

Recent Progress in Smart Polymeric Gel-Based Information Storage for Anti-Counterfeiting

Yu Sun, Xiaoxia Le,* Shiyu Zhou, and Tao Chen*

Information security protection has a tremendous impact on human life, social stability and national security, leading to the rapid development of anti-counterfeiting materials and related techniques. However, the traditional stored information on hard or dry media is often static and lacks functions, which makes it challenging to deal with increasing and powerful counterfeiting technologies. Modified intelligent polymeric gels exhibit color changes and shape morphing under external stimuli, which give them great potential for applications in information storage. This paper provides an overview of the latest progress in polymeric gel-based information storage materials in relation to counterfeiting. Following a brief introduction of anti-counterfeiting materials, the preparation methods for intelligent gels with adjustable colors (e.g., chemical colors and physical colors) and various encryption/decryption modes involving dimensions and diverse colors are outlined. Finally, the challenges and prospects for information storage and anti-counterfeiting based on smart gels are discussed.

decryption processes. Furthermore, these traditional anti-counterfeiting strategies are easily duplicated and are unable to counter the growing number of forgery techniques because they are widely recognized. Therefore, there is an urgent need to develop new anti-counterfeiting materials and innovative encryption/decryption approaches to endow stored information with higher security.

In recent decades, polymeric gels have been developed as novel materials with programmable 3D network structures that are adaptable and inclusive, showing great potential for applications in various fields such as soft robotics, tissue engineering and information storage.^[12–19] Among these, smart gels that exhibit shape morphing or color changes when exposed to external stimuli (e.g., light, heat, electricity, magnetism, mechanical

force, or chemicals) have gained much attention.^[20–23] Owing to its unique stimulus–responsiveness, a smart polymeric gel has been proven to be an excellent candidate for information encryption/decryption, exhibiting dynamic information output and a much higher security level. In general, an anti-counterfeiting process consists of three steps: coding, encryption, and decryption. For smart gel-based information storage devices, the external stimulus is the key to the decryption, and the tunable optical properties of the gel are utilized for coding. In other words, the information loaded on the gel is invisible or fake under normal circumstances, and the recipient can obtain the desired message only when the encrypted message is exposed to a particular external stimulus.

Although polymeric gel-based information storage devices (PGISDs) are still in their infancy, there has been strong worldwide interest in this field. However, no related review has provided an in-depth overview of gel-based information storage for anti-counterfeiting. This review provides a tutorial overview that summarizes the recent progress in PGISDs, focusing on the preparation methods for gels with adjustable optical properties, their encryption/decryption mechanisms, and how to improve the security level using their dimensions and colors. As depicted in **Figure 1**, anti-counterfeiting materials based on elaborate gel systems show excellent encryption/decryption behaviors by adjusting either their chemical colors in the presence or absence of UV irradiation or physical colors under visible light (absorption/transmittance, refraction/scattering, and interference/diffraction). Endowing gels that display polychromatic colors with stored information can achieve multilevel


1. Introduction

Counterfeiting is a worldwide problem that poses a severe threat to people's lives, social stability and even national security, which has prompted the development of anti-counterfeiting materials and corresponding encryption/decryption technologies in recent decades.^[1–6] A series of anti-counterfeiting materials and technologies, including watermarks,^[7] laser holograms^[8,9] and luminescent patterns,^[10,11] has been explored and utilized to tackle the challenges posed by false products or fake information. In general, stored information lacks encryption/

Y. Sun, X. Le, 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
E-mail: lexiaoxia@nimte.ac.cn; tao.chen@nimte.ac.cn

Y. Sun, X. Le, T. Chen
School of Chemical Sciences
University of Chinese Academy of Sciences
Beijing 100049, China

S. Zhou
St. Elizabeth Catholic High School
238 Westmount Blvd, Thornhill, ON L4J 7V9, Canada

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/adma.202201262>.

DOI: 10.1002/adma.202201262

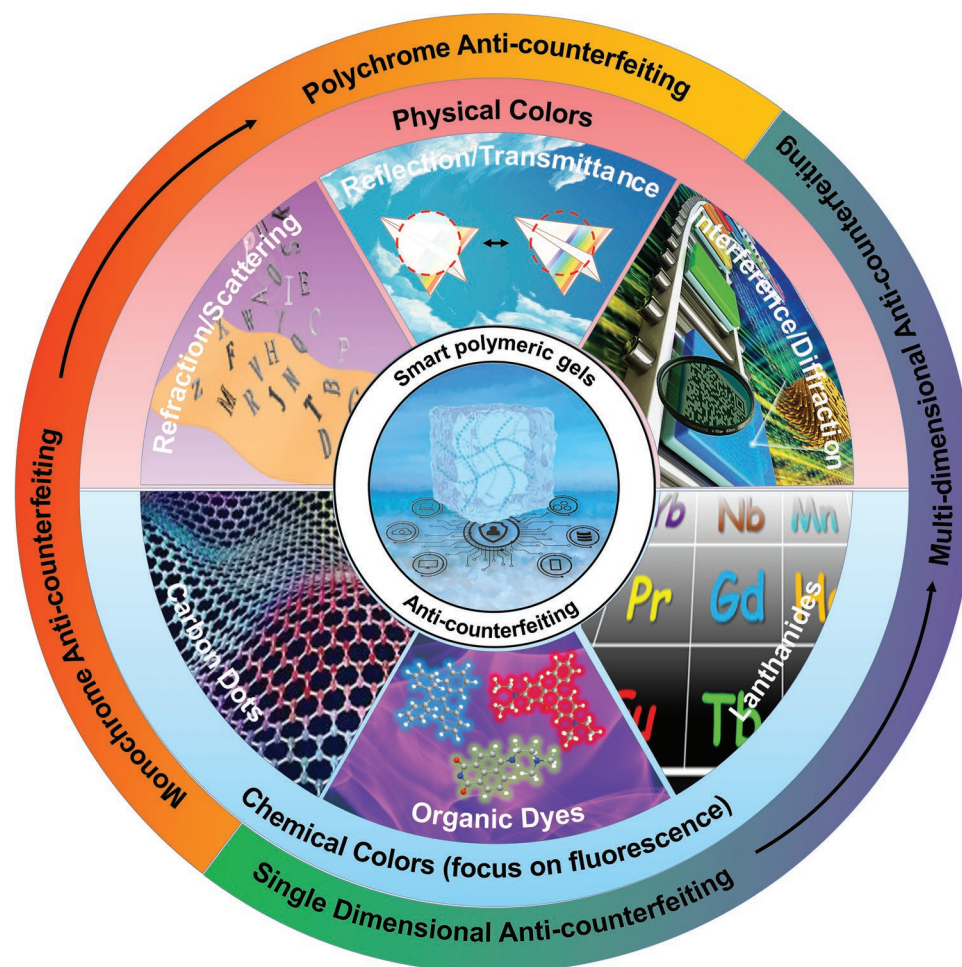


Figure 1. Schematic illustration of gels with adjustable optical properties, including chemical colors (focus on fluorescence) and physical colors (refraction/scattering, reflection/transmittance, interference/diffraction), that can be utilized for anti-counterfeiting (from monochrome to polychrome, single-dimension to multiple dimensions).

or multi-dimensional encryption/decryption processes through multifunctional synergy. Finally, we summarize the current challenges and future perspectives for gel-based information storage. We hope that their excellent modifiability and unique stimuli-responsive performance allow gel networks to advance information security systems and provide a new direction for future research.

2. Design and Construction of PGISDs

A crucial part of constructing PGISDs is the realization of adjustable optical properties. This type of anti-counterfeiting material can be roughly divided into the following two categories according to the coloration mechanism: chemical color, which depends on the chemical composition, and physical color, which relies on the microstructure. Specifically, gel-based information devices based on chemical colors can be constructed by simply introducing fluorescent units or stimulus-responsive pigment molecules. In this review, we mainly focus on fluorescence or fluorescent patterns, which can only be observed under certain conditions (such as a specific excitation

wavelength, temperature, and pH), giving them great potential for applications in the field of anti-counterfeiting.

As shown in **Figure 2**, emitting sources (e.g., carbon dots (CDs), dyes, lanthanides) are usually introduced to endow polymeric gels with fluorescent performance. CDs can directly serve as crosslinking points or can be modified (e.g., amide, hydroxy, or carboxy) before being grafted onto polymer chains via chemical bonding or physical interactions. For dyes and lanthanides, physical doping or chemical grafting approaches are often employed. Another straightforward method is to give dyes or ligands double bonds so that the fluorescent units can be directly introduced into the gel network through free radical copolymerization. In this type of system, appropriate approaches such as module assembly and ion printing are used to encode secret information, which can show up or fade away by adjusting either the swelling/deswelling state of the gel network or the fluorescent unit itself.

On the other hand, physical colors are generally produced by micro- or nanostructures that can modulate light (e.g., interference/diffraction, refraction/scattering, and reflection/transmittance). As representative and standard examples, structural color and grayscale are highlighted in this review because

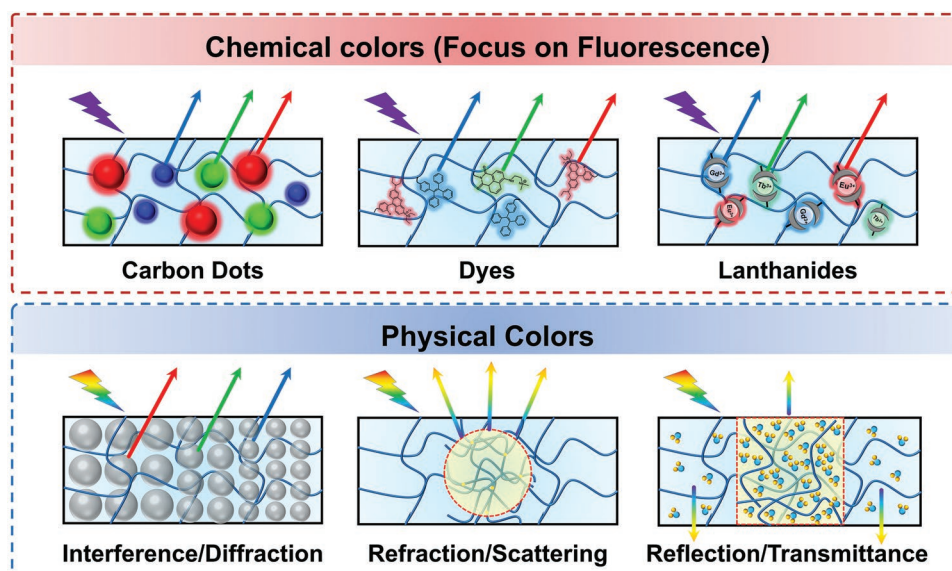


Figure 2. Cartoon figures of gel networks designed for anti-counterfeiting based on adjustable optical properties, including chemical colors (focus on fluorescence) and physical colors based on interference/diffraction, refraction/scattering and reflection/transmittance.

they have attracted much attention. Depending on the periodic spacing, refractive index, and viewing angle, gels with structural color can be designed and prepared by the in situ polymerization of a precursor solution based on photonic crystal arrays or patterned construction of opal/inverse opal structures. For grayscale, the coding patterns are obtained by spatially controlling the crosslinking density of the gel networks, and generating varying degrees of light scattering. Polymeric gels with different optical properties are first summarized and analyzed, along with their pros and cons, according to the recent progress in this area.

2.1. Polymeric Gel-Based Information Storage Based on Chemical Color

2.1.1. Chemical Color Based on CDs

CDs^[24] are one kind of novel 0D carbon material composed of discrete quasi-spherical nanoparticles that are less than 10 nm in size. CDs have attracted much attention as a new type of photoluminescence nanomaterial owing to their excellent properties, including high photostability, two-photon characteristics, excitation-light-dependent photoluminescence and good biocompatibility. Another exciting factor related to CDs is their cost-effective preparation method. Currently, CDs can be divided into the following three categories: graphene quantum dots,^[25] carbon nanodots (CNDs),^[26] and polymer dots.^[27] CNDs can be further grouped into carbon quantum dots (CQDs) and other carbon nanodots depending on the presence or absence of a crystal lattice. CDs have demonstrated many promising applications in bioimaging, optical devices, and anti-counterfeiting materials.

Wu et al.^[28] first prepared a series of glucose-based ionic liquid (IL) precursors via a hydrothermal method. Because of the tunable amphiphilicity of ILs, hydrophilic and hydrophobic

CQDs can be incorporated into hydrogel and organogel systems by in situ polymerization (Figure 3a). IL-modified CQDs can be firmly immobilized in a gel network by the hydrogen bonds between the amino groups in polyacrylamide (PAM) and the N and O atoms on the surface of the CQDs. Based on a sandwiched construction, the encoded information hidden in the inner layer can be decrypted after stretching and exposure to UV light. Recently, our group also synthesized one kind of vinyl-functionalized CDs (VCDs) that were crowned with rotatable hydrophobic groups and copolymerized with acrylamide (AM) and acrylic acid (AAc) (Figure 3b).^[29] The CDs in this system serve as crosslinkers and endow the as-prepared glycol gel with blue fluorescence, which can turn rose-red owing to the formation of aggregation-induced emission (AIE) aggregates after solvent exchange with water. Using its water-triggered fluorescence changing behavior, various fluorescent patterns can be printed on the gel by utilizing water as an “ink.” However, the encrypted information is unstable owing to the water–glycol exchange, which leads to the loss of definition or even the disappearance of the printed patterns.

In addition to simply anchoring CDs in the gel network via noncovalent bonding, CDs can also serve as gelation centers and contribute to the formation of crosslinked gels. A typical example presented by Qu et al.^[30] was CDs@silica composite gels fabricated via a reaction between the hydroxyl groups of CDs and tetraethyl orthosilicate (Figure 4). The obtained xerogel was not only loaded with a high fraction of CDs (19.2 wt%) without considering the aggregation-caused quenching effect, but also possessed high photoluminescence quantum yields exceeding 40%. Owing to the particularity of the preparation method, no relevant work on information anti-counterfeiting has been conducted.

Furthermore, even more interest has been generated by CD-doped stimulus-responsive gels, which exhibit apparent variations in their fluorescent intensity or color under external stimuli. Among these, temperature-sensitive hydrogel poly

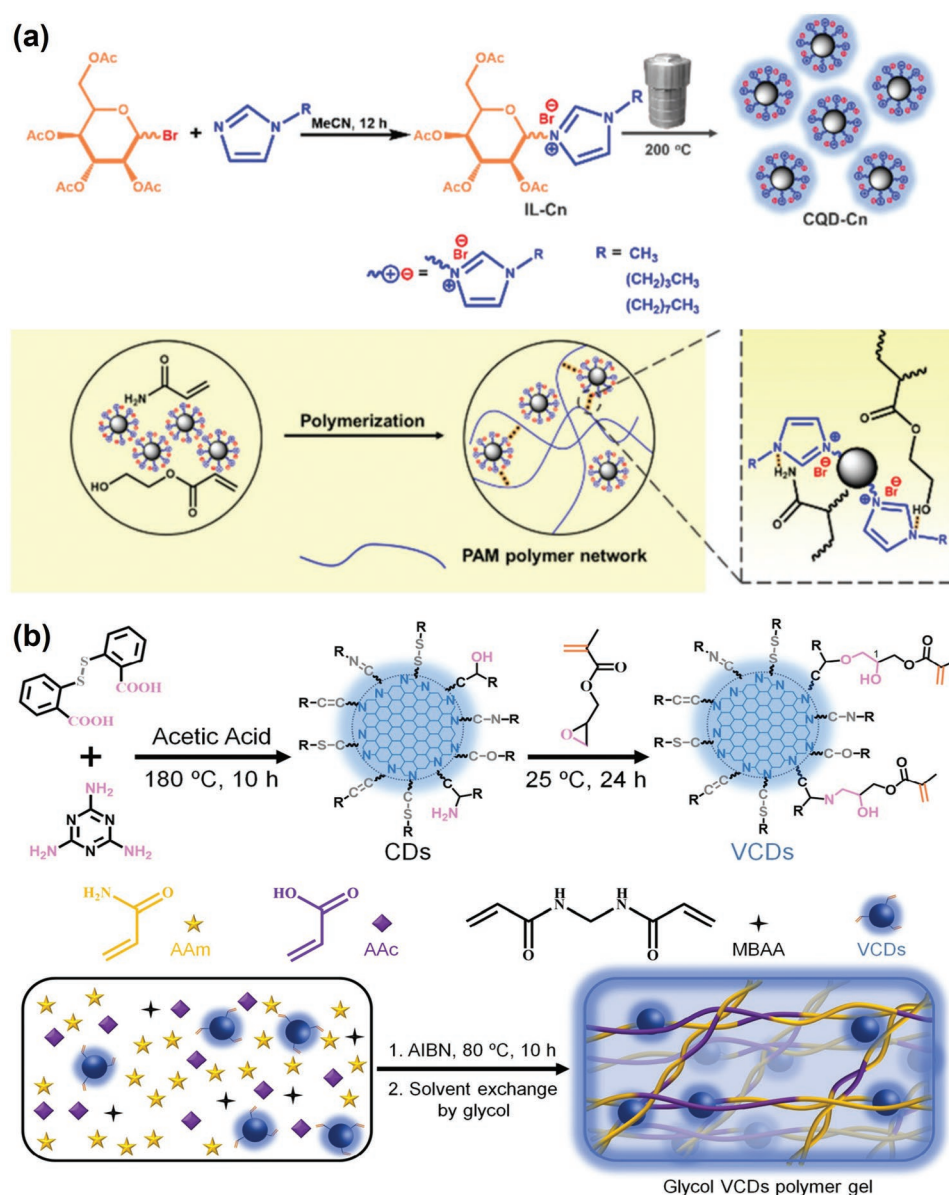


Figure 3. a) Preparation process for IL-based CQDs and CQD-doped PAM hydrogel (reproduced with permission.^[28] Copyright 2020, Royal Society of Chemistry). b) Synthetic procedure for CDs and VCDs, as well as the preparation of glycol VCD gels by radical polymerization (adapted with permission.^[29] Copyright 2021, John Wiley and Sons).

(*N*-isopropylacrylamide) (PNIPAM) is one of the most widely studied active matrices. For instance, Li et al.^[31] introduced CDs with strong fluorescence into PNIPAM hydrogels via atom transfer radical polymerization. The CD/PNIPAM hybrid hydrogel showed a dramatic change in its fluorescence intensity at a lower critical solution temperature of 33 °C. Similarly, Zhao et al.^[32] reported the one-step preparation of a green fluorescence-emission CD/PNIPAM hydrogel, which has been used for anti-counterfeiting identification, fluorescence imaging and ink. In summary, because some stimuli such as heat cannot be applied with spatial precision, the best way to achieve information encryption/decryption is to make gels smaller (e.g., microgels, nanogels) and use them as “inks.”

2.1.2. Chemical Color Based on Organic Dyes

Organic dyes^[33] possessing planar, rigid aromatic rings with conjugated structures can be divided into several types, including boron-dipyrromethene (BODIPY),^[34,35] rhodamine derivatives,^[36,37] coumarins^[38] and fluorescein.^[39] according to the differences in their chemical structures. Organic dyes can be introduced into gel systems through physical doping or chemical bonding. Wang et al.^[40] prepared a novel hydrogel by simply mixing a coumarin derivative (Pho-CA) with AM in water and exposing it to UV light in the absence of crosslinkers and initiators (Figure 5). The resultant hydrogel exhibited multi-functional characteristics, including stretchable properties, a self-healing behavior and water-controlled adhesiveness. The

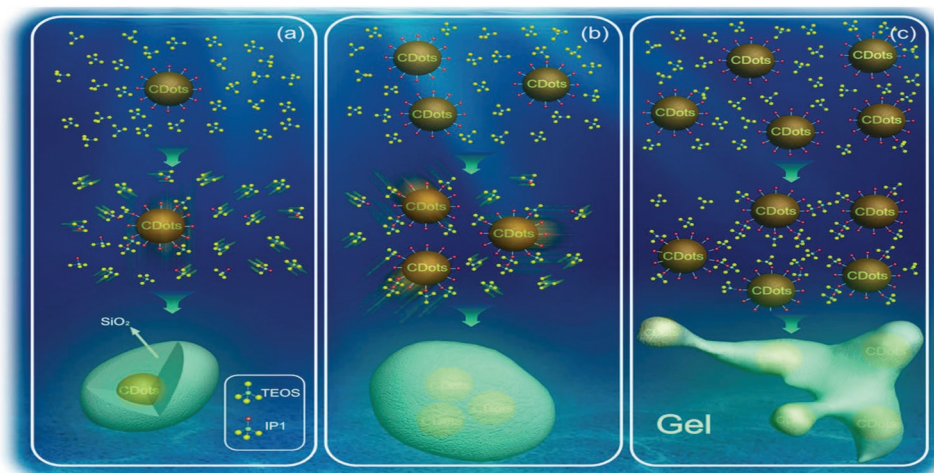


Figure 4. Formation of CDs@silica composite nanoparticles/gel via carbon dot-triggered silica gelation process (adapted with permission.^[30] Copyright 2017, American Chemical Society).

gelation process under UV irradiation, accompanied by blue fluorescent emission, can be utilized for information encryption and decryption. Nevertheless, the durability and stability of the encrypted content may be a challenging problem owing to the inevitable photobleaching, which is a universal phenomenon that exists in organic dyes.

Ji et al.^[41] first prepared a set of building blocks consisting of a PAM network, tethered tetracationic macrocyclic anion receptor, and pendant alkyl sulfonate subunits (Figure 6a). Organic dyes, including coumarin, BODIPY and rhodamine B, were incorporated into the backbones of the hydrogels to produce blue, green and red fluorescences. Through interfacial macrocycle/anion interactions, arrays of 3D color codes containing encoded information could be constructed, which could then be read by a smartphone app. Recently, they^[42] further designed a multifluorescent supramolecular hydrogel and

employed the “Codes in Code” method to improve the storage capacity. By introducing three kinds of AIE-gens (AIE-R, AIE-Y, AIE-B) into a poly(vinyl alcohol) (PVA) solution, hydrogels emitting red, yellow and blue light could be prepared through the formation of intermolecular hydrogen bonds (Figure 6b). Hydrogels containing 1D barcodes and 2D codes were then assembled into hydrogels with 3D information, leading to a large amount of information storage. To implement module assembly, gels must possess self-healing properties, which is a limitation of this anti-counterfeiting material.

2.1.3. Chemical Color Based on Lanthanides

Lanthanide ions and their corresponding complexes exhibit distinct optical properties such as a large Stokes shift, high

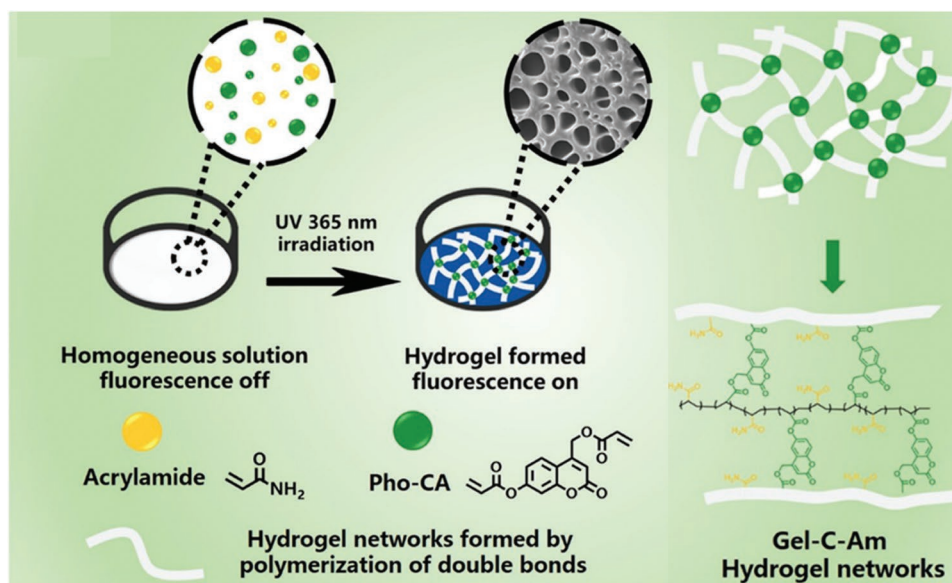


Figure 5. Schematic illustration of preparation process and chemical composition of Gel-C-AM hydrogel (reproduced with permission,^[40] Copyright 2020, American Chemical Society).

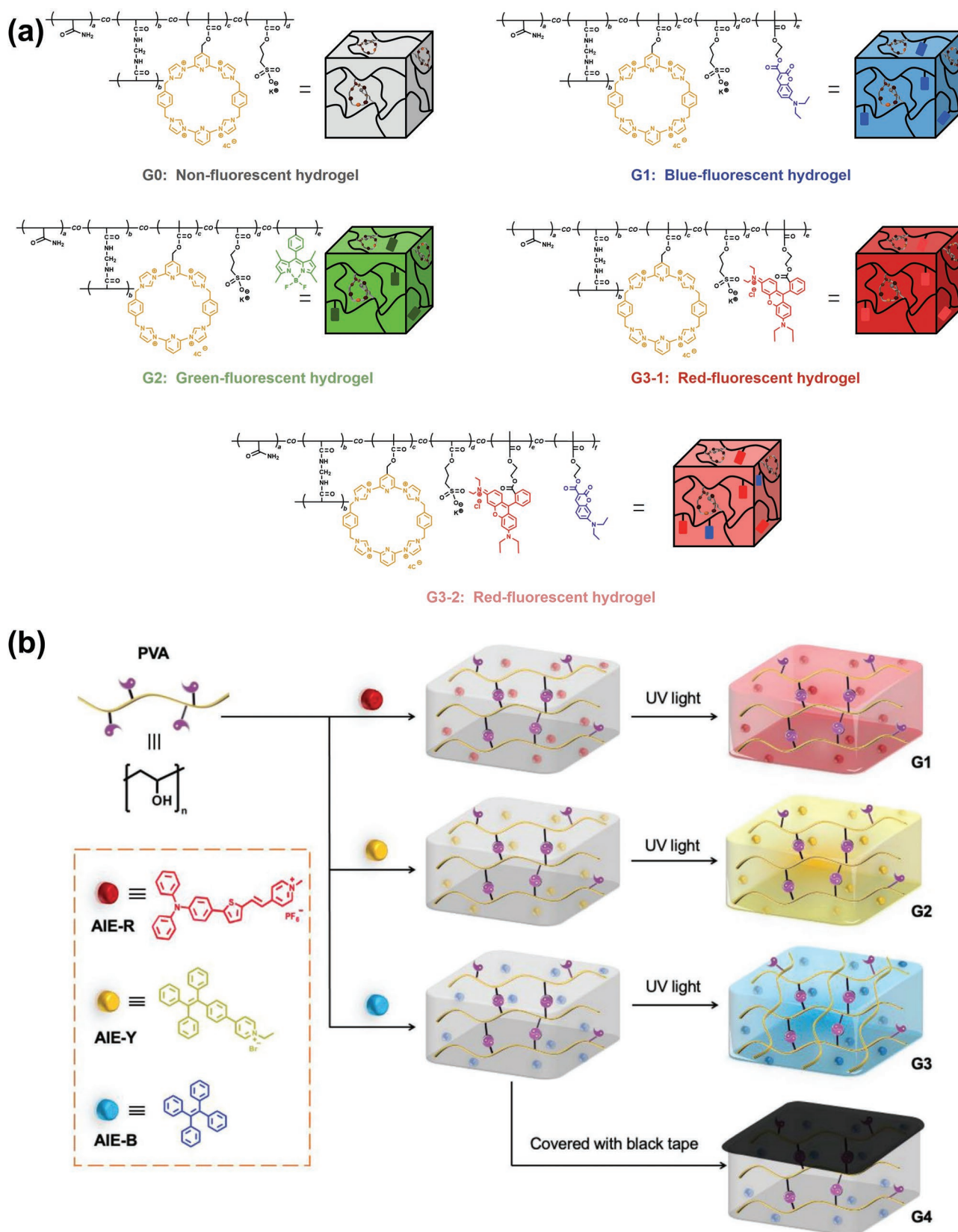


Figure 6. a) Chemical structures and cartoon representations of multifluorescent supramolecular polymeric hydrogels emitting no fluorescence, blue fluorescence, green fluorescence, and red fluorescence in response to UV light (adapted with permission.^[41] Copyright 2018, John Wiley and Sons). b) AIE supramolecular adhesive hydrogels made up of PVA and different organic dyes, including AIE-R, AIE-Y and AIE-B (adapted with permission.^[42] Copyright 2021, John Wiley and Sons).

quantum efficiency, narrow emission bands, and photochemical stability. Thus, they possess an attractive potential for organic photoelectric, luminescent coating, and fluorescent anti-counterfeiting applications.^[43–45] However, lanthanide ions always have a small absorption coefficient in the UV region because of the forbidden *f–f* transition, resulting in a low luminous efficiency. A practical method to overcome this drawback is the integration of organic ligands to lanthanide ions by the “antenna effect,” through which the former absorbs the UV illumination energy and transmits it to the latter, causing fluorescence emission. Another advantage of lanthanides is their variety of colors corresponding to different ions such as Eu^{3+} , Tb^{3+} , Sm^{3+} and Dy^{3+} , with their compounds exhibiting red, green, purple and yellow emissions under UV excitation, respectively (Figure 7a).^[46] Therefore, combining lanthanides and gels is a promising anti-counterfeiting strategy.

Because of dynamic lanthanide coordination, lanthanide-based gels generally exhibit stimulus–responsiveness, including a tunable fluorescence, self-healing performance and shape-memory behavior. For example, our group prepared hydrogels by copolymerizing NIPAM and the fluorescent ligand potassium 6-acrylamidopicolinate (K6APA).^[47] Following treatment with Eu^{3+} or Tb^{3+} , the obtained hydrogels displayed red or green emissions, which is characteristic of color shifting in response to acidity/alkalinity or metal ions (Figure 7b). Adopting a facile strategy, Xu et al.^[48] successfully fabricated a dual-emitting Eu^{3+} -functionalized hydrogen-bonded organic framework hydrogel film composed of melamine (MA), isophthalic acid (IPA), and sodium alginate. In this system, Eu^{3+} ions not only acted as a crosslinker for the hydrogel, but also selectively chelated with flumequine (FQ), producing red fluorescence. In addition, the fluorescence resonance energy transfer (FRET) process could occur between the D–A dual-component MA-IPA and ofloxacin (OF), successively quenching the blue emission but enhancing the green emission. Considering the unique fluorescence response of the hydrogel to OF and FQ, the authors fabricated a series of anti-counterfeiting platforms by arranging different types of arrays (Figure 7c). Wang et al.^[49] also reported a multi-responsive luminescent hydrogel that was obtained by mixing catechol-modified carboxymethyl chitosan, phenylboronic acid-modified gelatin, 3,5-dinitrosalicylic acid (DNSA), and Eu^{3+} ions using a simple heating–cooling process (Figure 7d). The resultant hydrogel showed color, fluorescence and phase changes in response to certain triggers such as temperature, acid/base, salt and redox stimuli. Thus, it has potential applications in sensors, medicine, self-healing materials and anti-counterfeiting.

2.1.4. Chemical Color Based on Two or More Emitting Sources

Currently, a single emitting source can no longer meet the requirements for advanced information security, which has promoted the development of multicolor hydrogels. For instance, Zhao et al.^[50] constructed a series of luminescent hydrogels with light-controlled on–off switches via the copolymerization of AM, a lanthanide complex, and a photochromic diarylethene unit (Figure 8a). The closed form of the diarylethene ring under UV irradiation could conduct a FRET with the lanthanide com-

plex, resulting in the luminescence quenching of the hydrogel. Once exposed to visible light, the diarylethene rings turned into the open form, and the luminescence of the hydrogels was recovered, allowing confidential information to be readable.

A double-layer mechanochromic hydrogel was presented by Ali's group,^[51] in which CDs and a non-luminescent absorber (BHEA) were incorporated in the top layer, and lanthanide ions coordinated with terpyridine were in the bottom layer. When an external strain was applied, the thickness of the top layer decreased, which increased the light transmittance and enhanced emission from the bottom layer (Figure 8b). This mechanochromic characteristic could easily be tuned by changing the composition of the top layer (the concentration of either the CDs or BHEA). Both stretching and pressing encryption devices can be constructed by adopting this type of strain-dependent discoloration. Similarly, they also developed a facile method for the fabrication of white-light-emitting hydrogels^[52] composed of a PAM/poly(acrylic acid) (PAAc) hydrogel network incorporating lanthanide ions (Eu^{3+} and Tb^{3+}), “antenna” dyes (terpyridine), and CDs (Figure 8c). The lanthanide ions were stabilized by coordination with the carboxylic groups of PAAc, whereas the methacrylate-CDs were covalently bonded in the gel network. By tuning the stoichiometry between the lanthanide ions and CDs, the obtained white luminescence showed an optical response to multiple stimuli, including heat, pH, organic vapors and metal ions. Owing to the synergy of the different emission sources, this type of gel-based anti-counterfeiting material exhibits a wider range of tunability in fluorescent colors, showing a more attractive performance during the information encryption/decryption process.

2.1.5. Other Chemical Color

In addition to the methods mentioned above for changing the optical properties, a change in the chemical structure or state of a specific molecule accompanied by a color transition can also be used for information storage.^[53,54] Because of the photoinduced ring-opening merocyanine (MC, purple) and ring-closing spiro (SP, colorless) forms of spiropyrans, they have been widely applied in the information storage field.^[55,56] For example, Long et al.^[56] reported an ion-crosslinked photochromic hydrogel fabricated via micellar copolymerization. In this system, hydrophobic methyl acrylate and a spiropyran-modified acrylate derivative formed micelles connected by hydrophilic sodium polyacrylate chains, which were further crosslinked by calcium ions. SP-MC conversion occurs upon exposure to UV light, which makes it possible to record programmable information. Owing to their excellent resistance to light fatigue and high color conversion reversibility, hydrogels have application potential in repeatable optical displays. A different approach was taken by Wang et al.^[57] involving the synthesis of photochromic hydrogels by the polymerization of *N,N'*-bisacrylylcystamine (BACA), AM and sodium *p*-styrene-sulfonate (NASS) in the presence of silver nanoparticles. Photogate coordination switching between the AgNPs and disulfide bond of BACA could be realized in this hydrogel system, reversibly altering the color between reddish-brown and gray-white. With the assistance of high-precision masks, desirable information

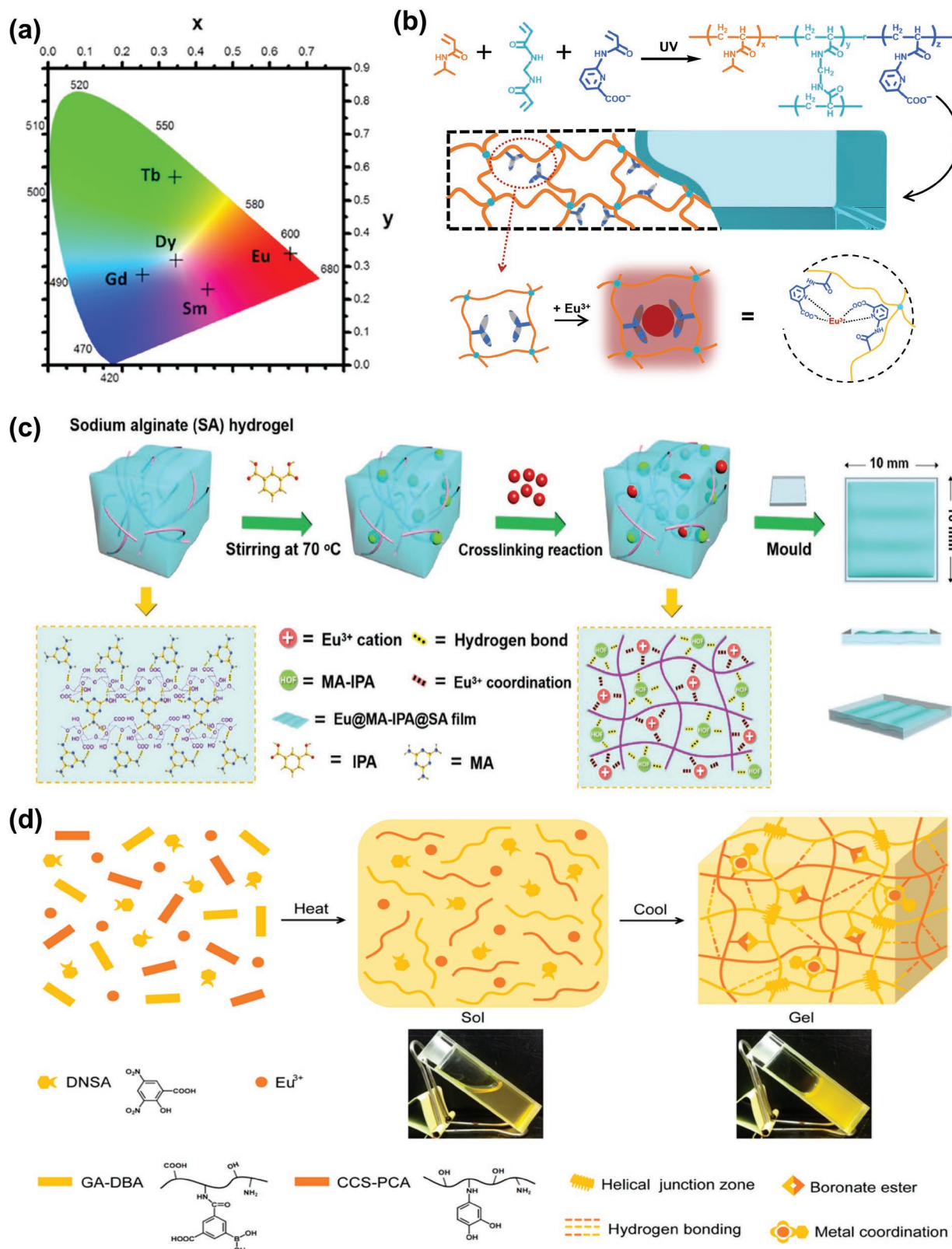


Figure 7. Schematic illustrations showing synthesis of fluorescent polymeric gels containing lanthanides. a) Colorimetric coordinates of various lanthanides (Ln = Sm-Dy) under 312 nm (adapted with permission.^[46] Copyright 2016, John Wiley and Sons). b) Illustration showing preparation of PNIPAM-K6APA hydrogel via UV polymerization, which shows red fluorescence after chelating with Eu^{3+} ions (adapted with permission.^[47] Copyright, John Wiley and Sons). c) Synthesis of Eu@MA-IPA@SA film by the crosslinking reaction of MA-IPA@SA hydrogel and Eu^{3+} ions (adapted with permission.^[48] Copyright 2021, John Wiley and Sons). d) Preparation of GA/CCS/DNSA/ Eu^{3+} hydrogel through a heating–cooling process (reproduced with permission.^[49] Copyright 2020, American Chemical Society).

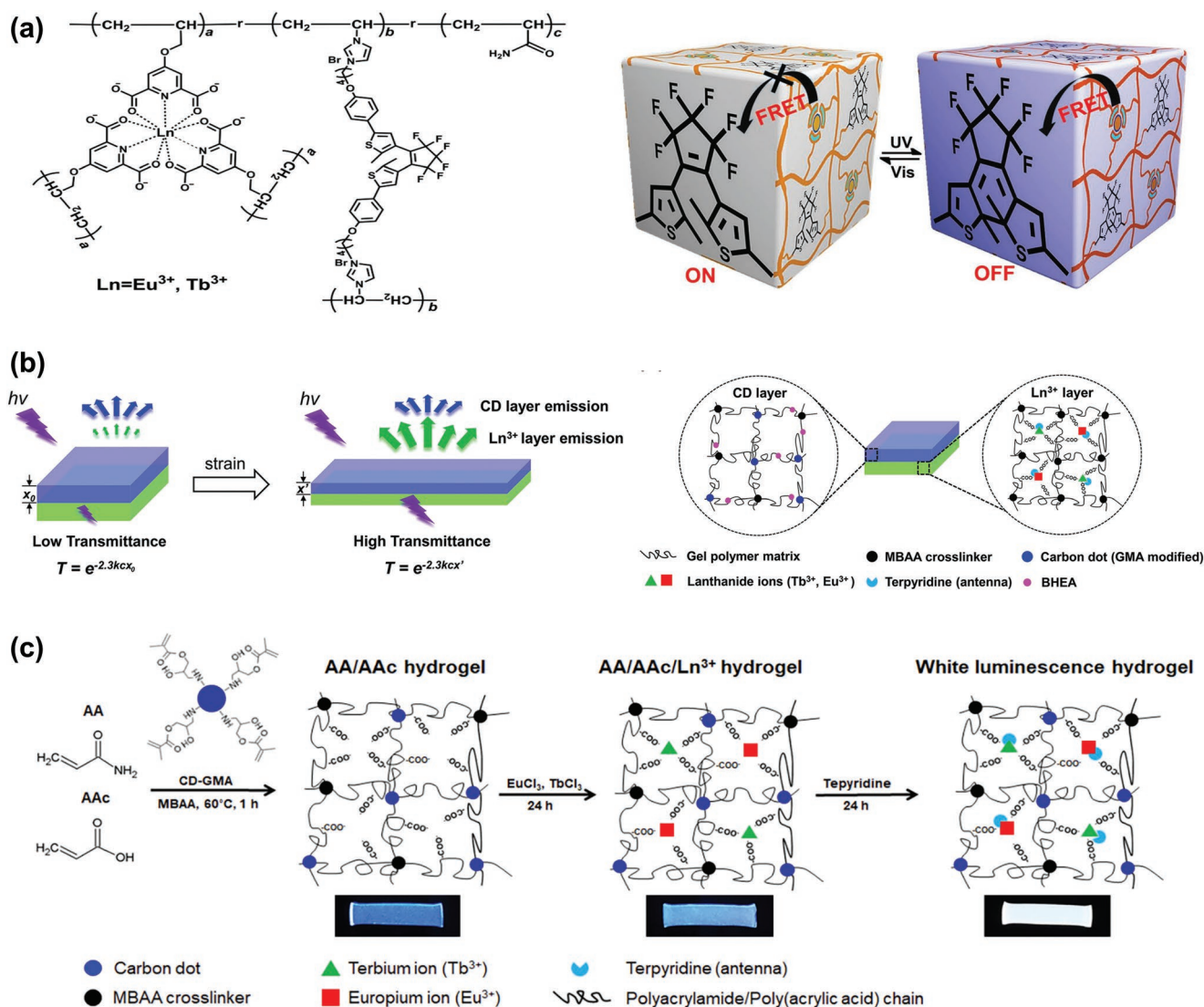


Figure 8. Fluorescent polymeric hydrogels based on mixed fluorescent centers. a) Chemical structure of luminescent polymeric hydrogel and its on–off photoswitchable behavior (adapted with permission.^[50] Copyright 2019, John Wiley and Sons). b) Design and chemical components of double-layer mechanochromic hydrogel (adapted with permission.^[51] Copyright 2019, John Wiley and Sons). c) Fabrication of white luminescence hydrogel with multi-stimuli-responsiveness (reproduced with permission.^[52] Copyright 2018, American Chemical Society).

could be written on the hydrogel after exposure to UV light and erased in the dark. Compared with fluorescent patterns that require UV irradiation, patterns with color transitions under visible light have the advantage of easy manipulation.

2.2. Polymeric Gel-Based Information Storage Based on Physical Color

2.2.1. Physical Color Based on Interference/Diffraction

In contrast to organic dyes based on the absorption of light, structural color originates from periodic micro-/nanostructures that block the propagation of certain wavelengths of light, displaying the corresponding colors.^[58,59] When these structural color materials are combined with intelligent gels, the obtained

hybrid materials exhibit tunable optical properties under external stimulation due to variations in the refractive index or lattice constant. Taking advantage of this feature, responsive structural color gels have shown good potential for display materials, anti-counterfeiting labels, sensors, and imaging.

Generally, the methods reported for constructing hydrogels with structural colors can be classified into 1D lamellar gels and 3D opal gels according to the periodicity dimension. A typical example of a lamellar photonic gel was reported by Haque et al.,^[60] in which a robust photonic hydrogel was prepared by assembling and stacking hydrophobic/hard poly(dodecylglyceryl itaconate) (PDGI) parallel bilayers into a hydrophilic/soft PAM network matrix. To endow the photonic gels with multi-responsiveness, they further introduced a secondary network of PAAc into the above PDGI/PAM gel to obtain an interpenetrating soft layer of PAM-PAAc (Figure 9a).^[61] In the soft layers, the

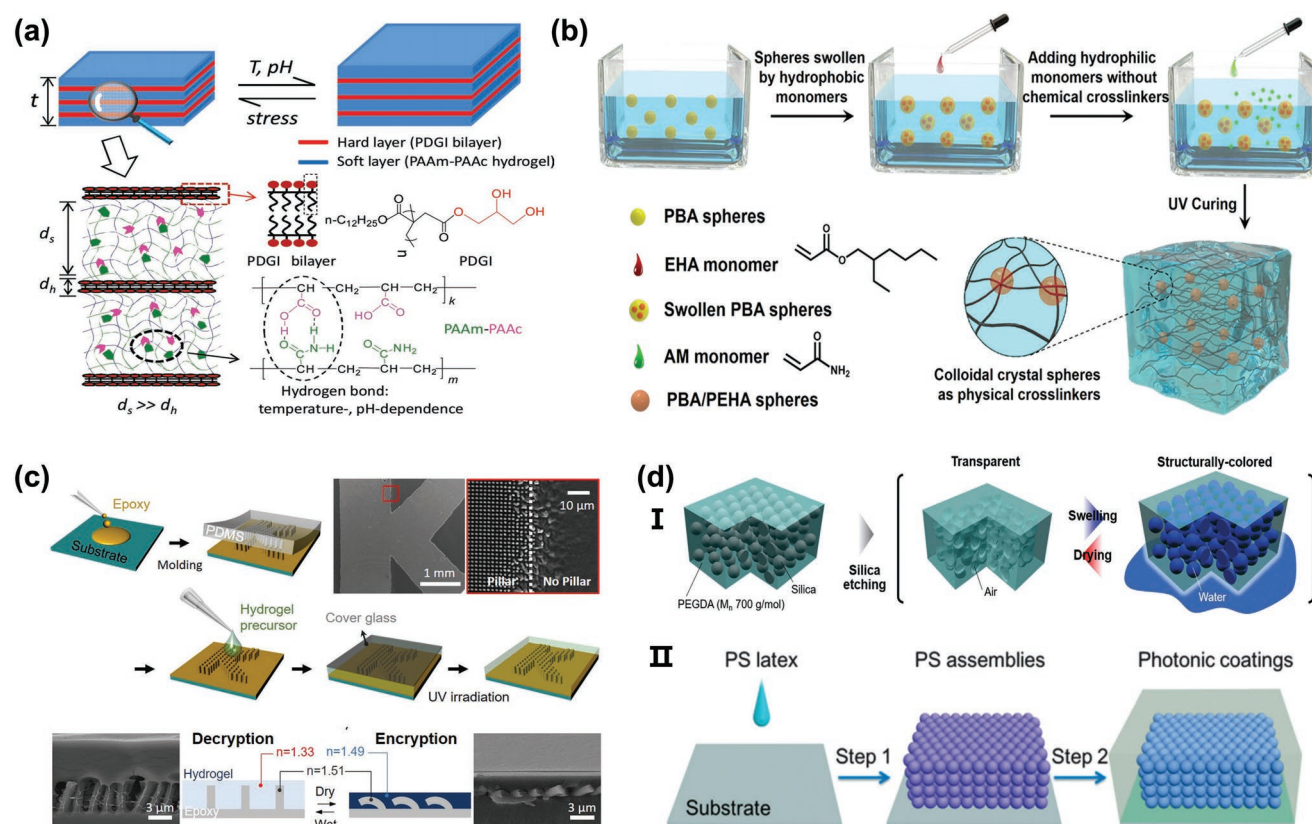


Figure 9. Methods for constructing gels with structural colors. a) Ternary stimuli-responsive photonic hydrogel PDGI/PAM-PAAc based on an alternating soft and hard lamellar structure (adapted with permission.^[61] Copyright 2013, John Wiley and Sons). b) Fabrication of photonic crystal hydrogel cross-linked by a colloidal array (reproduced with permission.^[62] Copyright 2019, American Chemical Society). c) Design and fabrication of hydrogel-based cryptographic surface with dynamic structural color (adapted with permission.^[63] Copyright 2019, John Wiley and Sons). d) Methods for constructing regular arrays by applying colloid particles, including assistance by capillary force (I) or dripping (II) (adapted with permission.^[64] Copyright 2020, John Wiley and Sons and reproduced with permission.^[65] Copyright 2015, Royal Society of Chemistry).

hydrogen bonds between the PAAc and PAM networks were weakened at high temperatures, and the dissociation of the carboxy groups of PAAc occurred at a high pH. As a result, in addition to mechanical stress/strain, an increase in the pH or temperature could also induce the swelling of the soft layers, accompanied by a red-shift of the photonic stop-band. As for 3D opal gels, Chen et al.^[62] synthesized a stretchable photonic hydrogel by directly cross-linking hydrophilic PAM chains with monodispersed poly(butyl acrylate) spheres, which were first swollen in 2-ethylhexyl acrylate monomers (Figure 9b). The fully physical network endowed the hydrogel with high elasticity, direct-printable processability and excellent optical qualities, exhibiting a broad photonic shift of 460 nm under minor compressive stress (kilopascal level). Because a simple press could verify the authenticity of the encoded information, this type of material is expected to be industrialized.

To apply them in information storage and anti-counterfeiting, facile and scalable strategies should be developed to obtain photonic patterns on gels. Micromolding processes such as imprinting and soft photolithography are the most commonly employed methods. As shown in Figure 9c, Choi et al.^[63] designed a water-responsive “hydrocipher” based on a hydrogel-coated micropillar array for the dynamic decryption of hidden photonic patterns. Specifically, the passive micropillar array was

made of epoxy and had an approximate refractive index compared with the dried hydrogel coat, making the pattern optically transparent during the encryption process. When triggered by water, the dehydrated hydrogel swelled, causing the bent pillars to become upright, accompanied by angle-dependent diffraction colors. Therefore, any patterns or figures composed of micropillar arrays could be used to conduct reversible encryption/decryption via dehydration–hydration cycles.

Similarly, Kim's group^[64] designed and produced macroporous hydrogels consisting of poly(ethylene glycol)diacrylate and a spontaneously formed regular array of silica particles (Figure 9d-I). Micropatterns could be loaded onto a hydrogel via multistep photolithography by selectively removing the silica particles. As the cavities collapsed randomly in the dry state, the entire material was highly transparent owing to the loss of long-range order. When the hydrogels were subjected to water, ethanol, or a mixture of these, the regular array was restored, leading to the appearance of an iridescent color. More interestingly, the composition of the water–ethanol mixture played an essential role in the resonant wavelength, thus endowing the encrypted patterns with advanced security. Although the above-encrypted patterns could be completely hidden and only shown under certain stimuli, the information was permanent, and new information could no longer be loaded. Du et al.^[65]

constructed a rewritable photonic paper by immobilizing ordered polystyrene particles into a CS matrix (Figure 9d-II). Using water as the ink, photonic patterns could be manifested owing to a swelling-induced lattice constant change in the PS assemblies. The brilliant colors could be tuned by changing either the particle size of the PS or the pH of the aqueous solution.

2.2.2. Physical Color Based on Refraction/Scattering

Another physical color is derived from the interaction (refraction/scattering) between electromagnetic waves and specific micro/nanostructures. As a typical manifestation of physical color based on refraction/scattering, spatiotemporally grayscale images are created by differences in the spatial cross-linking density of gel networks, which leads to the heterogeneity of local, visible light scattering (Figure 10). In addition to the physical mask-assisted patterning method,^[66,67] digital light processing^[68–70] is a mature technique for obtaining tailored patterns owing to its remarkable universality and higher definition. Recently, Jiang et al.^[66] utilized a grayscale exposure digital light processing method to fabricate 3D hydrogels with programmable patterns on or within them. The invisible patterns appeared once the printed hydrogel was immersed in water, which was ascribed to microphase separation and a tunable mesh size originating from the gradient cross-linking density. Moreover, the loaded patterns reversibly appeared or disappeared during the hydration/dehydration of the hydrogels.

Electrochemical methods can also induce changes in the crosslinking density and store complex information in hydrogels. In the early stages, Wu et al.^[71] prepared an agarose-based hydrogel interpenetrated with cationic CS chains. An electrode pen could be used to increase local regions of the hydrogel through electrolysis reactions, where the CS chains self-assembled into crystalline domains. The imparted structure and information could be erased, and new information could be written with the help of the reversible association–dissociation transition of the macromolecule. Recently, they created a CS hydrogel doped with epichlorohydrin for 2D and 3D structural information storage.^[67] By adopting electrical writing, the

generated hydroxyl ions could open the ring of epichlorohydrin, which led to the covalent crosslinking of CS chains. As a result, the invisible structural information could be decrypted via three different optical access methods: the differing absorption of colored molecules, transmittance, and solubility.

2.2.3. Physical Color Based on Reflection/Transmission

Transparent–opaque transition is another physical color change that is ascribed to the reflection or penetration of light. The significant changes in their optical properties allow gels with this property to be used for information storage.^[72–74] In general, changes in the turbidity or transmittance of a gel result from the formation of heterogeneous phases, either by microphase separation or hydrophobic association. Inspired by the memorizing–forgetting behavior of the brain, Gong's group synthesized a polyampholyte (PA) hydrogel made from methyl chloride-quaternized *N,N*-dimethylamino ethylacrylate and sodium *p*-styrenesulfonate, which showed distinct turbidity changes under sudden cooling (Figure 11a).^[75] Taking advantage of the asymmetric water absorption–release kinetics, the PA hydrogel could memorize 2D feature information with the assistance of hollowed-out patterns during the thermal learning process.

Interestingly, the memorizing–forgetting process is dependent on the learning time and temperature, which can be used for sequential information forgetting. Liu et al.^[76] designed and fabricated an ionic organohydrogel composed of hydrophilic AAC and hydrophobic 2-methoxyethyl acrylate in a mixed solvent of DMSO and water (Figure 11b). When treated with water, solvent displacement occurred, and the hydrophobic segments were separated and aggregated inside the organohydrogel, leading to a transparent-to-turbid transition. A series of printed patterns could be obtained through the water-writing process. Furthermore, writing–wiping cycles could be conducted with the organohydrogel by immersing it in a DMSO solution. Because the interaction between solvent and gel networks plays an essential role in information coding, the shortcomings of solvents, such as instability, will also have a certain impact on the information encryption/decryption procedure.

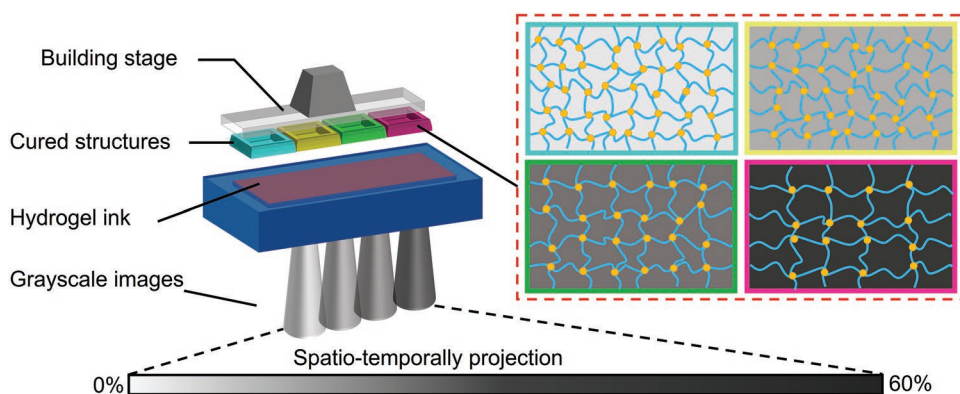


Figure 10. Digitally coded printing of hydrogels with spatiotemporal grayscale patterns (reproduced with permission.^[66] Copyright 2019, American Chemical Society).

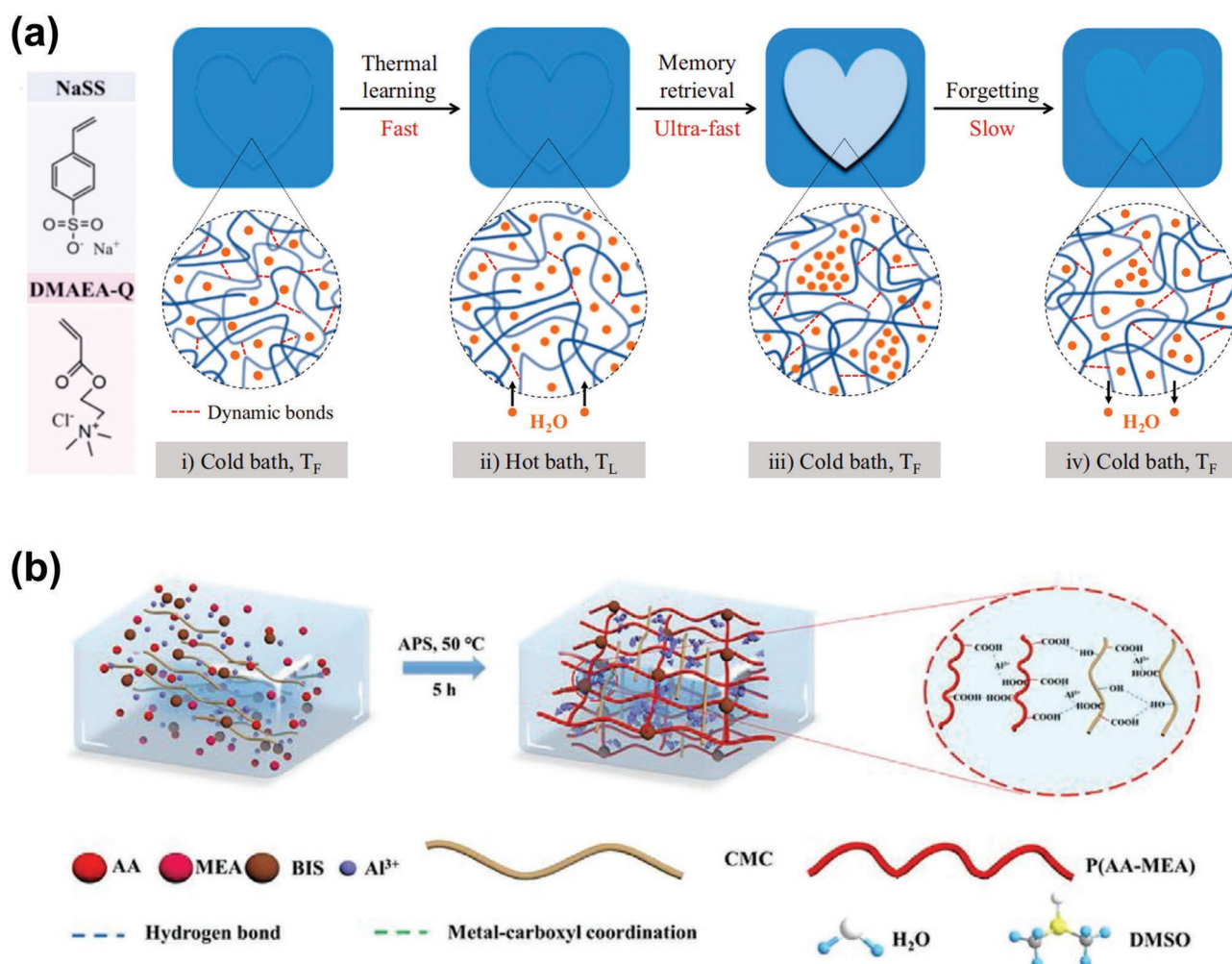


Figure 11. a) PA hydrogel with memorizing–forgetting behavior based on thermal stimulus (reproduced with permission.^[75] Copyright 2020, National Academy of Sciences). b) Organohydrogel with dynamic information loading and unloading through water-writing and DMSO wiping (adapted with permission.^[76] Copyright 2021, John Wiley and Sons).

3. Anti-Counterfeiting Applications

3.1. From Monochrome Anti-Counterfeiting to Polychrome Anti-Counterfeiting

Color change is a remarkable feature of intelligent gels for anti-counterfeiting. As 1D, color richness can improve the information capacity to some extent. In this section, we discuss hydrogels with monochrome, polychrome and white-light-emitting materials that are used for information storage.

3.1.1. Monochrome Anti-Counterfeiting

The initial polymeric gel-based information storage was monochrome, mainly depending on changes in transparency or on–off switchable fluorescent properties in response to external stimuli. Because a Pho-CA precursor solution can form a hydrogel and emit blue fluorescence after UV irradiation, Wang et al. constructed a lattice with specific points composed of a Pho-CA hydrogel to

encode the fluorescent letters “SCU”^[40] (Figure 12a). Meanwhile, a new encryption/decryption method has been established that uses a Pho-CA solution as “ink” and UV light as the key to decryption. As shown in Figure 12b, our group^[77] also reported a fluorescent hydrogel with a naphthalimide-based fluorophore (DEAN), whose fluorescence could be spatially and temporally quenched by OH[−]. As shown in Figure 11b, the ion-transfer-printing method was applied to locally control the fluorescence and produce desirable patterns such as a logo, panda, maple leaf, and the Chinese character “Fu.” All the patterns were invisible under visible light but appeared immediately under UV light at 365 nm. Although the encryption/decryption process worked well, the problem of easy ion diffusion always troubled us in this study.

The reversible on–off conversion of fluorescence can also be achieved by the formation or disintegration of luminescent complexes. As illustrated in Figure 12c, Hai and co-workers^[78] demonstrated the use of Tb³⁺-carboxymethyl cellulose (CMC) complex hydrogels for the encryption and decryption of fingerprint information. In their study, they used a lysozyme-binding aptamer to bind the lysozyme of fingerprint ridges, leading to

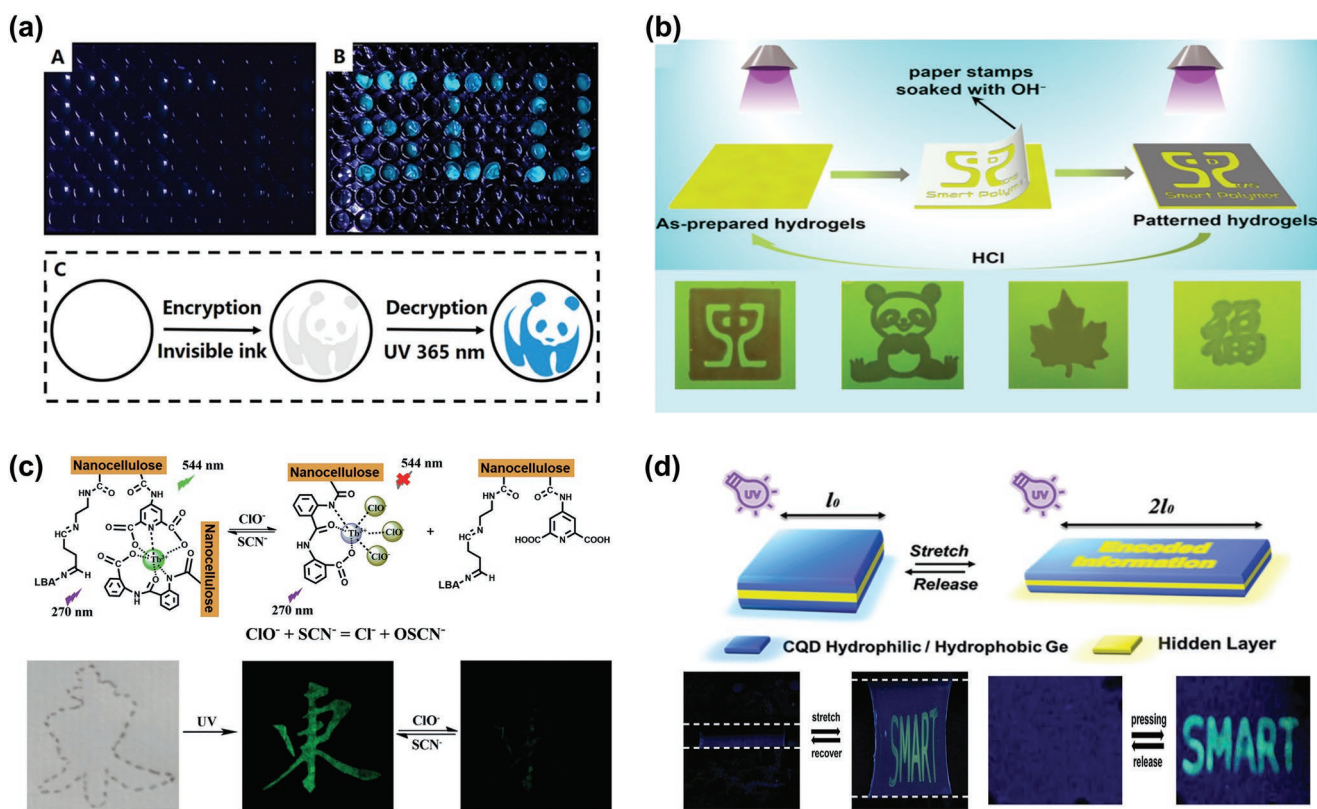


Figure 12. a) Photographs of hydrogel array containing letters "SCU," which was partially made up of Pho-CA, along with schematic diagram of encryption/decryption process (adapted with permission.^[40] Copyright 2020, American Chemical Society). b) Illustration of the information loading and decryption process and the designed patterns written on the fluorescent hydrogel (reproduced with permission.^[77] Copyright 2019, American Chemical Society). c) The composition and chromogenic mechanism of Tb³⁺-CMC complex hydrogel, along with fluorescent images of Chinese character "Fu" on paper (adapted with permission.^[78] Copyright 2018, John Wiley and Sons). d) Mechanochromic bilayer hydrogel with a "SMART" logo as an encryption device (adapted with permission.^[28] Copyright 2020, John Wiley and Sons).

the recording of the imaging information. Furthermore, using a ClO⁻/SCN⁻ trigger, the information could be effectively encrypted or decrypted by the quenching or recovery of the luminescence, respectively. As a practical application, they also loaded the Chinese character "Dong" on paper, which demonstrated the great application potential in information anti-counterfeiting.

Sometimes, hidden information cannot be decrypted under a certain condition. For example, Wu et al. reported a sandwich-type multilayer gel for storing confidential information (Figure 12d).^[28] When exposed to UV irradiation, the outer gel layer containing CQDs absorbed UV light and emitted blue fluorescence, but inhibited UV light penetration and obscured the yellow fluorescent information. When an external force was applied, the light transmittance increased because of a decrease in the thickness of the outer layer, leading to the inner information being revealed. Therefore, two conditions were required for information decryption in this system, which was conducive to protecting the secret information.

3.1.2. Polychrome Anti-Counterfeiting

The development of multicolor polymeric hydrogels provides a greater capacity and higher security for stored information,

thus making these a better choice for information storage and anti-counterfeiting. In general, traditional chromophores are introduced into the hydrogel matrix to produce a polychrome device.^[79–81] A series of studies was conducted by Ji's group in which hydrogel blocks that emitted various colors were assembled into multicolor fluorescent gel arrays (called 3D gel codes) for information storage.^[82,83] Upon UV irradiation, the encoded information could be read using a smartphone. Recently, a non-traditional multicolor fluorescent hydrogel was fabricated by Deng et al.,^[84] which was capable of excitation-dependent emission and metal ion responsiveness. Because it showed strong intrinsic fluorescence, the application of the prepared PAM/poly(itaconic acid) hydrogel to information encryption was investigated. In addition, using certain metal ions (Co²⁺, Mn²⁺, and Zn²⁺) as inks, a multi-ion inkjet printing technique was developed to print desirable patterns on the surfaces of hydrogels (Figure 13). A pattern that was invisible under natural light appeared when exposed to light with a short wavelength (UV, violet, or blue light). Different information could be observed under different excitation wavelengths, leading to multi-dimensional information decryption.

For information storage based on structural color, a polychromic property can commonly be realized by adjusting the refractive index, as well as the lattice constant.^[60,85–87] By

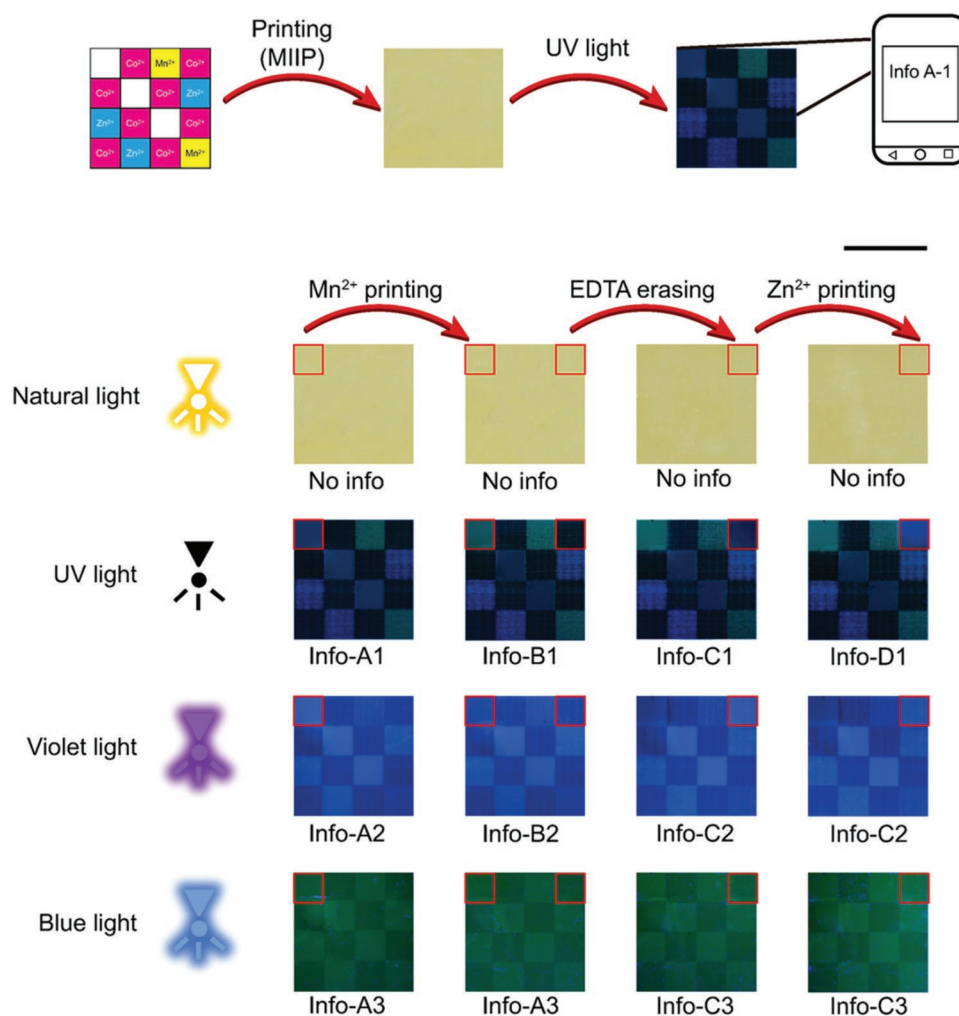


Figure 13. Multicolor fluorescent hydrogel with metal cation-responsiveness and excitation-dependence for multi-dimensional information encryption (reproduced with permission.^[84] Copyright 2021, American Chemical Society).

synthesizing monodisperse PS particles of various sizes (ca. 160, 174, and 225 nm), Du et al.^[65] obtained a series of CS hydrogels with different structural colors. As shown in **Figure 14a**, the letters “SIAT” were written with a Chinese ink brush using water as the ink, which faded away when the water evaporated. The showing-and-hiding processes provide a new strategy for pattern-on-demand printing. In this study, gel sheets acted as writing pads, and no information encryption/decryption process was involved. Zhang et al.^[88] developed an anti-counterfeit label by integrating ordinary angle-dependent colloidal crystal array films and angle-independent PNIPAM/GO hydrogels with inverse structures. When viewed from above, the pigeon pattern was hidden because the two materials had the same structural color (**Figure 14b**). When the viewing angle was changed, a green pigeon appeared, which could further undergo color migration to blue after irradiation with NIR light. This novel material is expected to open a new avenue for constructing anti-counterfeiting labels.

In addition to physical factor-induced structural color changes, chemicals can also influence photonic hydrogels. As presented in **Figure 14c**, the lamellar hydrogels reported

by Yue et al.^[61] exhibited ternary stimuli-responsive behavior, including stress/strain, pH and temperature responses. Based on a single photonic gel, different patterns (smiling face and crossed strips) could be obtained with various types of reflected light with the help of a silicone spacer with engraved patterns. Although the encrypted patterns were simple, this type of gel can inspire researchers in the fields of sensors and displays.

3.1.3. White-Light-Emitting Anti-Counterfeiting

White-light-emitting (WLE) gels^[89] are gaining increasing attention because of their sensitivity to external stimuli and obvious chromic shifts, which can be used to construct intelligent displays and information storage devices. A common strategy for preparing WLE gels involves the use of two or more fluorescent chromophores with three primary colors (red, yellow, and blue),^[52,90] or two complementary colors^[91] to cover the entire visible spectrum. For example, Bairi and colleagues^[90] fabricated various light-harvesting supramolecular hydrogels via the assembly of melamine-containing fluorescent dyes such as

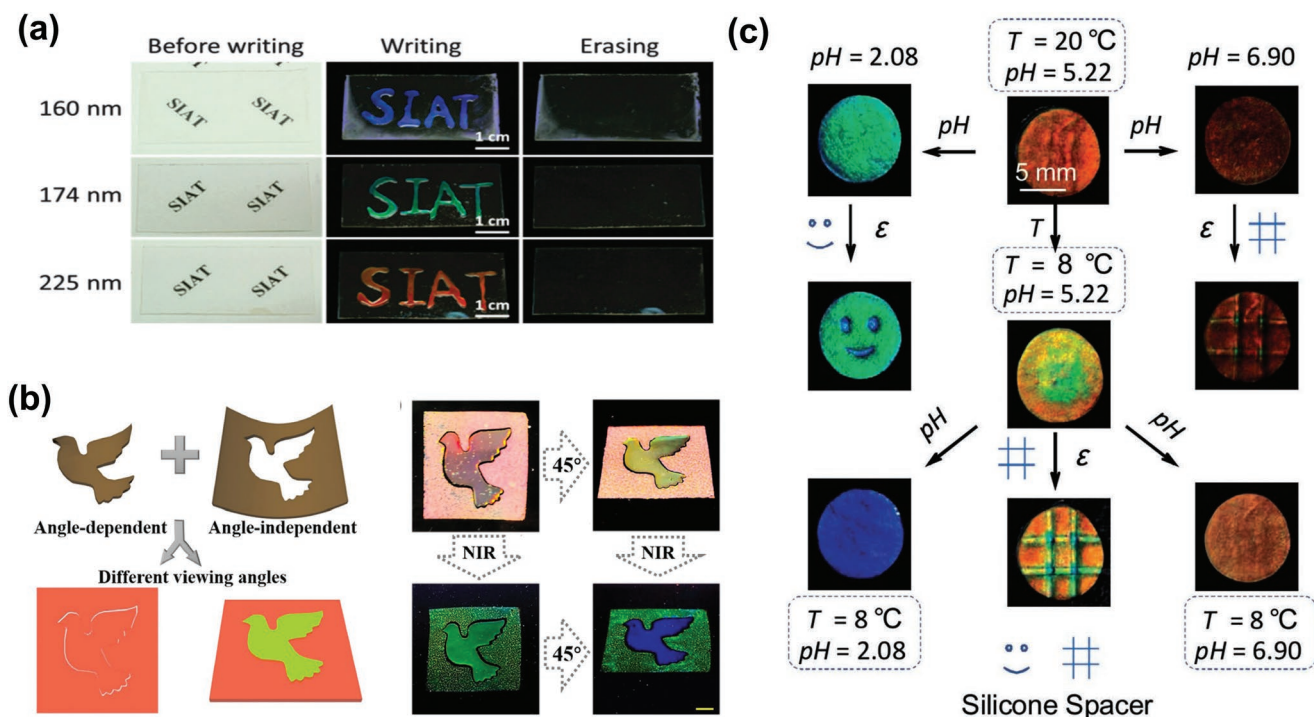


Figure 14. a) Images of photonic gels containing PS particles of different sizes, showing various colors when using water as ink (reproduced with permission.^[65] Copyright 2015, Royal Society of Chemistry). b) Pigeon patterned anti-counterfeit hydrogel label with thermal-responsive color change (adapted with permission.^[88] Copyright 2019, TSINGHUA university press). c) PDGI/PAM-PAAc photonic hydrogel with thermal-, pH-, and mechano-chromatic behaviors (adapted with permission.^[61] Copyright 2013, John Wiley and Sons).

riboflavin (R, green), 6,7-dimethoxy-2,4[1H, 3H]-quinazoline-dione (Q, blue), and rhodamine B (RhB, red). The MQ hydrogel showed blue fluorescence, whereas the R-doped MQ gel exhibited green fluorescence based on FRET. Furthermore, white-light emission was observed by varying the molar ratio of RhB and R. Similarly, Zhu et al.^[52] incorporated both lanthanide ions and CDs into a hydrogel network of PAM/PAAc. By adjusting the stoichiometry of the Eu^{3+} ions (red light), Tb^{3+} ions (green light) and CDs (blue emission), pure white luminescence was obtained through fluorescence energy transfer.

Alternatively, white light emission can also be achieved by a single chromophore, whose fluorescence depends on its state. Zhu et al.^[92] reported a WLE hydrogel prepared by the one-pot copolymerization of the hydrophobic chromophore monomer 4'-(*N*-vinyl benzyl-4-pyridinyl)-2,2':6',2''-terpyridine perchlorate (VPTP) and hydrophilic AM (Figure 15a). Owing to the coexistence of unimer (blue light) and dimer (green light) forms of the chromophore, the prepared transparent hydrogel showed strong white fluorescence under UV irradiation. Interestingly, the unimer–dimer transition of the chromophore occurred in response to a stimulus of heat or UV light, accompanied by a fluorescence variation from blue to white and then to yellow. Moreover, Cu^{2+} chelated with the terpyridine groups of the chromophore quenched the fluorescence of the hydrogel. This mechanism could be reversed by using ethylenediaminetetraacetic acid disodium salt to remove the Cu^{2+} ions. Therefore, employing either photolithography or wet stamping, this WLE hydrogel with tunable fluorescence is an ideal material for information storage with improved security levels.

According to Li's group,^[93] a vibration-induced emission molecule, an *N,N'*-disubstituted-dihydrophenazine derivative (DPAC-Ty), was embedded in a thermally responsive Pluronic F127 hydrogel. Because the DPAC-Ty molecule showed blue and orange fluorescence in the vibration-restricted and free-vibrating states, respectively, the fluorescence color of the resultant hydrogel could be adjusted by changing the temperature, with white light included (Figure 15b). They also introduced a protonation-sensitive fluorophore, 4,4-((1E,1E)-[2-(3-aminopropoxy)pyrimidine-4,6-diyl]bis(ethene-2,1-diyl))-bis(*N,N*-diethylaniline), into the Pluronic F127 hydrogel.^[94] The hydrophobic properties of F127 were adjusted by changing the temperature, leading to variations in the ratio of the protonated (blue light) and deprotonated (yellow light) states of the fluorophore. Owing to the changes in the fluorescence color, the hydrogel could achieve white-light emission at a certain temperature.

3.2. From Single-Dimensional Anti-Counterfeiting to Multi-Dimensional Anti-Counterfeiting

Because single-stage or single-dimensional encrypted information can easily be revealed via a chemical structure or composition analysis using well-known techniques, a single security element can no longer meet the needs of modern anti-counterfeiting. A step ahead is to fabricate more powerful fluorescent hydrogels possessing multiple colors or multifunctionality for multistage or multi-dimensional data security protection.^[95] A

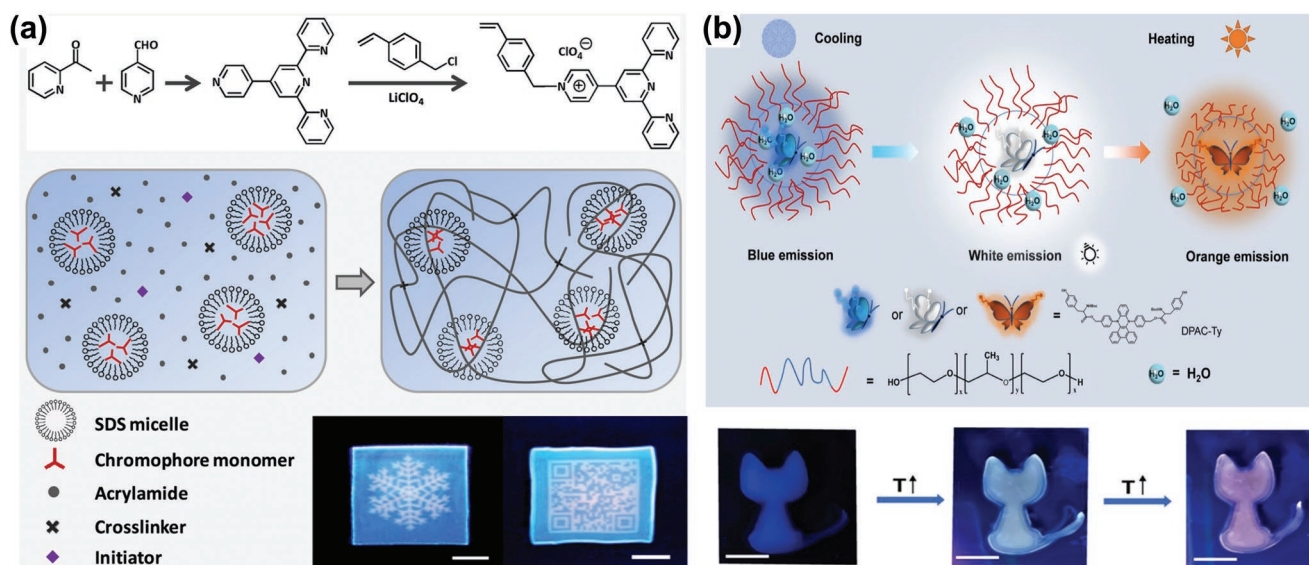


Figure 15. White-light-emitting hydrogels for anti-counterfeiting. a) Single chromophore-based hydrogel obtained by micellar copolymerization, exhibiting tunable fluorescence and patternability (reproduced with permission.^[92] Copyright 2018, American Chemical Society). b) White-light hydrogel with tunable fluorescence colors in response to temperature (reproduced with permission.^[93] Copyright 2020, American Chemical Society).

fluorescent hydrogel composed of AAC, AM, and pyrene-modified 2-hydroxyethyl methacrylate was prepared by our group.^[96] Using the ionoprinting technique, Fe³⁺ was introduced into the prepared hydrogel to partially quench the pyrene fluorescence and endow the gel with an anisotropic structure via AAC-Fe³⁺ chelation. As a result, fluorescence quenching-based text messages and actuation-based gesture information could be encoded on tailored filter paper containing Fe³⁺ ions, leading to hierarchical decryption when the stimuli of UV irradiation and water were applied (Figure 16a).

Taking advantage of the fluorescence variation as a function of time, a urease-containing fluorescent hydrogel was

selected as an information storage material that could self-erase decrypted information to avoid secondary information leakage.^[97] The hydrogel was first prepared by the polymerization of AAm and the fluorescent monomer DEAN in the presence of urease. As illustrated in Figure 16b, information could be loaded onto the fluorescent hydrogel via the ionoprinting method because of the coordination between the DEAN and metal ions (such as Zn²⁺ and Al³⁺). When exposed to a urea solution, the fluorescence intensity decreased as a result of the deprotonation of DEAN and the destruction of the metal coordination, which was ascribed to the NH₃ produced by the urease-urea catalytic reaction. Because the fluorescence

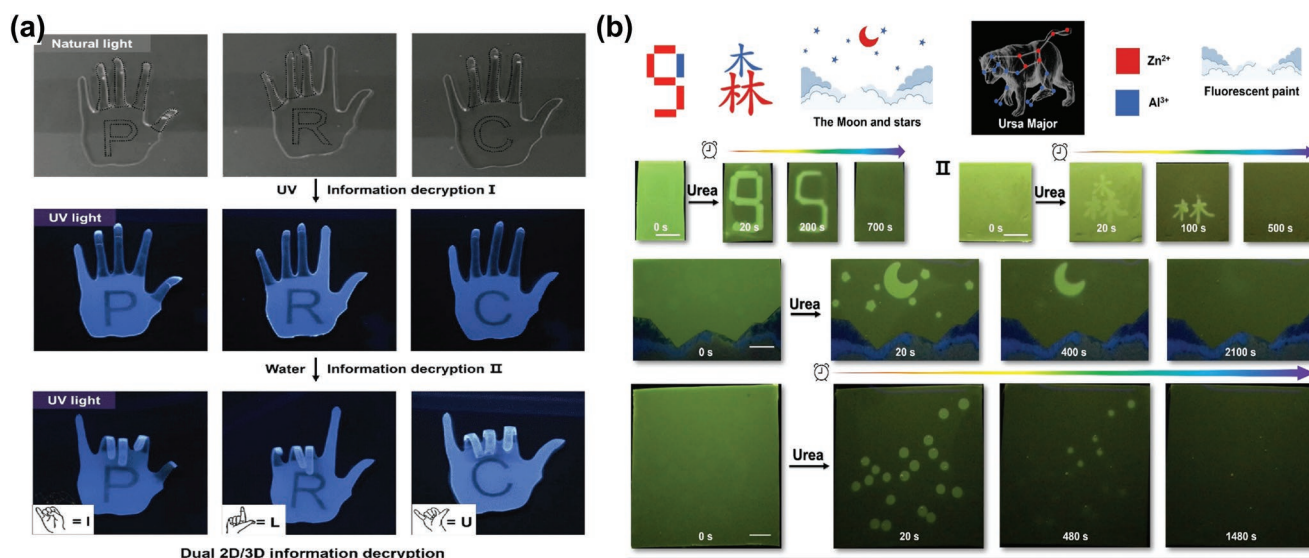


Figure 16. a) Hierarchical information decryption, including fluorescence quenching-based 2D information and actuation-based 3D information (reproduced with permission.^[96] Copyright 2019, Science China Press and Springer-Verlag GmbH Germany). b) Urease-containing fluorescent hydrogel for transient information storage (adapted with permission.^[97] Copyright 2021, John Wiley and Sons).

diminished at different rates, this type of hydrogel could achieve the dual-encryption of information with a self-erasure behavior.

Recently, we reported a fluorescent organohydrogel with interpenetrating heterogeneous networks consisting of a poly(*N,N*-dimethylacrylamide) hydrophilic network and poly-octadecyl methacrylate hydrophobic network.^[98] The former contained the green-yellow fluorescent monomer DEAN, and the latter contained spiropyran moieties with a photochromic performance. Under UV irradiation, SP units turned into MC, leading to a FRET between the DEAN and MC. As a result, the organohydrogel exhibited a continuous color change from green to yellow and finally to red. In addition, H⁺ ions could also open spiropyran rings into protonated merocyanine (MCH⁺), interrupting the FRET process. As depicted in **Figure 17**, various messages, including numbers, letters and QR codes, could be created by integrating the fluorescent organohydrogel in two different states. Stimulated by UV light, hidden information was revealed by the sequential variation of the fluorescent colors.

In another example, we developed a new photomechanically modulated fluorescent system consisting of a hollow window for display and an NIR-responsive fluorescent actuator, which was prepared by integrating a fluorescent glycol gel film, poly(dimethylsiloxane) film and carbon nanotube film.^[99] Owing to the difference in the thermal expansion performances of the two sides, the straight actuator could bend when exposed to NIR irradiation. In this system, on-demand decryption was realized by adjusting the display panels and time-and light-power-dependent actuating behaviors. As demonstrated in **Figure 18a**, with the assistance of a hollowed-out number “8” pattern, green fluorescent numbers such as “1”, “3”, and “8” could be displayed on the panel by tuning the NIR power from 0.2 to 0.8 W. Furthermore, complex and dynamic patterns such as a blossom (Figure 18b), as well as barcode labels for anti-counterfeiting (Figure 18c), could be achieved by endowing the fluorescent gels with different colors. The features of single-input and multiple-output systems are universal and hold promise for the design and fabrication of fluorescent display platforms.

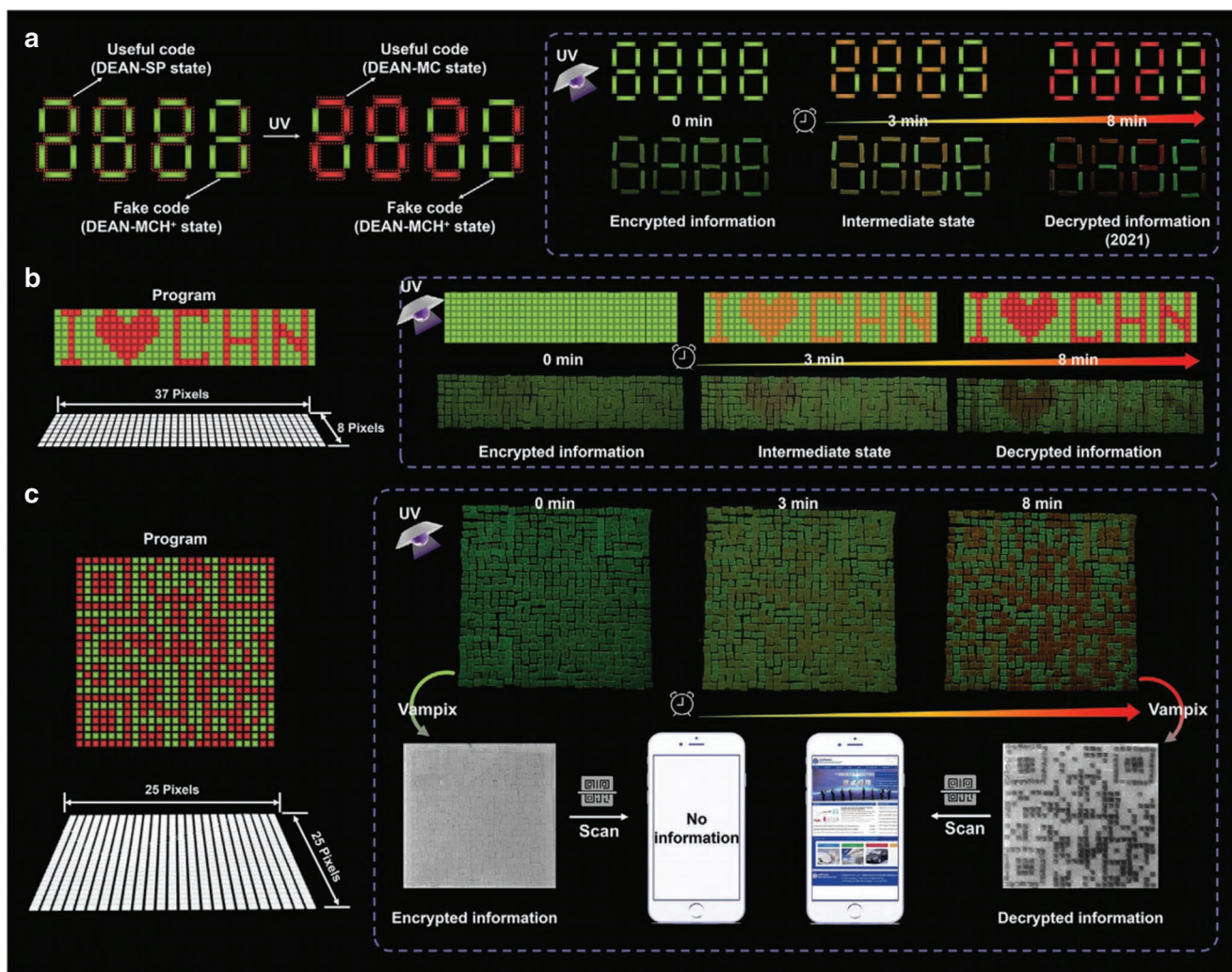


Figure 17. Advanced information anti-counterfeiting based on integration of fluorescent organohydrogels in DEAN-SP and DEAN-MCH⁺ states (adapted with permission.^[98] Copyright 2021, John Wiley and Sons).

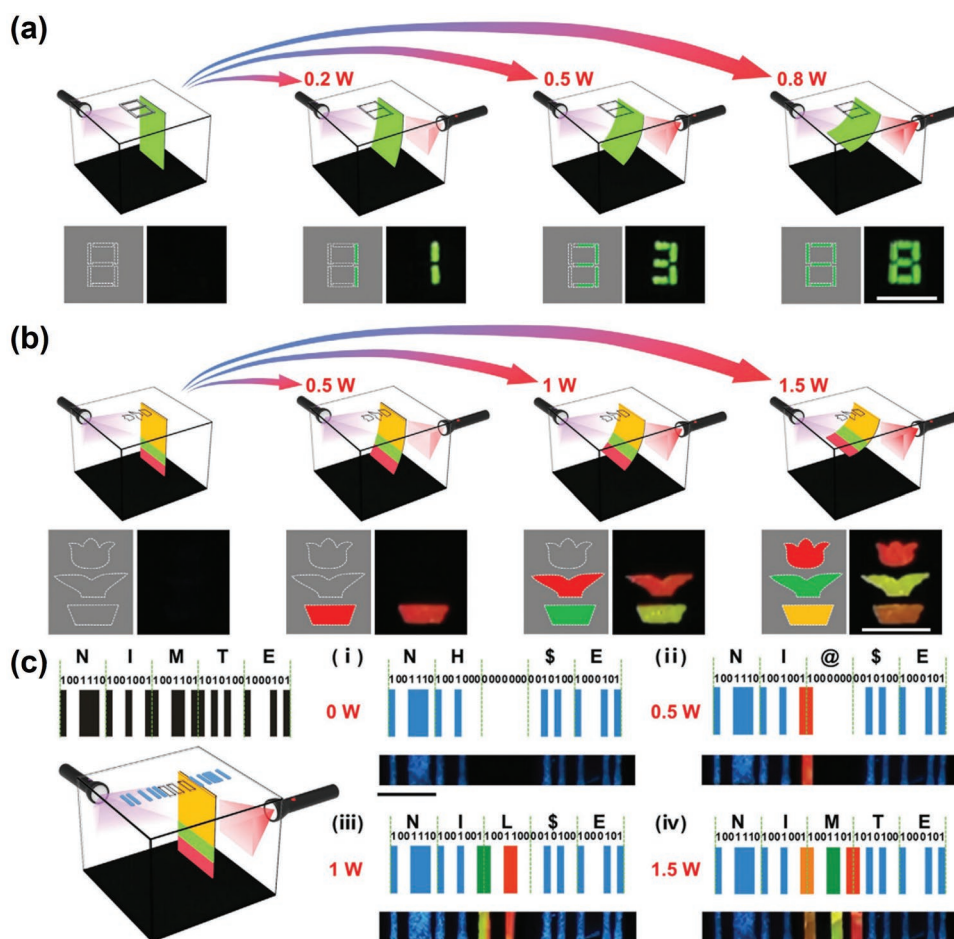


Figure 18. Schemes and illustrations of on-demand displays, including numbers, potted plants, and 2D barcodes, obtained by varying power of NIR light (adapted with permission.^[99] Copyright 2022, John Wiley and Sons).

A fluorescent hydrogel with a shape-memory behavior is another good choice for constructing advanced anti-counterfeiting platforms.^[100–103] One typical example^[102] demonstrated by our team was a PVA-based hydrogel interpenetrated with perylene tetracarboxylic acid-grafted gelatin (PTG) (Figure 19a). Taking Fe^{3+} as an “ink”, patterned fluorescence quenching endowed the as-prepared hydrogel with the ability to encode information. Owing to the formation of dynamic borate bonds between the borax and PVA chains, the hydrogel also exhibited an excellent self-healing behavior and shape memory performance. By integrating tunable fluorescence properties and fabricable origami structures, the protection message on hydrogels could be read after sequential shape recovery and UV irradiation.

The patterned information realized by ionoprinting or wet stamping was not stable and lost resolution once the solvent interfered. Recently, Zhu et al.^[103] incorporated photo-tuned fluorescent information into a shape-memory hydrogel to obtain stable and rewritable 2D secret patterns, as well as to improve the security level using reconfigurable 3D shapes (Figure 19b). The hydrogel was prepared by copolymerizing the fluorescent VPTP monomer with 1-vinylimidazole and methacrylic acid. On one hand, because of the dense hydrogen bonds that existed

in the system, the hydrogel was capable of temperature-mediated shape memory for constructing 3D shapes using origami or Kirigami technology. On the other hand, the photoinduced unimer–dimer transition of the VPTP corresponded to a blue–green shift, which could be used to create 2D patterns on the surface of the hydrogel by photolithography. By combining a tunable fluorescence and reconfigurable architecture, dual-encryption could be realized in this novel hydrogel system.

4. Conclusions and Perspectives

In this review, we systematically discussed the latest progress and promising applications of polymeric gels in the field of anti-counterfeiting, which can be achieved by adjusting chemical or physical colors. For chemical colors, gels containing fluorescent chromophores such as CDs, organic dyes, and lanthanides were mainly discussed because of their vivid colors and ease of manipulation. Polymeric gels can be endowed with fluorescence via chemical modifications or physical doping. On the other hand, physical colors are ascribed to the interactions (interference/diffraction, refraction/scattering, and reflection/transmittance) between light and the

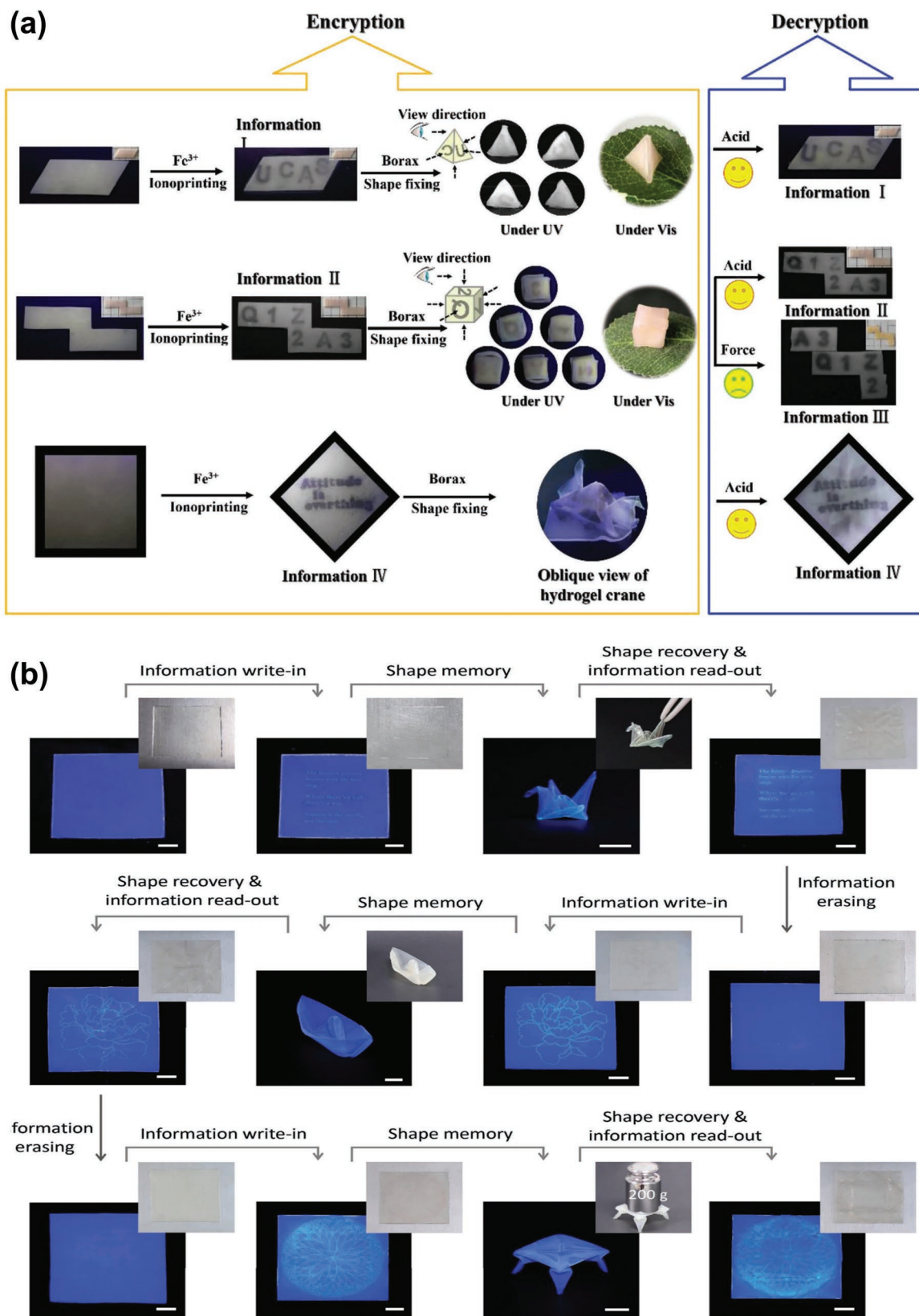


Figure 19. a) 3D fluorescent hydrogel for multistage data security protection (adapted with permission.^[102] Copyright 2019, John Wiley and Sons). b) Shape-memory hydrogel with dual-encryption performance (adapted with permission.^[103] Copyright 2021, John Wiley and Sons).

nano/microstructures in the hydrogel substrate. Specifically, the structure color, grayscale, and transparent–opaque transitions were taken as corresponding examples. Using photolithography and photopolymerization, permanent information can be stored on polymeric gels, while repeatable or rewritable information can be stored using ionoprinting or color block assembly. Using a certain stimulus as the key, the secret information can be encrypted and decrypted. This section discusses the challenges encountered in polymeric gel-based information storage devices and their prospects for future development.

Compared with other anti-counterfeiting materials, intelligent gel-based anti-counterfeiting systems possess extraordinary stimulus–responsiveness, resulting in a dynamic information output and an enhanced anti-counterfeiting performance. However, current gel-based systems have not been fully explored, and quite a few questions exist. This limits their application at an industrial scale and in daily life. The natural properties of swelling and shrinking in the presence of water and air associated with hydrogels could cause the disappearance of hidden information. The recently developed gels that are capable of anti-swelling^[104,105] or anti-hydration^[106,107] might be a good choice to address these issues.

In addition, attention should also be paid to improving the information storage capacity and resolution. One of the most effective and predictable approaches is to combine existing technologies, including inkjet printing, 4D printing, and various other printing techniques. In these systems, the gel can serve as either the “paper” or “ink.” It is worth noting that the gel should first be made into a thin film or integrated with another printable substrate to act as the “paper”, whereas a nano- or microgel needs to be fabricated to obtain an “ink.”

Last but not the least, there is an eternal pursuit in the anti-counterfeiting field to use the simplest method to achieve the highest security level. Combining different optical properties and the synergy of other functions (e.g., shape memory, shape morphing, and self-healing) could endow gel-based anti-counterfeiting systems with more complex and diversified forms in the encryption/decryption process, which could improve the information security level. Considering the most straightforward method for decryption, facile stimulations (e.g., light, moisture, and temperature) are the most commonly used and are also the future development trends for advanced anti-counterfeiting. However, achieving both the simplest anti-counterfeiting mode and highest security level remains a significant challenge.

Because the current gel-based anti-counterfeiting systems are primarily conceptual, they are a long way from being ready for large-scale practical applications. However, we believe that this review will benefit many research areas, including smart anti-counterfeiting materials, encryption/decryption technologies and flexible devices, thus sparking more novel ideas about intelligent materials to promote the development of information storage for anti-counterfeiting. Meanwhile, we hope that more researchers will be interested in intelligent polymeric gels for anti-counterfeiting and will work together to exchange excellent ideas to allow the development of this field to flourish.

Acknowledgements

The authors thank Israt Ali from Institute National de la Recherche Scientifique for his kind help with the revision to this manuscript. This work was supported by the National Natural Science Foundation of China (52103246), National Key Research and Development Program of China (2018YFC0114900, 2018YFB1105100), Zhejiang Provincial Natural Science Foundation of China (LQ22E030015), Youth Innovation Promotion Association of Chinese Academy of Sciences (2017337), Key Research Program of Frontier Science, Chinese Academy of Sciences (QYZDB-SSW-SLH036), Sino-German Mobility Program (M-0424), and K. C. Wong Education Foundation (GJTD-2019-13).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

anti-counterfeiting, fluorescent information storage, multi-dimensional encryption/decryption, physical colors, smart polymeric gels

Received: February 8, 2022

Revised: June 8, 2022

Published online: September 3, 2022

- [1] R. Arppe, T. Sørensen, *Nat. Rev. Chem.* **2017**, *1*, 0031.
- [2] H. Bae, S. Bae, C. Park, S. Han, J. Kim, L. Kim, K. Kim, S. Song, W. Park, S. Kwon, *Adv. Mater.* **2015**, *27*, 2083.
- [3] Y. Li, D. Young, X. Loh, *Mater. Chem. Front.* **2019**, *3*, 1489.
- [4] J. Miao, X. Ding, S. Zhou, C. Gui, *IEEE Access* **2019**, *7*, 142926.
- [5] B. Yoon, J. Lee, I. Park, S. Jeon, J. Lee, J. Kim, *J. Mater. Chem. C* **2013**, *1*, 2388.
- [6] X. Yu, H. Zhang, J. Yu, *Aggregate* **2021**, *2*, 20.
- [7] H. Hu, H. Zhong, C. Chen, Q. Chen, *J. Mater. Chem. C* **2014**, *2*, 3695.
- [8] F. Ruffato, R. Rossi, M. Massari, E. Mafakheri, P. Capaldo, G. Romanato, *Sci. Rep.* **2017**, *7*, 18011.
- [9] W. Ye, F. Zeuner, X. Li, B. Reineke, S. He, C.-W. Qiu, J. Liu, Y. Wang, S. Zhang, T. Zentgraf, *Nat. Commun.* **2016**, *7*, 11930.
- [10] P. She, Y. Ma, Y. Qin, M. Xie, F. Li, S. Liu, W. Huang, Q. Zhao, *Matter* **2019**, *1*, 1644.
- [11] C. Zhang, B. Wang, W. Li, S. Huang, L. Kong, Z. Li, L. Li, *Nat. Commun.* **2017**, *8*, 1138.
- [12] X. Hao, Z. Xu, C. Li, W. Hong, Q. Zheng, Z. Wu, *Adv. Mater.* **2020**, 2000781.
- [13] Y. Jian, S. Handschuh-Wang, J. Zhang, W. Lu, X. Zhou, T. Chen, *Mater. Horiz.* **2021**, *8*, 351.
- [14] Z. Jiang, B. Diggle, I. C. G. Shackelford, L. A. Connal, *Adv. Mater.* **2019**, *31*, 1904956.
- [15] M. Liu, Y. Ishida, Y. Ebina, T. Sasaki, T. Hikima, M. Takata, T. Aida, *Nature* **2015**, *517*, 68.
- [16] A. Nojoomi, H. Arslan, K. Lee, K. Yum, *Nat. Commun.* **2018**, *9*, 3705.
- [17] H. Yuk, B. Lu, X. Zhao, *Chem. Soc. Rev.* **2019**, *48*, 1642.
- [18] X. Le, H. Shang, S. Gu, G. Yin, F. Shan, D. Li, T. Chen, *Chin. J. Chem.* **2021**, *40*, 337.
- [19] M. Zhang, S. Wang, Y. Zhu, Z. Zhu, T. Si, R. Xu, *Mater. Horiz.* **2021**, *8*, 1756.
- [20] G. Lin, M. Si, L. Wang, S. Wei, W. Lu, H. Liu, Y. Zhang, D. Li, T. Chen, *Adv. Opt. Mater.* **2022**, *10*, 2102306.
- [21] W. Lu, M. Si, H. Liu, H. Qiu, S. Wei, B. Wu, R. Wang, G. Yin, J. Zhang, P. Theato, Y. Wei, T. Chen, *Cell Rep. Phys. Sci.* **2021**, *2*, 100417.

- [22] S. Wei, H. Qiu, H. Shi, W. Lu, H. Liu, H. Yan, D. Zhang, J. Zhang, P. Theato, Y. Wei, T. Chen, *ACS Nano* **2021**, *15*, 10415.
- [23] B. Wu, X. Le, Y. Jian, W. Lu, Z. Yang, Z. Zheng, P. Theato, J. Zhang, A. Zhang, T. Chen, *Macromol. Rapid Commun.* **2018**, *40*, 1800648.
- [24] S. Baker, G. Baker, *Angew. Chem., Int. Ed.* **2010**, *49*, 6726.
- [25] L. Li, G. Wu, G. Yang, J. Peng, J. Zhao, J. Zhu, *Nanoscale* **2013**, *5*, 4015.
- [26] H. Li, Z. Kang, Y. Liu, S. Lee, *J. Mater. Chem.* **2012**, *22*, 24230.
- [27] N. Gupta, Y. Chan, S. Saha, M. Liu, *ACS Appl. Polym. Mater.* **2020**, *2*, 4195.
- [28] Y. Wu, Y. Ren, J. Guo, Z. Liu, L. Liu, F. Yan, *Nanoscale* **2020**, *12*, 20965.
- [29] S. Wu, H. Shi, W. Lu, S. Wei, H. Shang, H. Liu, M. Si, X. Le, G. Yin, P. Theato, T. Chen, *Angew. Chem., Int. Ed.* **2021**, *60*, 21890.
- [30] D. Zhou, D. Li, P. Jing, Y. Zhai, D. Shen, S. Qu, A. L. Rogach, *Chem. Mater.* **2017**, *29*, 1779.
- [31] Y. Zhang, X. He, W. Li, *RSC Adv.* **2015**, *5*, 71030.
- [32] D. Zhao, W. Ma, R. Wang, X. Yang, J. Li, T. Qiu, X. Xiao, *Polymers* **2019**, *11*, 1171.
- [33] H. Langhals, *Phys. Sci. Rev.* **2020**, *5*, 20190100.
- [34] N. Boens, V. Leen, W. Dehaen, *Chem. Soc. Rev.* **2012**, *41*, 1130.
- [35] H. Lu, J. Mack, Y. Yang, Z. Shen, *Chem. Soc. Rev.* **2014**, *43*, 4778.
- [36] H. Kim, M. Lee, H. Kim, J. Kim, J. Yoon, *Chem. Soc. Rev.* **2008**, *37*, 1465.
- [37] M. Rajasekar, *J. Mol. Struct.* **2021**, *1235*, 130232.
- [38] D. Cao, Z. Liu, P. Verwilst, S. Koo, P. Jangjili, J. Kim, W. Lin, *Chem. Rev.* **2019**, *119*, 10403.
- [39] S. Keerthana, B. Sam, L. George, Y. N. Sudhakar, A. Varghese, *J. Fluoresc.* **2021**, *31*, 1251.
- [40] N. Wang, K. Yu, K. Li, M. Li, X. Wei, X. Yu, *ACS Appl. Mater. Interfaces* **2020**, *12*, 57686.
- [41] X. Ji, R. Wu, L. Long, X. Ke, C. Guo, Y. Ghang, V. Lynch, F. Huang, J. Sessler, *Adv. Mater.* **2018**, *30*, 1705480.
- [42] Y. Yang, Q. Li, H. Zhang, H. Liu, X. Ji, B. Tang, *Adv. Mater.* **2021**, *33*, 2105418.
- [43] J. Bunzli, C. Piguet, *Chem. Soc. Rev.* **2005**, *34*, 1048.
- [44] F. Wang, X. Liu, *Acc. Chem. Res.* **2014**, *47*, 1378.
- [45] W. Zheng, P. Huang, D. Tu, E. Ma, H. Zhu, X. Chen, *Chem. Soc. Rev.* **2015**, *44*, 1379.
- [46] O. Guillou, C. Daiguebonne, G. Calvez, K. Bernot, *Acc. Chem. Res.* **2016**, *49*, 844.
- [47] 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.
- [48] X. Xu, J. Wang, B. Yan, *Adv. Funct. Mater.* **2021**, *31*, 2103321.
- [49] Q. Zhou, X. Dong, Y. Xiong, B. Zhang, S. Lu, Q. Wang, Y. Liao, Y. Yang, H. Wang, *ACS Appl. Mater. Interfaces* **2020**, *12*, 28539.
- [50] Z. Li, H. Chen, B. Li, Y. Xie, X. Gong, X. Liu, H. Li, Y. Zhao, *Adv. Sci.* **2019**, *6*, 1901529.
- [51] Q. Zhu, K. Van Vliet, N. Holten-Andersen, A. Miserez, *Adv. Funct. Mater.* **2019**, *29*, 1808191.
- [52] Q. Zhu, L. Zhang, K. Van Vliet, A. Miserez, N. Holten-Andersen, *ACS Appl. Mater. Interfaces* **2018**, *10*, 10409.
- [53] J. Chen, L. Xu, X. Lin, R. Chen, D. Yu, W. Hong, Z. Zheng, X. Chen, *J. Mater. Chem. C* **2018**, *6*, 7767.
- [54] H. Wen, X. Zeng, X. Xu, W. Li, F. Xie, Z. Xiong, S. Song, B. Wang, X. Li, Y. Cao, *J. Mater. Chem. C* **2021**, *9*, 2455.
- [55] A. Abdollahi, K. Sahandi-Zangabad, H. Roghani-Mamaqani, *ACS Appl. Mater. Interfaces* **2018**, *10*, 39279.
- [56] S. Long, Z. Ye, Y. Jin, J. Huang, Y. Huang, Y. Liao, X. Li, *Macromol. Rapid Commun.* **2021**, *42*, 2000701.
- [57] F. Wang, A. Cui, Z. Hu, L. Zhang, *Adv. Opt. Mater.* **2021**, *9*, 2101505.
- [58] G. Chen, W. Hong, *Adv. Opt. Mater.* **2020**, *8*, 2000984.
- [59] C. Zhou, Y. Qi, S. Zhang, W. Niu, S. Wu, W. Ma, B. Tang, *Chem. Eng. J.* **2021**, *426*, 131213.
- [60] M. Haque, G. Kamita, T. Kurokawa, K. Tsujii, J. Gong, *Adv. Mater.* **2010**, *22*, 5110.
- [61] Y. Yue, M. Haque, T. Kurokawa, T. Nakajima, J. Gong, *Adv. Mater.* **2013**, *25*, 3106.
- [62] J. Chen, L. Xu, M. Yang, X. Chen, X. Chen, W. Hong, *Chem. Mater.* **2019**, *31*, 8918.
- [63] J. Choi, M. Hua, S. Y. Lee, W. Jo, C. Lo, S. Kim, H. Kim, X. He, *Adv. Opt. Mater.* **2019**, *8*, 1901259.
- [64] J. Kim, G. Lee, J. Kim, S. Kim, *Adv. Funct. Mater.* **2020**, *30*, 2001318.
- [65] X. Du, T. Li, L. Li, Z. Zhang, T. Wu, *J. Mater. Chem. C* **2015**, *3*, 3542.
- [66] P. Jiang, C. Yan, Z. Ji, Y. Guo, X. Zhang, X. Jia, X. Wang, F. Zhou, *ACS Appl. Mater. Interfaces* **2019**, *11*, 42586.
- [67] C. Yang, X. Shi, L. Qi, X. Zhu, J. Tong, H. Deng, Y. Du, *ACS Appl. Mater. Interfaces* **2021**, *13*, 36538.
- [68] K. Hribar, Y. Choi, M. Ondeck, A. Engler, S. Chen, *Adv. Funct. Mater.* **2014**, *24*, 4922.
- [69] G. Peterson, J. Schwartz, D. Zhang, B. Weiss, M. Ganter, D. Storti, A. Boydston, *ACS Appl. Mater. Interfaces* **2016**, *8*, 29037.
- [70] G. Zhang, W. Peng, J. Wu, Q. Zhao, T. Xie, *Nat. Commun.* **2018**, *9*, 4002.
- [71] S. Wu, K. Yan, Y. Zhao, C. Tsai, J. Shen, W. Bentley, Y. Chen, H. Deng, Y. Du, G. Payne, X. Shi, *Adv. Funct. Mater.* **2018**, *28*, 1803139.
- [72] Q. Hu, Y. Zhang, T. Wang, W. Sun, Z. Tong, *Macromol. Rapid Commun.* **2021**, *42*, 2000747.
- [73] C. Yu, K. Cui, H. Guo, Y. N. Ye, X. Li, J. Gong, *Macromolecules* **2021**, *54*, 9927.
- [74] Y. Zhang, Y. Li, K. Chen, Z. Ma, X. Wang, L. Shi, R. Ran, *Polymer* **2019**, *179*, 121637.
- [75] C. Yu, H. Guo, K. Cui, X. Li, Y. N. Ye, T. Kurokawa, J. Gong, *Proc. Natl. Acad. Sci. USA* **2020**, *117*, 18962.
- [76] J. Liu, Z. Chen, Y. Chen, H. U. Rehman, Y. Guo, H. Li, H. Liu, *Adv. Funct. Mater.* **2021**, *31*, 2101464.
- [77] P. Li, D. Zhang, Y. Zhang, W. Lu, J. Zhang, W. Wang, Q. He, P. Theato, T. Chen, *ACS Macro Lett.* **2019**, *8*, 937.
- [78] J. Hai, T. Li, J. Su, W. Liu, Y. Ju, B. Wang, Y. Hou, *Angew. Chem., Int. Ed.* **2018**, *57*, 6786.
- [79] L. Jia, B. Zhang, J. Xu, T. Zhu, R. Chen, F. Zhou, *ACS Appl. Mater. Interfaces* **2020**, *12*, 19955.
- [80] J. Sun, J. Wang, M. Chen, X. Pu, G. Wang, L. Li, G. Chen, Y. Cai, X. Gu, B. Tang, *Chem. Mater.* **2019**, *31*, 5683.
- [81] S. Xie, B. Ren, G. Gong, D. Zhang, Y. Chen, L. Xu, C. Zhang, J. Xu, J. Zheng, *ACS Appl. Nano Mater.* **2020**, *3*, 2774.
- [82] X. Ji, W. Chen, L. Long, F. Huang, J. Sessler, *Chem. Sci.* **2018**, *9*, 7746.
- [83] X. Ji, B. Shi, H. Wang, D. Xia, K. Jie, Z. Wu, F. Huang, *Adv. Mater.* **2015**, *27*, 8062.
- [84] J. Deng, H. Wu, W. Xie, H. Jia, Z. Xia, H. Wang, *ACS Appl. Mater. Interfaces* **2021**, *13*, 39967.
- [85] F. Fu, Z. Chen, H. Wang, C. Liu, Y. Liu, Y. Zhao, *Nanoscale* **2019**, *11*, 10846.
- [86] D. Yang, S. Ye, J. Ge, *Adv. Funct. Mater.* **2014**, *24*, 3197.
- [87] J. Zhang, Y. Qin, Y. Shen, C. Jiang, Y. Tao, S. Chen, B. Xu, Z. Yu, *Adv. Mater. Interfaces* **2021**, *8*, 2001201.
- [88] Z. Zhang, Z. Chen, L. Sun, X. Zhang, Y. Zhao, *Nano Res.* **2019**, *12*, 1579.
- [89] V. Praveen, C. Ranjith, N. Armaroli, *Angew. Chem., Int. Ed.* **2014**, *53*, 365.
- [90] P. Bairi, B. Roy, P. Chakraborty, A. Nandi, *ACS Appl. Mater. Interfaces* **2013**, *5*, 5478.
- [91] Q. Zhao, Y. Chen, S. Li, Y. Liu, *Chem. Commun.* **2018**, *54*, 200.
- [92] C. Zhu, T. Bai, H. Wang, W. Bai, J. Ling, J. Sun, F. Huang, Z. Wu, Q. Zheng, *ACS Appl. Mater. Interfaces* **2018**, *10*, 39343.
- [93] S. Liu, J. Wang, F. Tang, N. Wang, L. Li, C. Yao, L. Li, *ACS Appl. Mater. Interfaces* **2020**, *12*, 55269.
- [94] J. Wang, F. Tang, Y. Wang, S. Liu, L. Li, *Adv. Opt. Mater.* **2020**, *8*, 1901571.
- [95] X. Zhang, X. Xu, L. Chen, C. Zhang, L. Liao, *Dyes Pigm.* **2020**, *174*, 108042.

- [96] X. Le, W. Lu, J. He, M. Serpe, J. Zhang, T. Chen, *Sci. China Mater.* **2019**, 62, 831.
- [97] X. Le, H. Shang, H. Yan, J. Zhang, W. Lu, M. Liu, L. Wang, G. Lu, Q. Xue, T. Chen, *Angew. Chem., Int. Ed.* **2021**, 60, 3640.
- [98] X. Le, H. Shang, S. Wu, J. Zhang, M. Liu, Y. Zheng, T. Chen, *Adv. Funct. Mater.* **2021**, 31, 2108365.
- [99] H. Shi, S. Wu, M. Si, S. Wei, G. Lin, H. Liu, W. Xie, W. Lu, T. Chen, *Adv. Mater.* **2022**, 34, 2107452.
- [100] Y. Jian, X. Le, Y. Zhang, W. Lu, L. Wang, J. Zheng, J. Zhang, Y. Huang, T. Chen, *Macromol. Rapid Commun.* **2018**, 39, 1800130.
- [101] H. Qiu, S. Wei, H. Liu, B. Zhan, H. Yan, W. Lu, J. Zhang, S. Wu, T. Chen, *Adv. Intell. Syst.* **2021**, 3, 2000239.
- [102] Y. Zhang, X. Le, Y. Jian, W. Lu, J. Zhang, T. Chen, *Adv. Funct. Mater.* **2019**, 29, 1905514.
- [103] C. Zhu, T. Bai, H. Wang, J. Ling, F. Huang, W. Hong, Q. Zheng, Z. Wu, *Adv. Mater.* **2021**, 33, 2102023.
- [104] L. Xu, S. Gao, Q. Guo, C. Wang, Y. Qiao, D. Qiu, *Adv. Mater.* **2020**, 32, 2004579.
- [105] Z. Xu, C. Fan, Q. Zhang, Y. Liu, C. Cui, B. Liu, T. Wu, X. Zhang, W. Liu, *Adv. Funct. Mater.* **2021**, 31, 2100462.
- [106] H. Gao, J. Mao, Y. Cai, S. Li, Y. Fu, X. Liu, H. Liang, T. Zhao, M. Liu, L. Jiang, *Adv. Funct. Mater.* **2021**, 31, 2007664.
- [107] T. Zhu, C. Jiang, M. Wang, C. Zhu, N. Zhao, J. Xu, *Adv. Funct. Mater.* **2021**, 31, 2102433.



Yu Sun graduated from Wuhan University with a bachelor degree in 2020. Currently, she is a Ph.D. student at the Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, under the supervision of Professor Tao Chen. Her current research interests include fluorescent hydrogels and their applications in anti-counterfeiting.



Xiaoxia Le received her Ph.D. degree in polymer chemistry and physics from the Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences (2019). She then joined Tao Chen's group as a postdoctoral research fellow. Currently, she is an associate professor at NIMTE. Her research focuses on the construction and functionalization of stimuli-responsive hydrogels for applications in the soft actuator and fluorescent information anti-counterfeiting fields.



Tao Chen (FRSC) received his Ph.D. from Zhejiang University (China) in 2006. After his postdoctoral training at the University of Warwick (UK), he joined Duke University (USA) as a research scientist. He then moved to Technische Universität Dresden (Germany) as an Alexander von Humboldt research fellow. Since 2012, he has been a full-time professor at the Ningbo Institute of Materials Technology and Engineering (NIMTE), Chinese Academy of Sciences. He has published more than 200 papers in the fields of functional and smart polymers. His research interests include smart hydrogels with applications in soft actuators and gel-based anti-counterfeiting, etc.