

Aggregation-Caused Quenching-Type Naphthalimide Fluorophores Grafted and Ionized in a 3D Polymeric Hydrogel Network for Highly Fluorescent and Locally Tunable Emission

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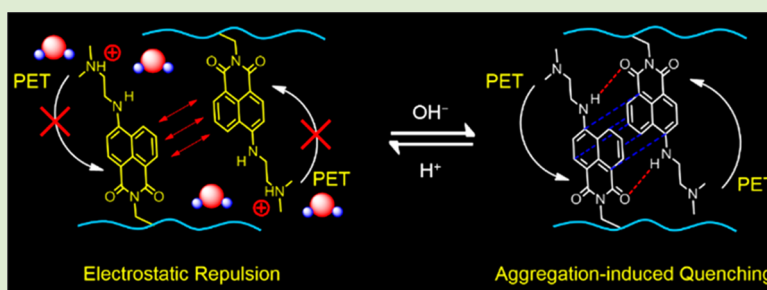
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Supporting Information



ABSTRACT: Polymer hydrogels with intense yet tunable fluorescence are of great research interest due to their wide potential use in biological imaging, sensing, information storage, etc. However, the conventional fluorophores such as naphthalimide and its derivatives are usually not recommended to prepare highly fluorescent hydrogels because of their aggregation-caused quenching (ACQ) nature and spontaneous tendency to undergo fluorescence self-quenching in quasi-solid-state hydrogel systems. Additionally, local regulation over fluorescent behavior of hydrogels, despite being important, still remains underdeveloped. Herein, we report highly fluorescent polymeric hydrogels based on conventional ACQ-type naphthalimide fluorophores, followed by spatial and temporal control of their fluorescent behavior. The hydrogels were prepared by one-pot radical copolymerization of naphthalimide-containing monomer and acrylamide in chitosan–acetic acid solution. Their intense emission comes from synergetic anchoring and diluting effect of the protonated naphthalimide moieties grafted on polymer chains, which result in the electrostatic repulsion among ACQ luminogens and reduced PET (photoinduced electron transfer) effect from adjacent dimethylamine groups to naphthalimide fluorophores. After being deprotonated in alkaline conditions, both PET and the ACQ effect work again to greatly quench fluorescence, endowing the hydrogels with pH-sensitive emission behavior. These properties encourage us to develop a diffusion-reaction (D-R) method to spatially and temporally control their fluorescent behavior. Based on these results, the ion-transfer-printing-assisted D-R method was further developed to fabricate many high-precision and meaningful fluorescent patterns on hydrogels. These fluorescent patterns are invisible under daylight but become vivid under specific UV light illumination, suggesting their wide potential applications in information security and transmission.

Fluorescent polymeric hydrogels are highly swollen and hydrophilic three-dimensional (3-D) networks with tunable luminescent properties. Their chemical structures and fluorescent features could be facily tailored as occasion demands.^{1–4} Especially, their hydrophilic 3-D polymeric network structure significantly facilitates the substance exchange with surrounding aqueous solutions to induce visible

fluorescence response, making them particularly useful for biological imaging, luminescent sensing, information encoding, and transforming, etc.^{1,4} Over the past decade, a variety of

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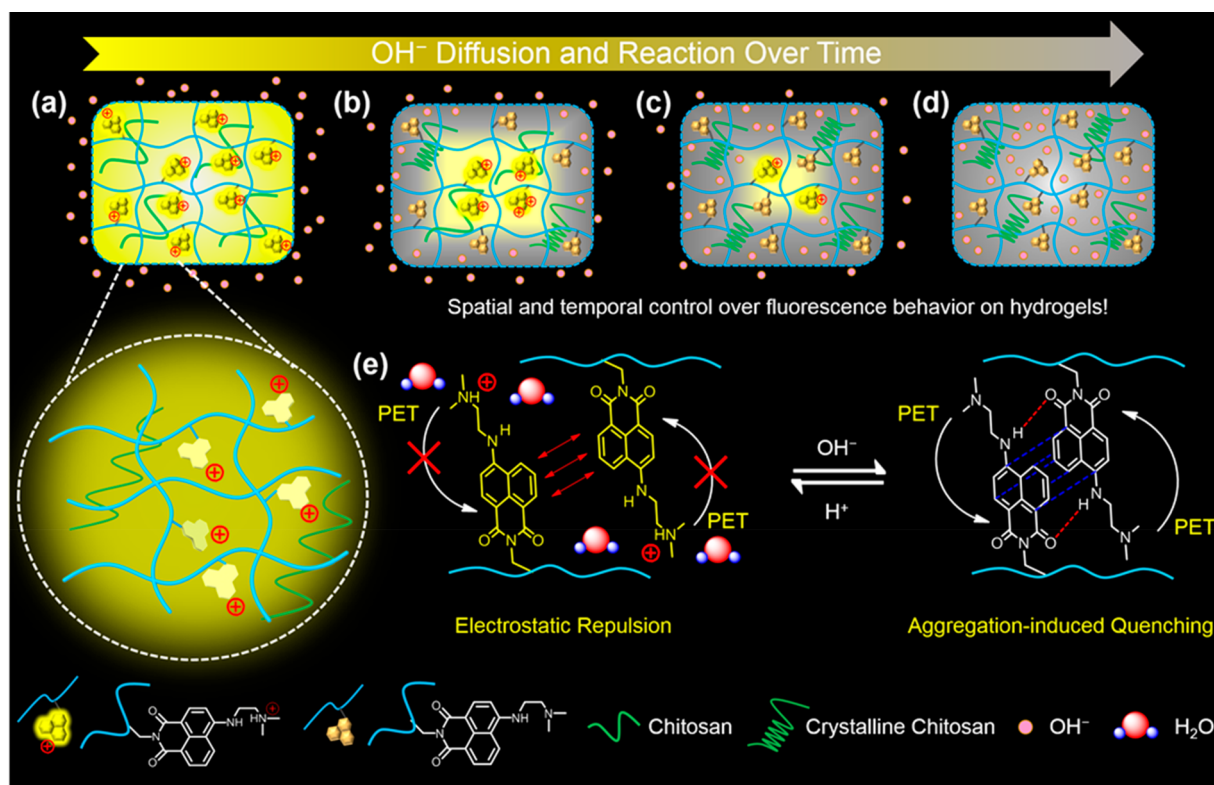


Figure 1. Illustration showing (a–d) the spatial/temporal control of emission behavior by the D-R method, as well as (e) the mechanism of strong fluorescence emission of the hydrogels. The as-prepared hydrogels are highly fluorescent because of synergetic anchoring and the diluting effect of the protonated naphthalimide moieties, which result in the electrostatic repulsion among ACQ luminogens and reduced PET effect from adjacent dimethylamino groups to naphthalimide fluorophores. After being deprotonated, both PET and the ACQ effect work again to greatly quench fluorescence, endowing the hydrogels with pH-sensitive emission behavior. Therefore, when aqueous NaOH solution is placed around and left to diffuse and react over time, the peripheral part becomes dark, and the dark part gradually grows, finally reaching the entire hydrogel.

fluorescent polymeric hydrogels have thus been developed by incorporating organic fluorophores,^{5–18} lanthanide chelates,^{19–23} or luminescent nanoparticles^{24–27} into hydrogel matrixes. For example, Tang and co-workers fabricated one luminescent hydrogel system based on the aggregation-induced emission (AIE)-type tetraphenylethene luminogens and realized the visualization of the entire gelation process of chitosan.¹⁵ The Huang and Sessler groups prepared blue-, green-, and red-light-emitting hydrogels by the covalent incorporation of coumarin, BODIPY, and rhodamine fluorophores, respectively, and demonstrated their use for information storage, modification, and readout.⁶ We also took advantage of the perylene bisimide-functionalized fluorescent polymer to fabricate an anisotropic hydrogel actuator with on–off switchable and color-tunable fluorescence behaviors.²⁸ These impressive advances have greatly broadened the list of fluorescent hydrogels and widened their potential applications.

Compared with these intense studies in which the fluorescent behaviors of the whole hydrogels are globally tuned, few attempts have been conducted to locally regulate their luminescent behaviors to realize the spatial/temporal emission control on/within hydrogels.²⁹ Such spatial/temporal emission control is favorable to form fluorescent hydrogel materials with patterned heterogeneities and periodicities of high precision, providing well-defined areas with disparate functions on a high level of spatial resolution.³⁰ As demonstrated by the extensive studies in patterned fluorescent thin polymer films over the past decade,^{30–33} patterned fluorescent hydrogels are expected to hold great potential for high-tech applications, including

sensing/medicinal diagnostic chips, information storage, encryption, and displays. However, fabrication and patterning of fine fluorescent polymeric hydrogel films remain quite challenging, probably because of the difficulty facing the design and preparation of highly emissive hydrogels, as well as the lack of facile patterning approach.

Herein, we report the facile fabrication of a new type of highly luminescent polymeric hydrogel, followed by spatial/temporal control of their emissive behaviors to produce fluorescent patterns through the developed diffusion-reaction (D-R) method. The hydrogel was prepared by one-pot radical copolymerization of 4-(*N,N*-dimethylaminoethylene) amino-*N*-allyl-1,8-naphthalimide (DEAN) and acrylamide (AAM) in the presence of chitosan–acetic acid solution (Figure S1). Their intense emission stems from the covalently immobilized naphthalimide groups, which are typical ACQ luminogens.^{33,34} Usually, the ACQ luminogens are not recommended to prepare highly fluorescent hydrogels because of their tendency to undergo fluorescence self-quenching in quasi-solid-state hydrogel systems. However, the naphthalimide fluorophores are covalently grafted and ionized in our hydrogel system, resulting in the synergy of electrostatic repulsion, anchoring, and a diluting effect (Figure 1a and 1e). The aggregation-induced fluorescence quenching is thus greatly reduced. Further deprotonation of this ACQ luminogen in alkaline conditions will induce their aggregation again. Meanwhile, the deprotonated dimethyl amino groups act as strong quenchers to the naphthalimide fluorophores via a known photoinduced electron transfer (PET) mechanism.³⁴ Therefore, our hydrogel becomes

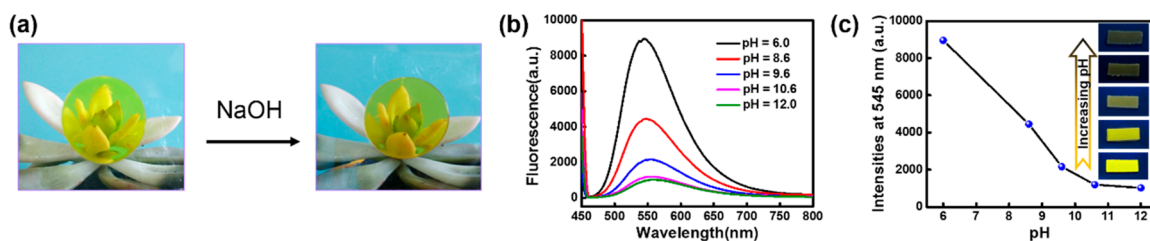


Figure 2. (a) Photos of the hydrogel samples before and after being treated by aqueous NaOH solutions (0.1 M); (b) fluorescence spectra of the hydrogel samples treated by various buffered solutions; and (c) the peak fluorescence intensities of the hydrogel samples treated by various buffered solutions, as well as their photos taken under 365 nm UV lamp.

nearly nonfluorescent in alkaline conditions, indicating that its emission is typically pH-sensitive. Based on this fluorescence switching mechanism, spatial/temporal control over its fluorescence behavior was realized by the local diffusion of OH^- and the subsequent deprotonation reaction (D-R) method (Figure 1a–d). As a result, reversible fluorescent patterns can be facilely fabricated onto the hydrogels as demanded using the D-R method.

The key step to preparing the hydrogel is synthesis of the fluorescent DEAN monomer. Figure S2 depicts its synthetic procedure. Briefly, 4-bromo-1,8-naphthalic anhydride is heated with allylamine in ethanol to produce *N*-allyl-4-bromonaphthalimide, which then reacts with excess *N,N*-dimethylethylenediamine to give the yellowish DEAN monomer in high yield. Its chemical structure was verified by the ^1H NMR spectrum (Figure S3), which was consistent with the reported result.³⁴ To realize suitable cross-linking density and hardness of the hydrogels, feed ratios were then optimized to be as follows (Table S1 and Figure S4): AAm: 1200 mg, Bis: 2.4 mg, DEAN: 15 mg, KPS: 12 mg, chitosan solutions (4 wt %): 4 mL. The obtained hydrogels (Figure 2a), having typically porous cross-linked network (Figure S5), are transparent (Figure S6a) and yellowish, as evidenced by the observed UV absorption band around 440 nm that is similar to that of the DEAN monomer (Figure S6b). These results, together with the FT-IR measurement (Figure S7), indicate the successful incorporation of naphthalimide fluorogens into the hydrogel matrix. It should be noted that chitosan polymer plays a vital role in improving moldability of the hydrogels, as demonstrated by the control experiments shown in Table S2 and Figure S8. This is because high-density O/N-containing groups grafted on chitosan polymer chains could form abundant hydrogen bonds between the chemically cross-linked PAAm network, resulting in significantly improved modulus (Figure S8). Therefore, the chitosan-incorporated hydrogel was used and subjected to systematical investigation herein.

Fluorescent properties of the hydrogels were studied. The as-prepared hydrogels were found to emit intense yellow-green light under UV illumination, accompanied with a strong fluorescence band around 550 nm (Figure 2b,c). The observed bright emission is believed to stem from the anchored naphthalimide luminogens, which exist at the ionized state and repel each other at acid conditions to reduce the ACQ effect (Figure 1e). At the same time, the PET effect from adjacent dimethyl amino groups to naphthalimide luminogens is also blocked by protonation. Therefore, it is the synergy of the suppressed ACQ and PET effects that endows the hydrogels with highly luminescent features. Further evidence for this proposed mechanism comes from their pH-switchable fluorescence behavior. As shown in Figure 2b, the emission

intensities of the hydrogels gradually weaken with increasing pH value. When pH reaches above 10.6, the hydrogels become nearly nonfluorescent (Figure 2c, inset) because of the significantly enhanced ACQ and PET effects. The pH-controlled emission intensity change is so large (~ 9 times) that vivid color contrast was observed by the naked eye. Interestingly, in spite of the remarkable pH-triggered fluorescence change, no pH-controlled transparency/color variation is noticed during day light (Figure 2a). The pH-responsive luminescent behavior of the hydrogel then encourages us to explore their potential utility for Morse and ASCII binary information security (Supplementary Note 1 and Figure S9),³⁵ as well as for remote pH detection in aqueous solutions (Supplementary Note 2 and Figures S10–11).

Based on the tunable fluorescence property of the whole hydrogel stripes, we further tried to develop a D-R method to realize the spatial/temporal control of their emission behavior. As shown in Figure 3a, a rectangle-shaped hydrogel sample was prepared and adhered onto a flat Petri dish. Then aqueous NaOH solution (0.1 M) was placed around the hydrogel and left to diffuse and react over time (Figure 3a, right). It was observed that the peripheral part soon becomes dark, while the inner part remains highly luminescent. The dark part is gradually growing

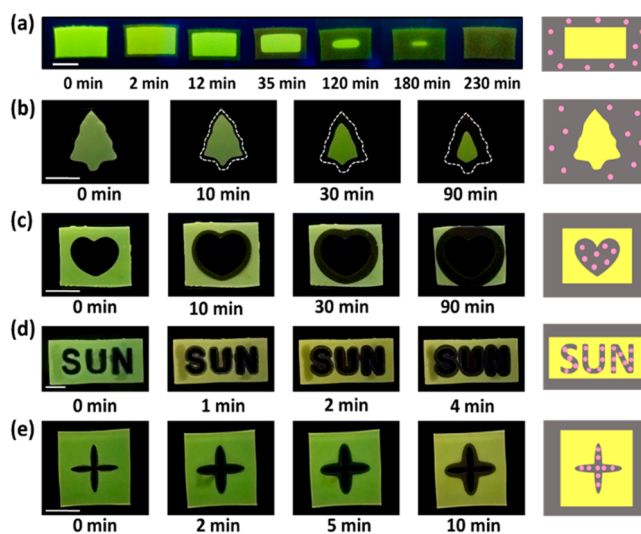


Figure 3. Locally regulating fluorescence behavior of the hydrogels by the D-R method. In all figures, the gel structure formed through the D-R method resulted from a starting point configuration as shown in the right cartoon. In the cartoons, the red dots represent hydroxide ions (OH^-): (a,b) NaOH (0.1 M) solutions were placed outside of the hydrogel samples and then diffuse from outside to inside; (c–e) NaOH (0.1 M) solutions were placed in the predesigned holes of the hydrogel samples and then diffused from inside to outside. Scale bars: 1 cm.

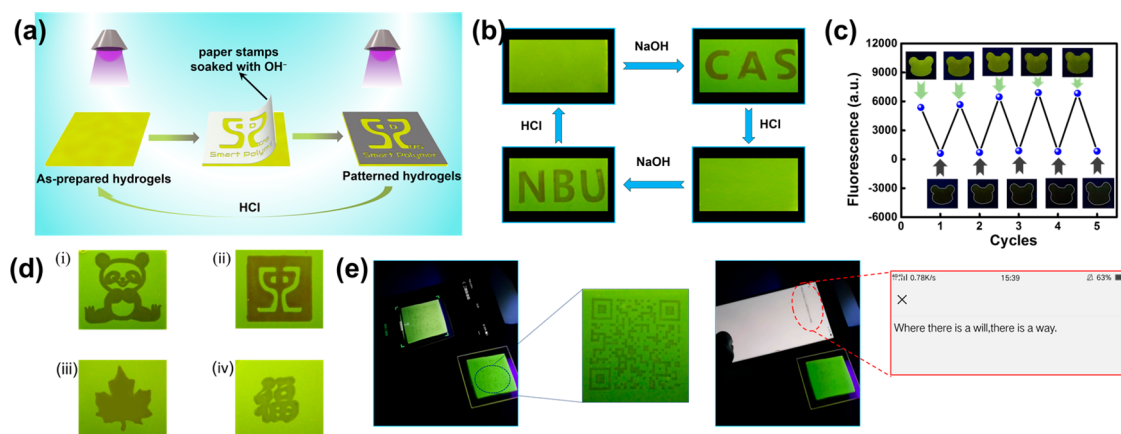


Figure 4. (a) Illustration of the ion-transfer-printing-assisted R-D method to produce fluorescent patterns on hydrogels. Cellulose paper stamps soaked with OH⁻ ions were placed onto the surface of the as-prepared hydrogel samples for 10 s. During this period, OH⁻ diffuses into the hydrogel to quench fluorescence. After peeling the stamps off, desirable fluorescence patterns were printed. (b) Photos showing the “printing–erasing” cycle. The printed CAS letters could be facilely erased by acid solutions (0.1 M HCl) and rewritten as NBU letters by NaOH solutions (0.1 M). (c) Fluorescence intensity change of the hydrogels at 545 nm after being treated sequentially by NaOH and HCl solutions (0.1 M). (d) Photos of the printed fluorescent patterns on hydrogels. The process could be cycled for several times. (e) QR-coded information encryption and transmission (taken under 365 nm UV light).

over time and finally reaches the whole hydrogel. When using hydrogel samples of different shapes, it is possible to obtain more complex or meaningful fluorescent shapes (Figure 3b–e).

We have demonstrated the ability to regulate the emission behavior of our hydrogels locally via the developed D-R method by using aqueous NaOH solution as the ink. However, it seems quite difficult to produce arbitrary patterns with precise resolution, which is vital for message display applications. To this end, an ion-transfer-printing-assisted R-D strategy was further developed.³⁶ As illustrated in Figure 4a, cellulose paper stamps soaked with OH⁻ ions were placed onto the surface of the as-prepared hydrogel films for 10 s. During this period, OH⁻ ions spontaneously diffuse into the hydrophilic hydrogel matrix and react to turn off the fluorescence. After peeling the stamps off, desirable fluorescence patterns were obtained. Notably, due to highly reversible nature of the pH-sensitive emission response, the fluorescent patterns can be sequentially redefined. For example, the printed CAS letters could be facilely erased by acid solutions (0.1 M HCl) and rewritten as NBU letters (Figure 4b). This “printing–erasing” cycle was proved to be repeated for many times (Figure 4c). Besides simple English letters, patterns that are more complex could also be printed onto our hydrogels, including a panda, logo of our group, rabbit, maple leaf, Chinese character “Fu”, and hand (Figures 4d i–iv and S12). Interestingly, it was found that these fluorescent patterns are transient, and their lifetimes can be tuned from several to tens of minutes (Figures S13–14) because they are stabilized by deprotonation reaction and thus typically exist in states far from equilibrium, just like biological nonequilibrium structures fueled by ATP.³⁷

We sought out the applicability of our hydrogel with transient fluorescent patterns as a carrier for a temporary message with a tunable lifetime.³⁷ As a proof-of-concept, the “CNITECH” and “NBU” messages were printed onto the hydrogel samples (Figures S13–14) by using paper stamps soaked in 1 and 0.1 M NaOH solutions, respectively. Both of the printed letters were very clear at the beginning but gradually autoerased over time owing to depletion of the OH⁻ “fuel”. The lifetimes of these fluorescent messages could be tuned from roughly several minutes to half an hour by altering the concentration of the OH⁻ fuel. Furthermore, high-precision QR code with a presupposed

message could also be facilely printed on our hydrogels (Figure 4e). The printed QR code was completely invisible under ambient light and not easy to be noticed. However, it could be scanned by a smartphone upon exposure to portable 365 nm UV light and immediately linked to the predesigned sentence “Where there is a will, there is a way”. It is worth mentioning that this kind of hydrogel-based message passing is superior to its paper-based counterparts in terms of timeliness. This is because the fluorescent patterns can self-erase quickly so that the printed message cannot be read soon. These results suggest that the fluorescent-hydrogel-based message passing approach is usually temporary, which may be particularly attractive for leaving transient messages in some special conditions.

In summary, we have fabricated a new class of fluorescent hydrogels by the radical polymerization of acrylamide and a specially designed naphthalimide-containing monomer in the presence of chitosan. The as-prepared hydrogels are highly luminescent at acid conditions because the naphthalimide groups, despite being ACQ-type, are protonated and repulsive to each other, resulting in synergy of suppressed ACQ and PET effects. Their fluorescence intensity is thus variable with the change of pH value. The localized tuning of fluorescent behaviors is thus demonstrated by the developed D-R method, which leads to the facile spatial/temporal control over their fluorescence property. Furthermore, transient fluorescent patterns with a tunable lifetime were fabricated on our hydrogel by an ion-transfer-printing-assisted D-R method. The patterned hydrogels are transparent and look homogeneous at ambient environment, yet are highly fluorescent and heterogeneous under UV light. Their potential applications for temporary information transmission and remote pH detection were also explored. In view of modular design of highly fluorescent hydrogels and facile operation of the D-R method, our strategy may inspire more powerful fluorescent materials with patterned heterogeneities and periodicities.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.9b00337.

Experimental section, synthesis of DEAN and hydrogels, information security, and remote pH detection applications (PDF)

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Notes

The authors declare no competing financial interest.

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