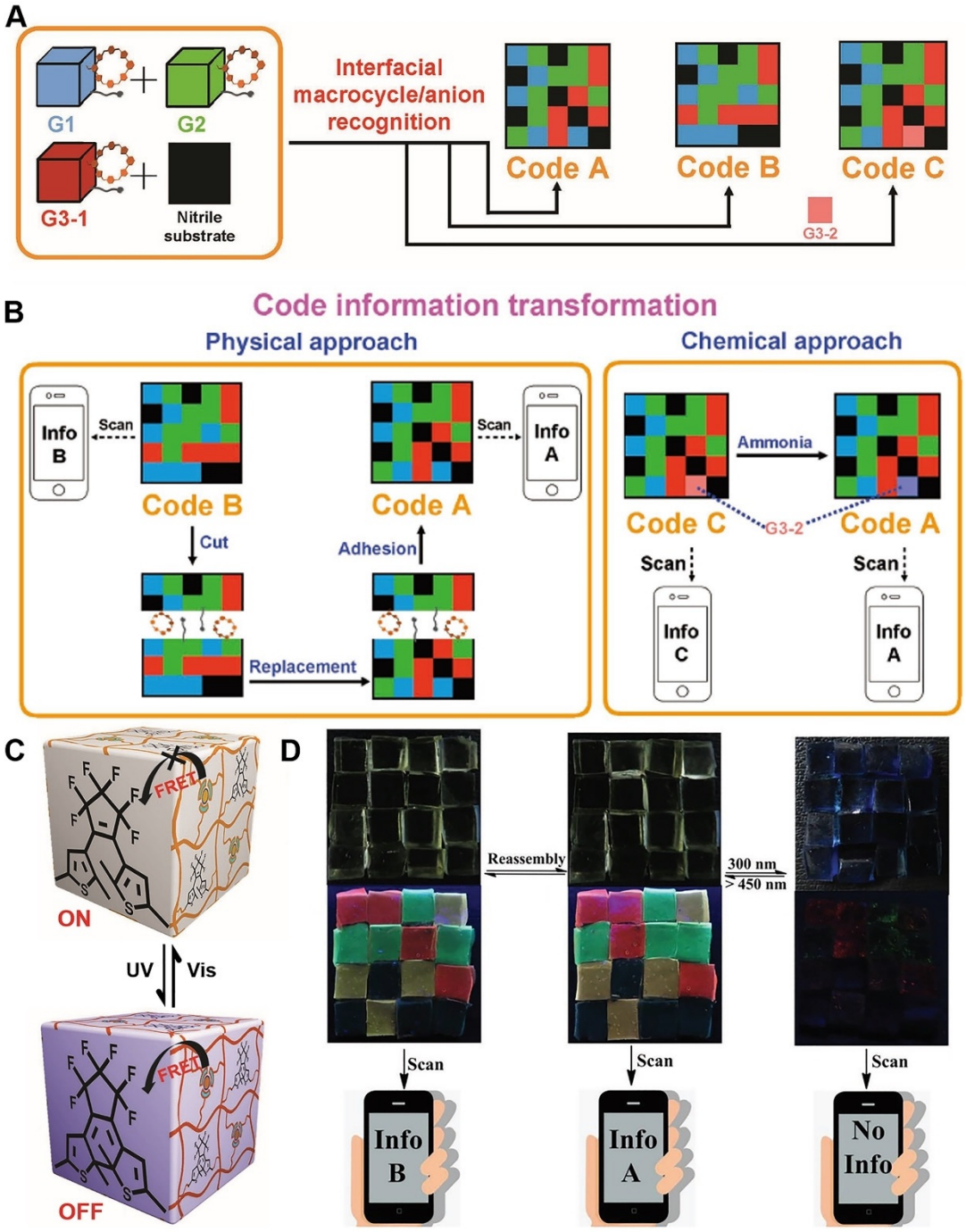


Figure 10. A) The formation of a 3D color code assembled by G1, G2, and G3 hydrogel blocks through physical adhesion. B) Schematic illustration of the transformation of code information triggered by physical and chemical approaches. Reproduced from Ref. [16] with permission. Copyright 2018 Wiley-VCH. C) Illustration showing the photoswitchable luminescence of MFPH building blocks consisting of diarylethene molecules and luminescent lanthanide complexes. D) Photographs of MPFH-based 3D code arrays exhibiting light-controlled encryption and decryption of information. Reproduced from Ref. [38b] with permission. Copyright 2019 Wiley-VCH.

grafting different fluorophores onto the hydrogel skeleton.[16] Specifically, the blue- (G1), green- (G2), and red-light-emitting (G3) hydrogels contain coumarin, boron-dipyrromethene, and rhodamine B domains, respectively. As shown in Figure 10A, these colorful building blocks were assembled on a black nitrile substrate through physical adhesion to form various 3D color code arrays, which represented predesigned information. Interestingly, information stored in these hydrogel codes can be recognized and read out by a smartphone under UV light. Moreover, the information could also be reprogrammed and transformed by rearrangement of these hydrogels blocks or control of their emission color by external chemical stimuli (Figure 10B). Potential use as wearable information storage and read-out was further demonstrated. By using a similar strategy, Zhao, Li, and colleges have recently reported another type of multicolor hydrogel block consisting of photoswitchable diarylethene molecules and luminescent lanthanide complexes.[38b] The open-close transition of the diarylethene ring could be controlled by irradiation with UV and visible light (Figure 10C). The closed form has been proved to induce FRET with the lanthanide complex and quench the emission. As a consequence, multicolor fluorescence of the assembled 3D code arrays could be effectively controlled by irradiation with UV and visible light. In this way, reversible information encryption and decryption are realized (Figure 10D).

Besides hydrogel arrays, fluorescent patterns on hydrogels could also be used for encoding and encrypting information. For example, Wu and co-workers recently reported a one-pot micellar copolymerization method to prepare MFPHs containing one single hydrophobic fluorogen: 4′-(*N*-vinylbenzyl-4-pyridinyl)-2,2′:6′,2″-terpyridine perchlorate (VPTP).[14c] The VPTP unimer and dimer emit blue and yellow light, respectively. It is thus possible to modulate the emission colors of the hydrogels by varying the ratio of unimer to dimer through the application of heat or light stimuli. This approach enables various types of 2D fluorescent patterns (e.g. quick response code), which represent different information, to be facilely produced using predesigned photo masks under irradiation with UV light, which actually modulates the ratio of VPTP unimer and dimer at the exposed regions.

To achieve more effective multistage data security, there has been recent research interest in expanding traditional 2D information encryption platforms to their 3D counterparts. In this regard, MFPHs are believed to be perfect candidate materials, because their soft and flexible nature enable them to be facilely programmed into various complex 3D geometries by employing such methods as "Lego" assembly[39] or the origami technique.[40] To this end, a proof-of-concept example has been demonstrated by us. As shown in Figure 11A, the MFPHs were prepared by repeated freezing/thawing cycles of perylene tetracarboxylic acid grafted gelatin (PTG) and poly(vinyl alcohol) (PVA) solutions, which exhibit a pH-triggered emission color change and typical Fe^{3+}-induced fluorescence quenching.[38c] The hydrogels also have a strong shape memory and self-healing properties because of the highly reversible borate bonds between the PVA and borax (Figure 11B). Therefore, it is possible to use Fe^{3+} as the "ink" to transform the 2D hydrogel films with printed information into 3D hydrogel information carriers with various complex shapes through a combination of shape memory and self-healing processes (Figure 11C,E). In this

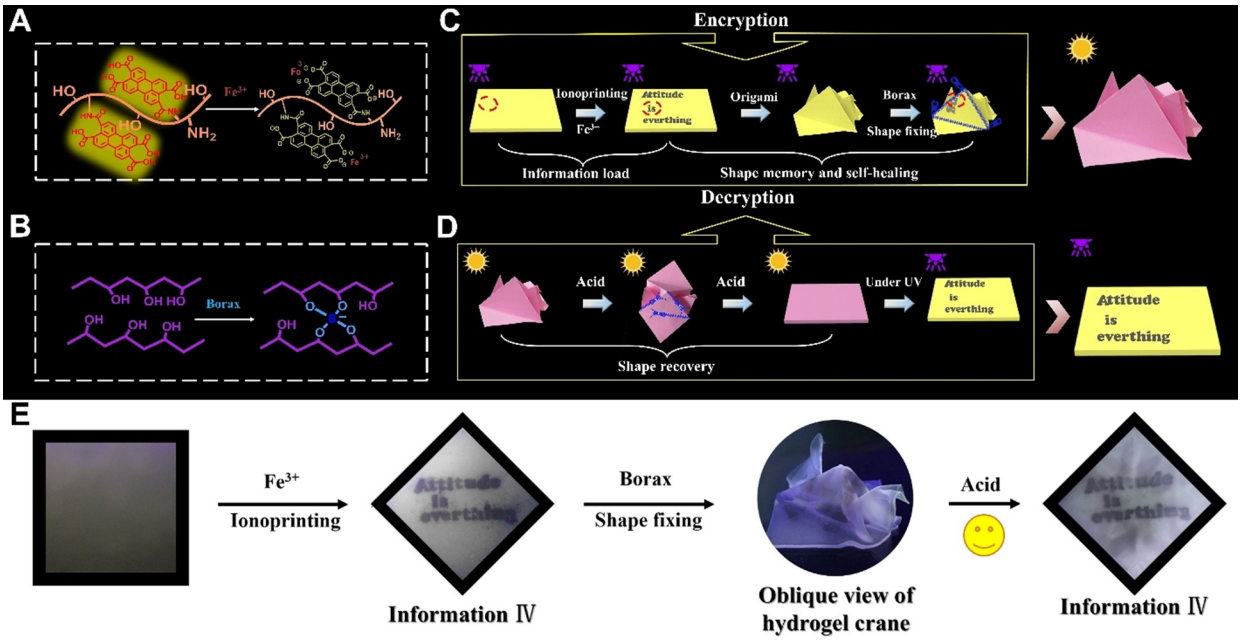


Figure 11. 3D fluorescent hydrogel origami for multistage data security. A) The Fe^{3+}-induced fluorescence quenching mechanism and B) the shape memory and self-healing mechanism through the formation of dynamic borate bonds between the PVA and borax. C,D) Schematic illustration of the information encryption and decryption process of the designed 3D fluorescent hydrogel origami, as well as E) the corresponding photographs taken under UV light. Specifically, the information can be loaded into the hydrogel films by ionoprinting and the Fe^{3+} ions can induce fluorescence quenching. Then 3D crane-shaped hydrogel origami structure was constructed by combining the origami technique, shape memory, and self-healing processes. Reproduced from Ref. [38c] with permission. Copyright 2019 Wiley-VCH.

way, information was successfully protected in three dimensions, which can only be decrypted following very specially predesigned procedures (e.g. under UV irradiation after shape recovery in acid solutions; Figure 11 D,E). Clearly, the encryption security of our 3D hydrogel platform is superior to its traditional 2D counterparts. All of these recent advances have preliminarily demonstrated the huge potential applications of MFPHs for data encoding and encryption. We also hope these examples could open up the possibility of utilizing multicolor fluorescent hydrogels for data storage, transmission, and protection.

3.4. Biomimetic Actuators

Many natural organisms (e.g. cephalopods, chameleons, frogs, and flowers) have amazing control over their color and morphology for camouflage, communication, and reproduction. These interesting motile plant/animal structures usually perform complex tasks by synergistic shape/color-changing functions. Synthetic counterparts are expected to form the next generation of smart materials that can function more closely to living organisms and have more practical applications. Compared with the widely studied polymer films and elastomers, polymer hydrogels—which have a tissue-like modulus and soft wet characteristics[41]—are more suitable for the construction of biomimetic color-changing soft robots. For example, we have made an attempt to combine a pH-responsive perylene bisimide (PBI) functionalized fluorescent hydrogel layer with a thermoresponsive graphene oxide/poly(*N*-isopropylacrylamide) hydrogel layer to produce biomimetic color-changing actuators.[5a] However, despite having the capability to undergo many different complex 3D deformations, the bilayer actuators can only exhibit an "on/off" emission response, not the preferable color change. They are thus far behind the abilities of natural creatures, such as chameleons, which can exhibit variations of skin color in different surroundings. Very recently, a big step forward was made by us. As shown in Figure 12 A, we first synthesized a fluorescent hydrogel by grafting the specially designed 6-acrylamidopicolinic moiety onto the chemically crosslinked PNIPAM network.[23] Its interfacial composition with pan paper (the passive layer) produced a bilayer hydrogel actuator, which could be endowed with bright red or green fluorescence when doped with Eu^{3+} or Tb^{3+} ions to form in situ lanthanide complexes. Interesting chameleon-inspired synergistic color/shape-

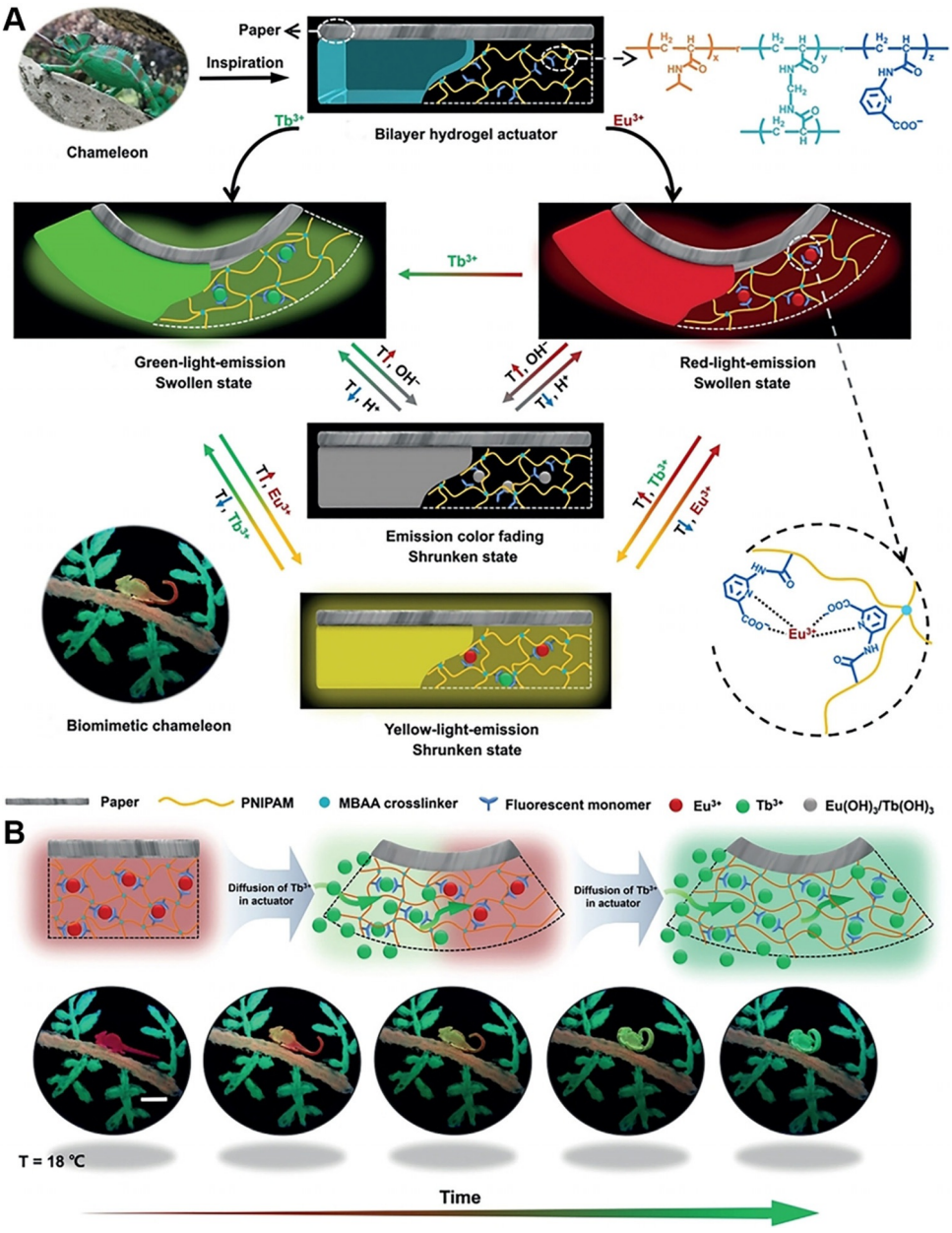


Figure 12. A) Schematic illustration of the structure and mechanism for the change in the emission color of the chameleon-inspired bilayer hydrogel actuator. B) Camouflage behavior of biomimetic hydrogel chameleons that can realize the gradual "red to yellow to green" color change and simultaneous body deformation in response to a subtle interplay between Tb^{3+} ions and temperature. Reproduced from Ref. [23] with permission. Copyright 2019 Wiley-VCH.

changing behaviors were achieved by utilizing both pH/metal ion-responsive variation of the emission color of the lanthanide complexes and the thermo-triggered volume change of the PNIPAM hydrogels (Figure 12B). Despite not being sufficiently elegant, the proposed demonstration has made color-changeable soft hydrogel robots accessible for the first time, thereby offering wide potential applications in biomimetic soft robotics, visual detection/display, camouflage, and so on.

In the above-mentioned soft actuator, the change in the shape and color is controlled by two different stimuli (e.g. temperature and metal ions, respectively). Such systems may sometimes suffer from a mismatch between shape deformation and color-shifting functions if the independent stimuli are not synchronized. It is thus advantageous to construct color-changing soft actuators that can be triggered by one single stimulus. To this end, we recently presented another bio-inspired anisotropic MFPHs actuator that can display a pH-controlled simultaneous change in the fluorescence color, the fluorescence brightness, and 3D shape deformation.[18] As shown in Figure 13A, this actuator also has a bilayer hydrogel structure, in which a pH-responsive AIEgen (tetra-(4-pyridylphenyl)ethylene, TPE-4Py) was introduced to impart the system with the fluorescence color and brightness response. In a neutral pH environment, the hydrophobic AIEgens tend to aggregate to produce a highly blue emission. In acid solutions, protonated TPE-4Py will form, which results in a noticeable red-shifted fluorescent emission and reduction of the fluorescence intensity. Meanwhile, protonated TPE-4Py can bind the benzenesulfonate groups of the poly(acrylamide/sodium 4-styrene sulfonate) network chains through electrostatic interactions, which induces shrinkage of the active layer as well as the enhancement of the fluorescence brightness. In this way, simultaneous color, brightness, and shape-changing behavior was realized in an acidic environment for the flower-shaped bilayer hydrogel actuator fabricated by 3D/4D printing (Figure 13B).

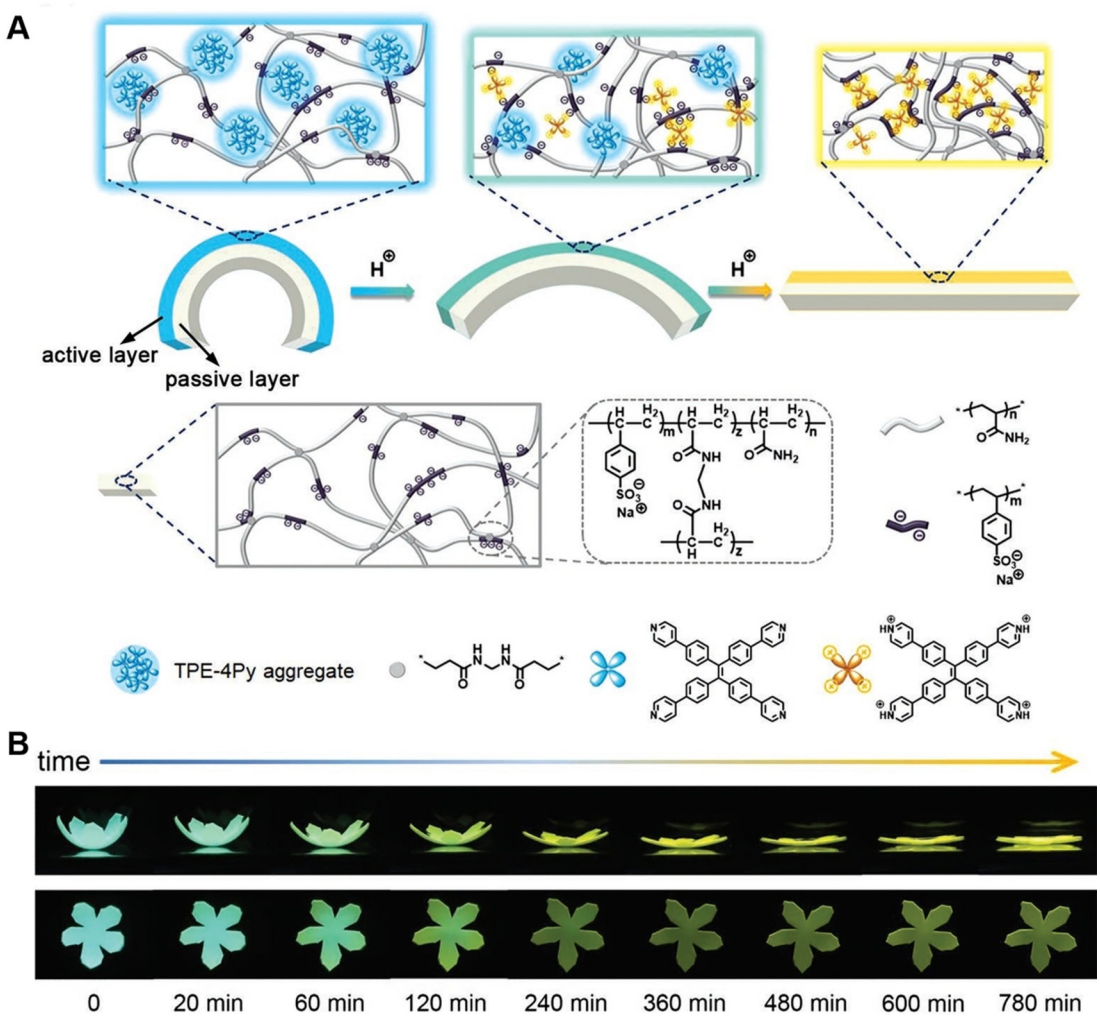


Figure 13. A) The chemical structure and multifunctional synergy mechanism of the biomimetic bilayer MFPHs actuators containing the pH-responsive AIEgen tetra-(4-pyridylphenyl)ethylene (TPE-4Py). B) Photographs of the flower-shaped bilayer hydrogel actuator displaying simultaneous fluorescence color, brightness, and shape-changing behavior in an aqueous solution at pH 3.12. Reproduced from Ref. [18] with permission. Copyright 2020 Wiley-VCH.

4. Summary and Outlook

In this Review, we have systemically summarized most of the recent progress in the design and preparation, as well as diverse functions and broad applications of MFPHs. MFPHs are generally fabricated by physical incorporation or chemical modification of two or more different fluorogens in the hydrogel matrix. The fluorogens are grouped into fluorescent protein, organic fluorophores, lanthanide complexes, and luminescent nanoparticles according to their structural features.

The use of such facile preparation approaches has enabled a number of robust multicolor fluorescent polymeric hydrogels with various chemical structures to be investigated. These MFPHs have been proved to be endowed with many extraordinary properties, including tissue-like mechanical properties, intrinsic soft and wet nature, biocompatibility with a high water content, diverse building blocks, along with responsive volume, shape, and fluorescence color changes. Notably, these advantageous properties make MFPHs unique from the classic and widely studied fluorescent materials used in the dry solid state or in solutions. MFPHs thus represent a quite promising class of luminescent materials that show great potential in many frontier applications such as sensing, bioimaging, biomimetic soft robotics, anti-counterfeit, and smart displays.

Despite there having been many impressive advances over the past decade, MFPHs are still a very young research area with numerous possibilities. First of all, new fabrication strategies have to be continually developed. In terms of the chemical structures of the fluorogens, although many classic organic fluorophores and lanthanide complexes have so far been employed to prepare MFPHs, the newly developed organic-inorganic hybrids and metal-containing materials (e.g. MOFs, perovskites) with excellent luminescence intensity and stability have not been introduced into polymeric hydrogel matrixes. The future marriage of MOFs or perovskites with MFPHs may open the way to many unforeseen properties and applications. Furthermore, the development of MFPHs with emission colors covering the full visible spectrum or far more into the near-IR region is also highly desired, especially for many bio-related uses.

Secondly, the future development of multifunctional MFPHs can bring new opportunities for practical applications. For example, as a consequence of their water-swollen soft and wet systems, MFPHs are of significant research interest in such biological areas as drug delivery, biosensing, and diagnosis. To this end, MFPHs with biodegradability and biocompatibility need to be considered. However, it has been found that most of the reported MFPHs have poor mechanical properties, which limits their potential applications especially in biomimetic actuators and soft robotics. More efforts should thus be devoted to constructing tough multicolor fluorescent polymeric hydrogels. Moreover, it would also be advantageous to design robust MFPHs with other functions, including self-healing, shape memory, electrical conductivity, or magnetism. Such multifunctional MFPHs may inspire innovative high-tech applications.

These proposed opportunities and challenges facing the field of MFPHs require continuous efforts from people with interdisciplinary backgrounds. As the saying goes, "Rome was not built in a day". We hope that this Review will build a solid platform to attract the wide interest of researchers, and lead to a boom in this field in the near future.

Acknowledgements

This work was supported financially by the National Natural Science Foundation of China (21774138, 51773215, 51873223), Key Research Program of Frontier Sciences, Chinese Academy of Sciences (QYZDB-SSW-SLH036), the National Key Research and Development Program of China (2018YFB1105100), Youth Innovation Promotion Association of Chinese Academy of Sciences (2019297, 2017337), the Open Fund of Guangdong Provincial Key Laboratory of Luminescence from Molecular Aggregates, South China University of Technology (2019B030301003), and Beijing Institute of Technology Research Fund Program for Young Scholars.

Conflict of interest

The authors declare no conflict of interest.

[1] W. Liu, W. Zhang, X. Yu, G. Zhang, Z. Su, *Polym. Chem.* **2016**, *7*, 5749 – 5762.

[2] a) N. Mehwish, X. Dou, Y. Zhao, C.-L. Feng, *Mater. Horiz.* **2019**, *6*, 14 – 44; b) Y. Li, D. J. Young, X. J. Loh, *Mater. Chem. Front.* **2019**, *3*, 1489 – 1502; c) Y. Xia, B. Xue, M. Qin, Y. Cao, Y. Li, W. Wang, *Sci. Rep.* **2017**, *7*, 9691.

[3] a) G. Weng, S. Thanneeru, J. He, *Adv. Mater.* **2018**, *30*, 1706526; b) P. Li, D. Zhang, Y. Zhang, W. Lu, J. Zhang, W. Wang, Q. He, P. Théato, T. Chen, *ACS Macro Lett.* **2019**, *8*, 937 – 942; c) J. Hai, T. Li, J. Su, W. Liu, Y. Ju, B. Wang, Y. Hou, *Angew. Chem. Int. Ed.* **2018**, *57*, 6786 – 6790; *Angew. Chem.* **2018**, *130*, 6902 – 6906; d) C. Madhu, B. Roy, P. Makam, T. Govindaraju, *Chem. Commun.* **2018**, *54*, 2280 – 2283; e) X.-X. Le, W. Lu, J. He, M. J. Serpe, J.-W. Zhang, T. Chen, *Sci. China Mater.* **2019**, *62*, 831 – 839.

[4] a) X. Zhang, K. Wang, M. Liu, X. Zhang, L. Tao, Y. Chen, Y. Wei, *Nanoscale* **2015**, *7*, 11486 – 11508; b) H. Wang, X. Ji, Y. Li, Z. Li, G. Tang, F. Huang, *J. Mater. Chem. B* **2018**, *6*, 2728 – 2733.

[5] a) 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; b) B. Wu, X. Le, Y. Jian, W. Lu, Z. Yang, Z. Zheng, P. Theato, J. Zhang, A. Zhang, T. Chen, *Macromol. Rapid Commun.* **2019**, *40*, 1800648.

[6] a) H. Chen, F. Yang, Q. Chen, J. Zheng, *Adv. Mater.* **2017**, *29*, 1606900; b) 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 – 4171; c) H. Jia, Z. Li, X. Wang, Z. Zheng, *J. Mater. Chem. A* **2015**, *3*, 1158 – 1163; d) Z. Wang, J. Nie, W. Qin, Q. Hu, B. Z. Tang, *Nat. Commun.* **2016**, *7*, 12033.

[7] a) Z. Li, Z. Hou, H. Fan, H. Li, *Adv. Funct. Mater.* **2017**, *27*, 1604379; b) J. Hai, X. Zeng, Y. Zhu, B. Wang, *Biomaterials* **2019**, *194*, 161 – 170; c) H. Zhi, X. Fei, J. Tian, M. Jing, L. Xu, X. Wang, D. Liu, Y. Wang, J. Liu, *J. Mater. Chem. B* **2017**, *5*, 5738 – 5744; d) D. Fan, X. Fei, J. Tian, H. Zhi, L. Xu, X. Wang, Y. Wang, *Polym. Chem.* **2016**, *7*, 3766 – 3772.

[8] a) A. Cayuela, S. R. Kennedy, M. L. Soriano, C. D. Jones, M. Valcarcel, J. W. Steed, *Chem. Sci.* **2015**, *6*, 6139 – 6146; b) A. Cayuela, M. L. Soriano, S. R. Kennedy, J. W. Steed, M. Valcarcel, *Talanta* **2016**, *151*, 100 – 105.

[9] a) P. Bairi, B. Roy, P. Chakraborty, A. K. Nandi, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5478 – 5485; b) Q. Zhu, L. Zhang, K. Van Vliet, A. Miserez, N. Holten-Andersen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 10409 – 10418; c) J. M. Galindo, J. Leganes, J. Patino, A. M. Rodriguez, M. A. Herrero, E. Diez-Barra, S. Merino, A. M. Sanchez-Migallon, E. Vazquez, *ACS Macro Lett.* **2019**, *8*, 1391 – 1395; d) K. Benson, A. Ghimire, A. Pattammattel, C. V. Kumar, *Adv. Funct. Mater.* **2017**, *27*, 1702955.

[10] E. A. Widder, *Science* **2010**, *328*, 704 – 708.

[11] M. D. Weber, L. Niklaus, M. Proschel, P. B. Coto, U. Sonnewald, R. D. Costa, *Adv. Mater.* **2015**, *27*, 5493 – 5498.

[12] a) Z. Wang, Y. Zhang, J. Zhang, L. Huang, J. Liu, Y. Li, G. Zhang, S. C. Kundu, L. Wang, *Sci. Rep.* **2014**, *4*, 7064; b) X. Ma, X. Sun, D. Hargrove, J. Chen, D. Song, Q. Dong, X. Lu, T.-H. Fan, Y. Fu, Y. Lei, *Sci. Rep.* **2016**, *6*, 19370.

[13] G. Feng, R. T. K. Kwok, B. Z. Tang, B. Liu, *Appl. Phys. Rev.* **2017**, *4*, 021307.

[14] a) L. Xiong, J. Feng, R. Hu, S. Wang, S. Li, Y. Li, G. Yang, *Anal. Chem.* **2013**, *85*, 4113 – 4119; b) L. Cao, X. Li, S. Wang, S. Li, Y. Li, G. Yang, *Chem. Commun.* **2014**, *50*, 8787 – 8790; c) 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 – 39352; d) J. Wang, F. Tang, Y. Wang, S. Liu, L. Li, *Adv. Opt. Mater.* **2020**, *8*, 1901571.

[15] a) E. Bat, E. W. Lin, S. Saxer, H. D. Maynard, *Macromol. Rapid Commun.* **2014**, *35*, 1260 – 1265; b) R. Nishiyabu, S. Ushikubo, Y. Kamiya, Y. Kubo, *J. Mater. Chem. A* **2014**, *2*, 15846 – 15852; c) H. S. Peng, J. A. Stolwijk, L. N. Sun, J. Wegener, O. S. Wolfbeis, *Angew. Chem. Int. Ed.* **2010**, *49*, 4246 – 4249; *Angew. Chem.* **2010**, *122*, 4342 – 4345; d) D. Wang, T. Liu, J. Yin, S. Liu, *Macromolecules* **2011**, *44*, 2282 – 2290; e) R. Merindol, G. Delechiave, L. Heinen, L. H. Catalani, A. Walther, *Nat. Commun.* **2019**, *10*, 528.

[16] X. Ji, R.-T. Wu, L. Long, X.-S. Ke, C. X. Guo, Y.-J. Ghang, V. M. Lynch, F. Huang, J. L. Sessler, *Adv. Mater.* **2018**, *30*, 1705480.

[17] 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.

[18] 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.

[19] 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 – 1100.

[20] a) P. Kumar, S. Soumya, E. Prasad, *ACS Appl. Mater. Interfaces* **2016**, *8*, 8068 – 8075; b) S. V. Eliseeva, J. C. Bunzli, *Chem. Soc. Rev.* **2010**, *39*, 189 – 227.

[21] a) M. X. Wang, C. H. Yang, Z. Q. Liu, J. Zhou, F. Xu, Z. Suo, J. H. Yang, Y. M. Chen, *Macromol. Rapid Commun.* **2015**, *36*, 465 – 471; b) W. Lu, C. Ma, D. Zhang, X. Le, J. Zhang, Y. Huang, C.-F. Huang, T. Chen, *J. Phys. Chem. C* **2018**, *122*, 9499 – 9506; c) C. Hu, M. X. Wang, L. Sun, J. H. Yang, M. Zrinyi, Y. M. Chen, *Macromol. Rapid Commun.* **2017**, *38*, 1600788; d) M. Wang, X. Li, W. Hua, L. Shen, X. Yu, X. Wang, *ACS Appl. Mater. Interfaces* **2016**, *8*, 23995 – 24007.

[22] A. P. S. Samuel, J. D. Xu, K. N. Raymond, *Inorg. Chem.* **2009**, *48*, 687 – 698.

[23] 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 – 16251; *Angew. Chem.* **2019**, *131*, 16389 – 16397.

[24] a) Q.-F. Li, X. Du, L. Jin, M. Hou, Z. Wang, J. Hao, *J. Mater. Chem. C* **2016**, *4*, 3195 – 3201; b) Z. Li, G. Wang, Y. Wang, H. Li, *Angew. Chem. Int. Ed.* **2018**, *57*, 2194 – 2198; *Angew. Chem.* **2018**, *130*, 2216 – 2220; c) J. Wang, S. Sun, B. Wu, L. Hou, P. Ding, X. Guo, M. A. Cohen Stuart, J. Wang, *Macromolecules* **2019**, *52*, 8643 – 8650.

[25] K. Meng, C. Yao, Q. Ma, Z. Xue, Y. Du, W. Liu, D. Yang, *Adv. Sci.* **2019**, *6*, 1802112.

[26] R. Dong, Y. Li, W. Li, H. Zhang, Y. Liu, L. Ma, X. Wang, B. Lei, *J. Rare Earths* **2019**, *37*, 903 – 915.

[27] E. Petryayeva, W. R. Algar, I. L. Medintz, *Appl. Spectrosc.* **2013**, *67*, 215 – 252.

[28] a) U. Resch-Genger, M. Grabolle, S. Cavaliere-Jaricot, R. Nitschke, T. Nann, *Nat. Methods* **2008**, *5*, 763 – 775; b) W. R. Algar, K. Susumu, J. B. Delehanty, I. L. Medintz, *Anal. Chem.* **2011**, *83*, 8826 – 8837.

[29] a) Q. Li, Y. W. Zhang, C. F. Wang, D. A. Weitz, S. Chen, *Adv. Mater.* **2018**, *30*, 1803475; b) D. Su, L. Wang, M. Li, S. Mei, X. Wei, H. Dai, Z. Hu, F. Xie, R. Guo, *J. Alloys Compd.* **2020**, *824*, 153896.

[30] S. Bera, A. Chakraborty, S. Karak, A. Halder, S. Chatterjee, S. Saha, R. Banerjee, *Chem. Mater.* **2018**, *30*, 4755 – 4761.

[31] L. Zhang, S. R. Jean, S. Ahmed, P. M. Aldridge, X. Li, F. Fan, E. H. Sargent, S. O. Kelley, *Nat. Commun.* **2017**, *8*, 381.

[32] a) Y. Lu, W. Chen, *Chem. Soc. Rev.* **2012**, *41*, 3594 – 3623; b) J. Li, J.-J. Zhu, K. Xu, *TrAC Trends Anal. Chem.* **2014**, *58*, 90 – 98.

[33] N. Goswami, F. Lin, Y. Liu, D. T. Leong, J. Xie, *Chem. Mater.* **2016**, *28*, 4009 – 4016.

[34] W. Lu, J. Zhang, Y. Huang, P. Theato, Q. Huang, T. Chen, *ACS Appl. Mater. Interfaces* **2017**, *9*, 23884 – 23893.

[35] a) M. Liras, I. Quijada-Garrido, O. García, *Polym. Chem.* **2017**, *8*, 5317 – 5326; b) X. Y. Xu, X. Lian, J. N. Hao, C. Zhang, B. Yan, *Adv. Mater.* **2017**, *29*, 1702298.

[36] Q. Zhu, K. Van Vliet, N. Holten-Andersen, A. Miserez, *Adv. Funct. Mater.* **2019**, *29*, 1808191.

[37] a) Y.-H. Tsou, X.-Q. Zhang, X. Bai, H. Zhu, Z. Li, Y. Liu, J. Shi, X. Xu, *Adv. Funct. Mater.* **2018**, *28*, 1802607; b) 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 – 5863.

[38] a) B. Chen, H. Xie, S. Wang, Z. Guo, Y. Hu, H. Xie, *Luminescence* **2019**, *34*, 437 – 443; b) Z. Li, H. Chen, B. Li, Y. Xie, X. Gong, X. Liu, H. Li, Y. Zhao, *Adv. Sci.* **2019**, *6*, 1901529; c) Y. Zhang, X. Le, Y. Jian, W. Lu, J. Zhang, T. Chen, *Adv. Funct. Mater.* **2019**, *29*, 1905514.

[39] C. Ma, T. Li, Q. Zhao, X. Yang, J. Wu, Y. Luo, T. Xie, *Adv. Mater.* **2014**, *26*, 5665 – 5669.

[40] X. P. Hao, Z. Xu, C. Y. Li, W. Hong, Q. Zheng, Z. L. Wu, *Adv. Mater.* **2020**, *32*, 2000781.

[41] a) K. Lei, Z. Li, D. Zhu, C. Sun, Y. Sun, C. Yang, Z. Zheng, X. Wang, *J. Mater. Chem. B* **2020**, *8*, 794 – 802; b) Z. Li, Z. Zheng, S. Su, L. Yu, X. Wang, *Macromolecules* **2016**, *49*, 373 – 386.

Manuscript received: May 25, 2020
Revised manuscript received: July 3, 2020
Accepted manuscript online: August 30, 2020
Version of record online: October 27, 2020

