# Optically Switchable Luminescent Hydrogel by Synergistically Intercalating Photochromic Molecular Rotor into Inorganic Clay

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Photomodulated luminescent hydrogels are of great potential for construction of functional soft materials. Herein a simple yet effective approach, by synergistically intercalating the dithienylethene-bridged bispyridinium dye into the inorganic clay of Laponite, is proposed to immobilize the dye's molecular conformation and then to activate the hydrogel's fluorescence emission. The incorporation with dithienylethene unit can not only increase the  $\pi$ -conjugation of organic dye but also endow the obtained supramolecular hydrogel with desirable photoswitchable capability. It can be envisioned that this organic–inorganic hybrid hydrogel featuring reversible luminescence switching behavior, high water content, good transparency, and mouldability may offer a practical strategy to create more advanced intelligent materials.

Luminescent hydrogels have aroused tremendous interest, mainly due to their unique physiochemical properties and inventive applications in life and material science, such as fluorescent sensors,<sup>[1]</sup> bioimaging agents,<sup>[2]</sup> tissue engineering,<sup>[3]</sup> and 3D printing.<sup>[4]</sup> In this regard, organic dyes,<sup>[5]</sup> quantum dots,<sup>[6]</sup> and rare-earth metal complexes<sup>[7]</sup> are frequently used as emitting sources to fabricate luminescent water-based soft materials. Nevertheless, structural optimization and implementation challenges still remain for the development of such functional materials. For instance, conventional organic dves are always subjected to photobleaching and self-quenching, thus making them not suitable for practical use.<sup>[8]</sup> Moreover, the excited state of lanthanide complexes can be severely dissipated via through O-H vibrations in aqueous environment and some additional ligands should be required for the protection from the deactivating solvent attacks.<sup>[9]</sup> Meanwhile, the development of luminescent hydrogels as advanced optical materials is always subjected to the tedious chemical synthesis and overuse of organic components. Therefore, it is absolutely imperative to explore highly photostable and emissive hydrogels in a simple and controlled manner.

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To further improve the physicochemical performance of luminescent hydrogels, herein we proposed a feasible approach to reversibly modulate the fluorescence intensity of supramolecular hydrogels by integration of a photochromic molecular rotor with inorganic frameworks. In our study, the dithienylethene-bridged bispyridinium salt was utilized as the emission precursor whose luminescence was quenched arising from the intramolecular free rotation, while the exfoliated Laponite clay was employed as the inorganic matrix to immobilize the conformation of molecular rotor. As a result, the association of oxyanion-rich Laponite surface with pyridinium sites led to formation of

a stable transparent hydrogel and the inherent fluorescence of molecular rotor could be activated at the same time. It is also noteworthy that benefiting from the dithienylethene core,<sup>[10]</sup> the obtained organic-inorganic hybrid hydrogel gave rise to optically switchable fluorescence emission. In our case, the photoswitchable luminescent hydrogels were not formed by simply doping or mixing, but achieved in a cooperative manner; that is, (1) pyridinium salt provides the positively charged binding sites for the electrostatic attraction with negatively charged Laponite, which is beneficial to the improved mechanical property; (2) Laponite as a 3D inorganic network can greatly deter the central single chemical bond of molecular rotor from free intramolecular rotation, thus resulting in the unique fluorescence enhancement in the gel state. Since our fabricated luminescent hydrogels were formed via noncovalent electrostatic interaction, the structural integrity of luminescent hydrogels is unaffected by external light input and more importantly, the synthetic complexity is avoided and the photoresponsive property is maintained to a great extent.

The synthetic route of dithienylethene-bridged bispyridinium salt 1 is shown in Scheme S1 (Supporting Information) and the target guest compound was comprehensively characterized by nuclear magnetic resonance (NMR) and high resolution mass spectrometry (HR-MS) (Figures S7–S10, Supporting Information). Because of the dithienylethene core, the photoswitchable molecule 1 exhibited reversible photoisomerization and photochromic behaviors. As depicted in **Figure** 1b, the absorption maximum of the open form (OF) in 1 was observed at 274 and 354 nm, respectively. When irradiated at 254 nm, the UV absorption was gradually declined, and a new absorption band at 607 nm accordingly increased and reached a



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**Figure 1.** a) Chemical structures of molecular rotors 1, 2, and **3**. b) Absorption spectra of the switch 1 upon irradiation at 254 nm in water ( $[1] = 2 \times 10^{-5}$  m). Inset: change in the photographic images of 1 upon alternating UV and visible-light irradiation.

photostationary state (PSS) after 6 min (Figure S11, Supporting Information), which could be assigned to the close form (CF) of 1. Meanwhile, three isosbestic points were found at 293, 341, and 436 nm during the transformation process. Thus, the photocyclization quantum yield ( $\phi_{o-c}$ ) for the active component was detected as  $\approx$ 76% by NMR spectral examination of the irradiated sample (Table S1 and Figure S12, Supporting Information). More interestingly, a complete recovery of the original UV–vis and NMR spectra of OF-1 was achieved upon irradiation of CF-1 at >490 nm (Figure 1b, and Figures S11 and S13, Supporting Information). The cycloreversion quantum yield ( $\phi_{c-o}$ ) was determined as 0.0045 and the circulation could be

repeated for at least ten times without any apparent deterioration (Figure S14, Supporting Information). Intuitively, the color of the solution could be changed between colorless (OF-1) and blue (CF-1) states by alternate UV and visible light (Figure 1b, inset). The concrete photochromic mechanism of 1 was shown in the inset of Figure 1b.

From the viewpoint of structural feature, the photosensitive compound 1 could be considered as a fluorescent molecular rotor, in which benzothiophene and pyridinium were electronrich as electron-deficient units, respectively.<sup>[11]</sup> This identification was further validated by the spectroscopic experiments with different viscosity.<sup>[12]</sup> As shown in Figure S15 (Supporting Information), the fluorescence of OF-1 was gradually enhanced



by a factor of 10 and showed hypochromatic shift by 21 nm as the viscosity of solvent increased and meanwhile, the absorption maximum was bathochromically shifted by 9 nm. In the control experiments, the reference compound 2 was synthesized without fluorinated cyclopentene and as expected, the similar spectral changes were observed, further suggesting that the rotational center was originated from the benzothiophenepyridinium conjugation (Figure S16, Supporting Information). The intermolecular rotation of 1 was also verified by quantum chemical calculations (Figure S17, Supporting Information). The computational results indicate that the rotation of central bond between benzothiophene and pyridinium part could easily occur under moderate conditions and thus would lead to energy dissipation of the excited 2 molecule without fluorescence emission. Thus, when they were in low-viscosity solvent such as methanol or water, the C-C single bond between donor and acceptor could rotate freely, resulting in energy relaxation from S<sub>1</sub> to S<sub>0</sub> through nonradiation. In contrast, the intramolecular rotation was effectively restricted in the presence of high-viscosity solvent (glycerol), thus leading to an obvious fluorescence enhancement.

After confirming that compound 1 was a typical fluorescent molecular rotor, a meaningful idea emerged in our mind that implanting the molecular rotor into gel environment may lead to the restriction of intermolecular rotation because of the high viscosity of gel media. Therefore, Laponite (LA), a type of non-toxic, eco-friendly layered clay with easy gelation in water,<sup>[13]</sup> was selected to immobilize the rotor 1 in the LA's inorganic framework. To our surprise, the simple mixture of 1 with 3.8 wt% LA in water could form a gel phase material with very low gelation concentration, which possessed high water content up to 96.2% (**Figure 2**b, inset). Notably, in rheological tests, *G'* value apparently increased when compound 1 was implanted into LA, indicating that incorporation of 1 into LA could improve the mechanical strength of the hydrogel (Figure 2a).<sup>[13]</sup>



**Figure 2.** a) Frequency ( $\omega$ ) sweep tests at  $\omega = 1-100$  rad s<sup>-1</sup> and strain ( $\gamma$ ) = 0.5% at 25 °C of single LA (Laponite/water = 3.8/96.2 wt%) and 1-LA hydrogels (Laponite/1/water = 3.8/0.0019/96.1981 wt%). b) Absorption spectra of OF-1 in aqueous solution and OF-1-LA hydrogel; Inset: the photographic images of gel-forming and gel transparence of 1-LA. c) The fluorescence spectra of OF-1 in aqueous solution and OF-1-LA hydrogel, and corresponding fluorescent images. d) Fluorescence spectra of OF-1-LA hydrogel upon irradiation at 254 nm; Inset: Reversibility of fluorescence emission for 1-LA hydrogel monitored at 575 nm upon alternating 254 nm and > 490 nm light irradiation. ([1] = 2 × 10<sup>-5</sup> M; excitation at 400 nm; the slit width was 10 and 10 nm for excitation and emission, respectively).







Scheme 1. Optimized geometry of OF-1 and CF-1 and schematic illustration of the formation of 1-LA hydrogel and photoswitching fluorescence behavior.

superior to the ones formed through host-guest complexation.<sup>[14]</sup> Furthermore, when fixing strain amplitude sweep at  $\omega = 6.28$  rad s<sup>-1</sup>, the hydrogels underwent a gel to quasiliquid state transition at the critical strain region ( $\gamma = 27.4\%$ ), which disclosed the breakdown of the hydrogel framework (Figure S18, Supporting Information). In addition, benefitting from good water solubility of 1 and cooperative integration with LA, we could clearly catch the sight of the words through the hydrogel, indicating that the 1-LA hydrogel was transparent (Figure 2b, inset). It is known that LA is negatively charged and our synthetic molecular rotor 1 bearing two positive charges on its arms could be well embedded into LA layers through multiple electrostatic interactions (Scheme 1). Moreover, the powder X-ray diffraction (XRD) experiments were performed in the LA and 1-LA xerogels. As shown in Figure S19 (Supporting Information), the broad diffraction pattern at  $2\theta = \approx 6.68^{\circ}$  implied that the interlayer space in the pristine Laponite was ≈1.3 nm, which was basically consistent with the reported value. Moreover, the broad peak shifted to  $2\theta = 4.59^{\circ}$ , corresponding to an interlayer space of 1.9 nm in the 1-LA gel.<sup>[15]</sup> The enlarged interlayer space in 1-LA gel demonstrated that compound 1 was synergistically embedded between two LA layers via multiple electrostatic interactions.<sup>[13d]</sup> In addition, it is noted that some photochromic molecules could escape from the gel matrix after

swelling the composite gel in water as a result of high water content and relatively weak electrostatic interaction between the photochromic molecule and Laponite (Figure S20, Supporting Information). Nevertheless, the obtained hydrogels were placed and aged hermetically one month at room temperature and no obvious variation was observed relative to the original gel state.

As depicted in Figure 2b, the absorption maximums of hydrogel 1-LA (283 and 382 nm) exhibited bathochromic shift by 9 and 28 nm as compared to 1 in aqueous solution (274 and 354 nm), accompanied by the color change from colorless to yellow. These results implied the formation of the intermolecular nanoaggregates of 1 in the hydrogel. Moreover, the hydrogel 1-LA exhibited strong fluorescence at 575 nm due to the restriction of intramolecular rotation of OF-1 in hydrogel (Figure 2c), while the fluorescence of OF-1 in aqueous solution was suppressed by intramolecular free rotation of central chemical bond.<sup>[16]</sup> Visually, the formation of gel state turned on the orange fluorescence of 1 by naked-eye observation. Furthermore, the fluorescent intensity of 1-LA was slightly enhanced as the content of Laponite increased (Figure S21, Supporting Information). To further exploit this strategy, the reference 2 and a frequently used molecular rotor, thioflavin T (3 in Figure 1a), were mixed with LA under the same experimental condition and similar rheological and spectroscopic







**Figure 3.** a) 3D confocal fluorescence images of hydrogels 1-LA; *x*, 0; *y*, 0; *z*, 0; (left) *x*, -55; *y*, -40; *z*, -25 (right). b) Photoswitchable intelligent and moldable luminescent hydrogels upon alternating 254 and >490 nm light irradiation.

properties were presented (Figures S22–S24, Supporting Information). These results jointly demonstrated that the gel-assisted fluorescence enhancement as a first-suggested new and simple method may provide a powerful tool for the intramolecular restriction of various molecular rotors, thus making molecule rotors more rigidified for efficient fluorescence radiation. Moreover, the control experiments showed that when encapsulated in the guar gum hydrogel as neutral matrix, yellow fluorescence of OF-1 was also observed (Figure S25, Supporting Information). Therefore, it could be concluded that the fluorescence emission potential could be conserved when implanted into electronegative or neutral gel matrix without fluorescence quenchers.

Furthermore, in order to ascertain the distribution of these molecular rotors in hydrogels, 3D confocal fluorescence image experiments were performed. As can be seen from Figure 3a, a great deal of strong orange fluorescent points were observed and evenly distributed in the hydrogel from different angles of view, further corroborating the aggregate mode and the good transparency of the molecular rotors in gel state. Meanwhile,

the **2-LA** hydrogel displayed the similar orange fluorescence with **1-LA** and the **3-LA** gel gave blue fluorescence (Figures S26 and S27, Supporting Information), which were all consistent with their inherent fluorescent emission.

Subsequently, due to the good photoisomerization of 1, the photochromic behaviors were examined for 1-LA hydrogel. Upon irradiation at 254 nm, the absorption maximum of the open form of OF-1-LA was declined at 283 and 382 nm, whereas a new absorption peak appeared at 628 nm, corresponding to the closed form of 1-LA, and the gel color was instantly changed from yellow to blue (Figure S28, Supporting Information). Subsequently, the absorption spectrum and gel color were recovered to the original state upon visible light irradiation, indicating the regeneration from closed to open form. These phenomena jointly suggested that 1-LA hydrogel still maintained its inherent photochromic property. In addition, the gel strength and transparency remained unchanged before and after UV light irradiation (Figure 2a, and Figure S18a and S28, Supporting Information). This encouraged us to further investigate whether the fluorescence of 1-LA hydrogel could



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be reversibly regulated by UV and visible light. As shown in Figure 2d and Figure S29 (Supporting Information), the fluorescent intensity of the hydrogel was gradually quenched upon continuous irradiation of 254 nm light for 4 min as a consequence of the conversion from OF-1-LA to CF-1-LA. Moreover, the fluorescent intensity of the resultant hydrogel (CF-1-LA) was restored to the initial state upon >490 nm visible light irradiation arising from the regeneration of OF-1-LA (Figure S30, Supporting Information). Accordingly, the color of fluorescence emission in 1-LA gel was visually changed between orange and dark (Figure 2d, inset). Notably, this lightdriven fluorescence switching cycle was repeatable for at least seven times without apparent fatigue (Figure 2d, inset), which suggested the good reciprocation for the photoswitching fluorescence process. In addition, there was no obvious change in the fluorescence spectra when OF-1 or CF-1 was used as the initial state to incorporate into the LA matrix (Figure S31, Supporting Information). It should be noted that as compared to the spectroscopic behaviors of free 1 in aqueous solution, UV-vis absorbance changes from OF-1-LA to CF-1-LA hydrogels were relatively weaker and only 78% fluorescent intensity was gradually quenched in the hydrogel state. These phenomena indicated that the photoswitchable molecule 1 in hydrogel may have relatively lower conversion ratio than that in water.<sup>[17]</sup>

Finally, the obtained hydrogels in our work possessed good mouldability, by which we could make a variety of luminescent 3D letter models (Figure S32, Supporting Information). As compared to 2-LA and 3-LA hydrogels, only 1-LA equipped with dithienylethene group could exhibit photoswitching fluorescence behavior. (Figure 3b) Therefore, by incorporating photoswitchable fluorescent molecular rotor into inorganic clay, we successfully constructed a transparent stable moldable lightmodulated luminescent hydrogel.

In conclusion, a molecular rotor was synthesized, showing reversible photochromic behaviors by the ring-closing and ringopening reactions of perfluorocyclopentene-based skeleton. The coassembling of photoactive molecular rotor with exfoliated Laponite clay could form binary supramolecular hydrogel with improved mechanical performance. Our results also indicate that the photophysical properties of dithienylethene derivatives could be completely retained in the Laponite matrix and more importantly, the inherent fluorescence emission of molecular rotor can be activated in the gel environment arising from the restriction of intramolecular rotation. Thus, we can anticipate that this organic–inorganic self-assembling approach may open avenues to create next-generation, optically responsive, waterbased soft materials.

### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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## **Conflict of Interest**

The authors declare no conflict of interest.

#### Keywords

dithienylethene, hydrogels, Laponite, light control, optical switches

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