

Fully Reversible Multistate Fluorescence Switching: Organogel System Consisting of Luminescent Cyanostilbene and Turn-On Diarylethene

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Multicolor tunable and multistate switchable organogel is reported, which consists of a cyanostilbene organogelator showing aggregation-induced enhanced emission and a turn-on type photochromic diarylethene dye. The mixed organogel can be reversibly switched among four different states (blue-emitting gel, nonemissive sol, green-emitting gel, and green-emitting sol) modulated by a combination of orthogonal stimuli of heat and light. It is interestingly noted that this four-state switching constitutes a combinational logic circuit consisting of two stimuli inputs and three outputs. Reversible fluorescence writing, switching, erasing, and image patterning processes on this mixture gel system are demonstrated.

1. Introduction

Fluorescent low-molecular-weight gelators (LMWGs), which form a 3D network by noncovalent self-assembly, are drawing great attention due to their potential in broad range of applications including optical memory, logic gate, and sensing.^[1] Of particular interest are "smart" LMWGs bearing stimuliresponsive units because their fluorescence emission can be controlled reversibly in response to the external stimuli.^[2] Photoresponsive LMWGs, which contain photochromic compounds (e.g., azobenzene, spiropyran, and diarylethene), are the most appealing ones since light irradiation has many advantages over other stimuli such as versatility in tuning of wavelength, intensity, and focusing while demanding no physical contact with the samples.^[1,3]

Many luminescent LMWGs admixed with photochromic molecules have been reported to date which mostly demonstrated single-color fluorescence on/off photoswitching.^[4–7] In these systems, photochromic molecules can switch on/off the fluorescence of the gel through light stimulus by modulating off/on energy transfer (ET) between the excited state of fluorophore and the isomeric ground states of photochromic dye. However, multicolor fluorescence photoswitching in LMWGs are still rare although it could make a breakthrough in optical

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memory, sensing, and logic gates. To the best of our knowledge, there has been only one example of the multicolor tunable photoresponsive LMWG reported so far. Chen et al. successfully demonstrated a multicolor fluorescent LMWG by utilizing spiropyrans as a photochromic switch.^[8] In this system, a mixture containing a dendron-substituted tetraphenylene organogelator and a spiropyran, as a fluorophore and a photochromic dye, respectively, has been used. A transparent and nonfluorescent spiropyran is converted into a colored and fluorescent one upon light irradiation. Simultaneously, the

emission of the donor fluorophore is quenched by the occurrence of ET from the excited state of the fluorophore to the ground state of the colored photochrome, resulting in the fluorescence color change of the gel. Although the LMWG showed reversible fluorescence color change in the gel state upon light irradiation, they could not maintain the switched color in the course of the thermally induced gel-to-sol transition, which represents the lack of orthogonality between the heat and the light stimuli. Moreover, autonomous return to the original fluorescence color happened even at room temperature, because the colored form of the spiropyrans is not stable and thus thermally reverts to the initial colorless form.^[6,8,9]

On the other hand, several luminescent LMWGs exploiting photochromic diarylethenes, which have excellent reversibility and thermal stability, as an ET acceptor have been reported.^[4,5] The diarylethene in LMWGs maintain photoresponsive bistability independent from thermal stimulus, i.e., heating to induce gel-to-sol transition without change in the isomeric states of photochromic molecule. However, single color on/ off switching of the emission in gel state (or in solution state) has only been demonstrated thus far, because most of the diarylethenes have virtually no fluorescence in both photoisomeric forms. Recently, Ahn,^[10] and Irie^[11,12] groups reported that turn-on type diarylethenes bearing sulfone groups undergo a cyclization to form a highly fluorescent closed-ring isomer upon UV-light irradiation, which inspired us to develop a dual fluorescence and multistate fully reversible organogel system.

Here, we demonstrate a multicolor switchable LMWG that can reversibly switch among four different states by the orthogonal stimuli of heat and light for the first time. As shown in **Scheme 1**, 1-cyano-trans-1,2bis-(3',5'-bis-trifluoromethylbiphenyl)ethylene (CN-TFMBE) was again selected as an



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Scheme 1. a) Chemical structure and the photochromic reaction of CF₃-BPDBTEO. Green emission is switched on/off upon UV/vis irradiation. b) Chemical structure and thermal switching of CN-TFMBE. Blue emission is turned on/off upon cooling/heating.

outstandingorganogelator in this work, which had been successfully employed in the on/off fluorescence switching system.^[5] To impart the enhanced turn-on fluorescence behavior and also the compatibility with the CF₃ containing gelator group, we have designed and synthesized a novel turn-on type green fluorescent diarylethene, (3,3'-(perfluorocyclopent-1-ene-1,2-diyl)bis(6-(3,5bis(trifluoromethyl)phenyl)-2-ethylbenzo[b]thiophene1,1-dioxide) (CF₃-BPDBTEO), as a photochromic guest molecule in this work. By mixing CN-TFMBE and CF₃-BPDBTEO, we attempted to achieve multicolor multistate fluorescence switching system.

2. Results and Discussion

CF₃-BPDBTEO as a novel class of fluorescent diarylethene compound was synthesized as shown in **Scheme 2**. Compound **6**, which is sulfone-containing diarylethene iodide, was prepared as the synthetic route according to literatures $(1\rightarrow3,^{[13]} 3\rightarrow4,^{[14]} 4\rightarrow6^{[11]})$. Suzuki coupling reaction of compound **6** with CF₃containing aryl boronic acid in the presence of Pd₂(dba)₃, P(Cy)₃, and K₂CO₃ led to CF₃-BPDBTEO, which is CF₃-functionalized fluorescent turn-on diarylethene. The detailed synthesis and structure characterization are fully described in the Experimental Section.

Figures 1a and 2a show the UV-vis absorption and photoluminescence spectra of CF₃-BPDBTEO in 1,1,2,2-tetrachloroethane (TCE) solution. The open form of CF₃-BPDBTEO has absorption bands in the UV-region (<380 nm) and shows no fluorescence emission at all. However, upon UV-light irradiation, a new absorption band at around 443 nm gradually builds up by forming a closed isomer of CF₃-BPDBTEO with a strong green emission ($\lambda_{max} = 511$ nm, PLQY = 0.78 in TCE solution). The reverse photoreaction can be induced by visiblelight ($\lambda > 420$ nm) irradiation, which completely restores the initial absorption spectrum of the open form CF₃-BPDBTEO. It is noteworthy that this ring-closure and ring-opening reactions can be reversibly repeated more than 30 cycles without any photodegradation (Figure 2b). Interestingly, CF₃-BPDBTEO shows virtually identical absorption and emission spectra with strong fluorescence in the solid state ($\lambda_{max} = 517$ nm, PLQY = 0.65 in poly(methyl methacrylate) (PMMA) film) compared to those in the TCE solution (see Figure S1, Supporting Information). The photochromic conversion ratio at the photostationary state (PSS) upon 365 nm irradiation is calculated as 0.82 by



Scheme 2. The synthesis scheme of CF₃-BPDBTEO.



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Figure 1. a) Normalized UV–vis absorption (dashed lines) and photoluminescence (PL; solid lines) spectra of CN-TFMBE and CF₃-BPDBTEO. The red shaded region is spectral overlap between the emission of CN-TFMBE and the absorption of closed form CF₃-BPDBTEO. b) Photographs of photoswitching (ring opening-and-closing reaction) of CF₃-BPDBTEO (2×10^{-5} M in TCE) and thermal-switching (sol–gel transition) of CN-TFMBE (0.8 wt% in TCE).

high-performance liquid chromatography (Figure S2, Supporting Information). The photocyclization and the photocycloreversion quantum yields of CF₃-BPDBTEO in TCE solution were measured by the change of absorption spectrum upon light irradiation as 0.67 and 0.0016, respectively, according to the literature procedure (Figure S3, Supporting Information).^[15] It is particularly noteworthy that both cyclization and cycloreversion quantum yields of this CF₃ containing diarylethene (CF₃-BPDBTEO) are far higher than those of the reported reference diarylethene compound without CF₃ group,^[11] (see Figure S3, Supporting Information). Particularly, the photocycloreversion quantum yield is four times higher than the reference diarylethene without CF₃ group, which can facilitate a fast response in photonic applications including molecular switch, optical memory, and logic gate. The photochromic conversion between the open form and the closed form of CF₃-BPDBTEO is thus extensive and reversible enough, most likely attributed to the electron withdrawing CF₃ functionality, for use as a high performance fluorescence photoswitch.

To construct a multistate switchable organogel with CF₃-BPDBTEO, the organogelator should have strong self-assembly power to form a stable gel. In addition, most importantly, the emission spectrum of the organogelator should make a large overlap with the absorption spectrum of the CF₃-BPDBTEO to induce efficient intermolecular ET for fluorescence color switching. As the appropriate organogelator satisfying these conditions, CN-TFMBE, originally developed by us,^[16] is chosen in this study. CN-TFMBE was synthesized by the reported method. CN-TFMBE possesses strong self-assembly capability to form a gel, composed of the 3D fibrillar network in TCE with critical gelation concentration of 0.4 wt%. CN-TFMBE has no emission in the solution but turns to show strong blue fluorescence ($\lambda_{max} = 472$ nm, PLQY = 0.52) in the gel state (concentration = 0.8 wt% in TCE) due to the aggregation-induced enhanced emission characteristics (Figure 1).[16,17] This means that the blue emission of CN-TFMBE can also be switched on/ off by a thermal stimulus by triggering the gel to sol transition. The spectral overlap (see the red shaded region in Figure 1a) between the blue emission of CN-TFMBE gel and the absorption of the closed form of CF₃-BPDBTEO is quite large (spectral overlap integral, $I(\lambda) = 8.27 \times 10^{14} \text{ m}^{-1} \text{ cm}^{-1} \text{ nm}^{4}$) enough to bring about efficient ET.

To study ET efficiency between CN-TFMBE and CF₃-BPD-BTEO, three mixture gels were prepared in different weightbased mixing ratios of CN-TFMBE:CF₃-BPDBTEO = 1:1 for gel **1**, 1:2 for gel **2**, and 1:3 for gel **3**, respectively, while keeping concentration of CN-TFMBE = 0.8 wt% in respect to the TCE solvent. The mixtures are gently heated above 60 °C, which is



Figure 2. a) UV–vis absorption and photoluminescence (PL) spectra of CF₃-BPDBTEO in TCE solution ($c = 1 \times 10^{-5}$ M) upon UV and visible-light irradiation. b) Reversible test of photoswitching of CF₃-BPDBTEO in TCE solution for 30 cycles.

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Figure 3. a–c) Normalized PL spectra changes of the CN-TFMBE/CF₃-BPDBTEO mixture gel upon UV irradiation (weight ratio of the mixture = 1:1 for gel 1 (a), 1:2 for gel 2 (b), and 1:3 for gel 3 (c), respectively, concentration of CN-TFMBE: 0.8 wt% in respect to the TCE solvent). d–f) SEM images of the xerogel prepared from the organogel formed with CN-TFMBE/CF₃-BPDBTEO (weight ratio of the mixture = 1:1 for gel 1 (d), 1:2 for gel 2 (e), and 1:3 for gel 3 (g), respectively.

higher than the critical gelation temperature ($T_{\rm gel}$) of the mixtures (Figure S4, Supporting Information), and then cooled slowly down to room temperature. The morphology of these organogels are characterized by scanning electron microscope (SEM) (**Figure 3**d–f; Figure S8, Supporting Information). The images show that all the three gels irrespective of the mixing ratios are composed of interwoven nanofibers, which are also similar to the neat CN-TFMBE gel, which suggests that CF₃-BPDBTEO locates outside the CN-TFMBE nanofibers and does not contribute the formation of nanofibers.

Figure 3a-c and Figure S5a-c (Supporting Information) show fluorescence spectral changes of the three mixture organogels before and after UV-light irradiation. It is obvious that the blue emission of the gel becomes the more quenched due to the occurrence of the more efficient ET from CN-TFMBE to the closed-form CF₃-BPDBTEO as the amount of CF₃-BPDBTEO in the gel is increased. The actual values of ET efficiencies of the gels increase from 59% for the gel 1 to 98% for the gel 3, according to the calculation done by the decreased intensities of the CN-TFMBE emission. It should be noted that the gel 3 having a weight ratio of the mixture CN-TFMBE:CF₃-BPD-BTEO = 1:3 shows virtually perfect fluorescence color change from blue (denoted as 2G state) to green (denoted as 1G state) upon UV irradiation (see Figure 3; Figure S5, Supporting Information). Time-dependent density functional theory (TD-DFT) calculations also predict the possible occurrence of ET from the CN-TFMBE ($S_1 \rightarrow S_0$ energy of 2.73 eV) to the closed form CF₃-BPDBTEO ($S_0 \rightarrow S_1$ energy of 2.60 eV), but the absence of ET to the open form CF₃-BPDBTEO ($S_0 \rightarrow S_1$ energy of 3.70 eV) as shown in Figure S6 of the Supporting Information.

To get further insight into the mechanism of ET process, the fluorescence decay profiles of the organogels at 450 nm were recorded (Figure S7a–c, Supporting Information) before and after UV irradiation. These fluorescence lifetime changes of the energy donor (CN-TFMBE) upon UV irradiation and the corresponding lifetime-based ET efficiencies, which specifically

measures the nonradiative ET processes, for the three different gel systems are summarized in Table 1. It should be noted that while Förster type and/or Dexter type ET processes shorten the lifetime of energy donor, trivial ET process does not affect the lifetime of ET donor because it is a radiative mechanism.^[18] In the gel 1 with the 1:1 ratio, the lifetime of CN-TFMBE is slightly decreased by 7.5% upon UV irradiation, while 59% decrease of the CN-TFMBE emission intensity is observed in the PL spectrum shown in Figure S5a of the Supporting Information. This result implies that the ET in gel 1 occurs in much higher extent through the trivial pathway, but in the smaller extent by the nonradiative Förster type ET (FRET). This is because the concentration of CF3-BPDBTEO within the FRET radius is rather small in gel 1. By contrast, in the other two gels, the fluorescence lifetime of the donor is greatly decreased representing the significant increase of FRET process. The ET efficiencies calculated from the fluorescence lifetime results (52.4% for the gel 2 and 85.3% for the gel 3, respectively) are getting close to those from the PL results (71% for the gel 2 and 98% for the gel 3, respectively) with much smaller portion of trivial ET. This indicates

Table 1. Fluorescence lifetimes of CN-TFMBE (energy donor) and energy transfer efficiency in the mixture gels composed of CN-TFMBE and CF3-BPDBTEO. Monitored at 450 nm with 342 nm excitation. (τ : fluorescence lifetime, η : energy transfer efficiency.).

Mixture gel		τ[ns]	$ au_{av}\left[ns ight]$	$\eta^{ ext{a})}$
Gel 1	Open	8.45(78.5%)/1.45(21.5%)	6.94	7.5%
	PSS	7.13(87.2%)/1.63(12.8%)	6.42	
Gel 2	Open	7.19(79.1%)/1.64(20.9%)	6.03	52.4%
	PSS	6.41(34.5%)/1.00(65.5%)	2.87	
Gel 3	Open	7.80(49.1%)/1.32(50.9%)	4.50	85.3%
	PSS	5.85(3.1%)/0.49(96.9%)	0.66	

 $^{\rm a)}\eta = 1 - au_{\rm av,pss}/ au_{\rm av,open}$









Figure 4. a) Schematic illustration and b) photographs of the four states (2G, 0S, 1G, 1S) of the mixture. c) Truth table and d) schematic illustration for the organogel-based integrated logic circuit.

that significant portion of CF₃-BPDBTEO molecules are well located within the Förster distance in the gel **2** and gel **3**. This spatial proximity is most likely due to CF₃ group mediated specific intermolecular interactions such as $C-F\cdots F-C$ and $C-F\cdots \pi$ interactions, as was suggested in our previous study.^[5]

The green emissive gel **3** (denoted as **1G** state in Figure 4) is converted into a green fluorescent solution (denoted as **1S** state) upon heating. Because both isomeric forms of CF_{3} -BPDBTEO have high thermal stability, the green emission of the mixed system can be sustained. But, in sharp contrast to the photoinduced fluorescence color change between blue and green in the gel state, the fluorescence emission of the mixed system is turned off upon visible-light irradiation in solution (denoted as **0S** state in Figure 4 and Figure S9a–c of the Supporting Information for the emission spectra change). In

solution state, the CN-TFMBE and CF₃-BPDBTEO molecules should be far separated from each other in the TCE solvent. Upon visible-light irradiation, the closed form of CF₃-BPD-BTEO returns back to the nonemissive open form. In addition, the cyanostilbene unit of CN-TFMBE is significantly twisted in the solution, leading to torsion-induced nonradiative deactivation of the excited-states.^[16,19] Consequently, it brings about a complete off switching in the emission of the mixture system.

The reversible switching between different states is important for applying it to practical applications. To test the reversibility of the mixture system, fluorescence spectra are monitored upon repeated UV- and visible-light irradiation. As shown in **Figure 5** and Figure S10 (Supporting Information), the photoinduced color switching in both gel ($1G \leftrightarrow 2G$) and solution ($0S \leftrightarrow 2S$) could be reversibly switched for many cycles.



Figure 5. Reversibility test of the mixture in a) gel (1G \leftrightarrow 2G) and b) solution state (0S \leftrightarrow 2S) with alternation of UV and visible-light irradiation.





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Figure 6. Optical recording demonstration of the CN-TFMBE/CF₃-BPDBTEO mixture gel system (mixing ratio = 1:3, concentration of CN-TFMBE = 0.8 wt% in respect to TCE solvent) in a quartz cell.

This means that both the thermoresponsive emission on/ off switching of CN-TFMBE and the photoresponsive emission color switching of CF₃-BPDBTEO are fully reversible and also independent from each other enabling orthogonal responses to the different stimulus. Therefore, the four different states (**2G**, **0S**, **1G**, and **1S**) of the mixture can be fully addressable by the stimuli combinations of UV/vis light irradiation and heating/ cooling process.

By taking advantages of the reversible and orthogonal multistate switching, the mixed gel represents a combinational logic circuit consisting of two different inputs (input **A** and **B** for the light and the thermal stimuli, respectively) and three different outputs (output 1 and 2 for the on/off emission at 465 nm and at 530 nm, respectively, and output **3** for the gel/solution state) as shown in Figure 4d. It should also be noted that the combinations of the three output bits can be converted into four different output letters denoting the states of the mixture (see the truth table in Figure 4c). For example, applying UV light (1 in input **A**) and cooling process (0 in input **B**) to the mixture makes the output bits (0, 1; G) via a combination of NOR, NOT, and YES logic gates in the circuit. It is converted into the **1G** state, well indicating the green emissive organogel state in Figure 4b.

Finally, the rewritable optical recording process is demonstrated using the mixture system. Figure 6 shows the operational procedures for recording, color switching, and erasing of fluorescent images in the CN-TFMBE/CF₃-BPDBTEO the gel 3 system. It starts from the blue emissive gel state (2G). By irradiation of UV light through a mask containing the letters "GEL," a high contrast image of the letters is transcribed by forming the green fluorescence gel state (1G). This recorded image, green fluorescent "GEL" letter with blue fluorescent background, could also be written by irradiation of visible light from a whole green emissive gel with opposite phased "GEL" photomask (see Figure S11, Supporting Information). The whole fluorescence color can be changed into green upon further UV-light irradiation without the photomask. Otherwise, by heating, it can also be changed to the green solution state (1S). To erase the fluorescence, we turn off the emission of the mixture (0S) by visible light exposure. Subsequently, we can rewrite the blue fluorescence in the mixture system by a simple cooling down process.

3. Conclusion

In summary, we have developed reversible and multistate addressable fluorescent organogel, which is composed of a thermally switchable fluorescence organogelator and a photoswitchable turn-on diarylethene dopant with orthogonal responsibilities. By a combination of applying the two orthogonal stimuli (heat and light), we successfully demonstrated that four different states **(0S, 1S, 1G,** and **2G)** with three different fluorescence colors (off, green, and blue) are reversibly switchable in the mixture organogel through modulation of intermolecular ET. It is noteworthy that the four states switching of the mixture could be expressed through the com-

binational logic circuit. It is expected that this multistate fully addressable organogel system will be an important step toward future optoelectronic applications.

4. Experimental Section

Materials: All reagents and solvents obtained from commercial suppliers (Sigma-Aldrich, Alfa Aesar Co., and TCI Co.) were used without further purification unless otherwise stated. All glassware, syringes, magnetic stirring bars, and needles were thoroughly dried in a convection oven. Reactions were monitored using thin layer chromatography (TLC) with commercial TLC plates (silica gel 60 F254, Merck Co.). Silica gel column chromatography was performed with silica gel 60 (particle size 0.063–0.200 mm, Merck Co.).

Synthesis of CF_3 -BPDBTEO: Compound **6** was prepared according to the reported procedures.^[11,13,14] 1.5 g of **6** (1.85 mmol) and 1.19 g of 3,5-Bis(trifluoromethyl)phenylboronic acid (4.62 mmol) were dissolved in a THF solution (40 mL) at room temperature. To this solution, 40 mL of saturated aqueous K₂CO₃, 0.34 g of tris(dibenzylideneacetone) dipalladium(0) (0.37 mmol), and 1 mL of 18% tricyclohexylphosphine toluene solution were added. The mixture was stirred at room temperature for 3 h. After the reaction, the mixture was poured into a huge amount of water. The solution was neutralized with diluted hydrochloric acid and extracted with chloroform. The chloroform layer was concentrated, and silica gel column purification with hexane:ethyl acetate (30:1, v/v) was conducted. Reprecipitation in methanol from dichloromethane solution afforded a white powder (1.23 g, yield = 68%). ¹H NMR (300 MHz, CDCl₃, δ): 1.16 (t, J = 7.6 Hz, 3.7H (ap)), 1.45 (t, J = 7.6 Hz, 2.3H (p)), 2.43-2.54 (m, 1.6H (p)), 2.57-2.73 (m, 2.4H (ap)), 7.29 (d, J = 8.4 Hz, 0.8H (p)), 7.34 (d, J = 7.9 Hz, 1.2H (ap)), 7.69 (d, J = 8.0 Hz, 0.8H (p)), 7.86 (d, J = 8.0 Hz, 1.2 H (ap)), 7.93 (s, 3.2 H (p)), 7.98 (d, J = 6.0 Hz, 2.4 H(ap)), 8.02 (s, 2.4H). HRMS (FAB+, m/z): [M+H]⁺ calcd for C₄₁H₂₃F₁₈O₄S₂, 985.0750; found, 985.0757. Anal. calcd for C₄₁H₂₂F₁₈O₄S₂: C, 50.01; H, 2.25; S, 6.51. Found: C, 50.15; H, 2.33; S, 6.35.

Measurements: ¹H NMR spectra were recorded on a Bruker Avance 300 spectrometer. Mass spectra were acquired by employing JEOL JMS-600W/JMS-700GC, and elemental analyses were performed on a CE Instrument EA1110 instrument. High-performance liquid chromatography measurements were carried out using a Shimadzu LC-20AD chromatograph with an injection volume of 1 μ m. UVvis absorption spectra were collected on a Shimadzu UV-1650PC spectrophotometer. Fluorescence spectra were obtained by using a Varian Cary Eclipse fluorescence spectrophotometer. Absolute PL quantum yields were obtained using a Photon Technology International QM-40 spectrometer equipped with a 3.2 in. integrating sphere. A UV hand-held lamp (365 nm, 1.2 mW cm⁻²) was used as a UV-light source,



and a xenon arc lamp (300 W) was used as a visible light source through a color filter (>420 nm of Newport). Time-resolved fluorescence lifetime experiments were performed through the time-correlated single photon counting methods by using a FluoTime 200 instrument (Picoquant, Germany). A 342 nm pulsed light-emitting diode (LED) with a repetition rate of 10 MHz was used as an excitation source. Fluorescence decay profiles were analyzed by FluoFit Pro software, using exponential fitting models through deconvolution employing instrumental response functions. The fluorescence images were obtained with a digital camera (Canon PowerShot G6) under illumination at 365 nm. Field-emission SEM observation was carried out with SUPRA 55VP (Carl Zeiss). Fluorescence optical images were acquired with Nuance FX (Cambridge Research & Instrumentation).

Calculation: TD-DFT calculations were carried out in the gas phase using the Gaussian 09 quantum-chemical package.^[20] The geometry optimizations for the ground state of molecules were performed using B3LYP functionals with 6–31G(d,p) basis set.^[21] Vibration frequency calculations at the same level were performed for the obtained structures to confirm the stable minima.

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

aggregation-induced enhanced emission, diarylethene, fluorescence, logic gates, low molecular weight gelators

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- [1] S. S. Babu, V. K. Praveen, A. Ajayaghosh, Chem. Rev. 2014, 114, 1973.
- [2] a) N. M. Sangeetha, U. Maitra, Chem. Soc. Rev. 2005, 34, 821;
 b) C. D. Jones, J. W. Steed, Chem. Soc. Rev. 2016, 45, 6546;
 c) X. Yang, G. Zhang, D. Zhang, J. Mater. Chem. 2012, 22, 38;
 d) Z. Sun, Q. Huang, T. He, Z. Li, Y. Zhang, L. Yi, ChemPhysChem 2014, 15, 2421.
- [3] a) J. Eastoe, M. Sanchez-Dominguez, P. Wyatt, R. K. Heenan, *Chem. Commun.* 2004, 2608; b) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* 2014, 114, 12174; c) S. Bhattacharya, S. K. Samanta, *Langmuir* 2009, 25, 8378; d) S. Yagai, T. Karatsu, A. Kitamura, *Chem. Eur. J.* 2005, 11, 4054; e) J. Eastoe, A. Vesperinas, *Soft Matter* 2005, 1, 338; f) H. Tian, S. Wang, *Chem. Commun.* 2007, 781; g) C. J. Barrett, J.-i. Mamiya, K. G. Yager, T. Ikeda, *Soft Matter* 2007, 3, 1249; h) S. Yagai, A. Kitamura, *Chem. Soc. Rev.* 2008, 37, 1520; i) F. Ercole, T. P. Davis, R. A. Evans, *Polym. Chem.* 2010, 1, 37; j) M. M. Russew, S. Hecht, *Adv. Mater.* 2010, 22, 3348; k) E. R. Draper, D. J. Adams, *Chem. Commun.* 2016, 52, 8196.



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- [4] a) S. Wang, W. Shen, Y. Feng, H. Tian, Chem. Commun. 2006, 1497; b) S. Xiao, Y. Zou, M. Yu, T. Yi, Y. Zhou, F. Li, C. Huang, Chem. Commun. 2007, 4758; c) X. Cao, J. Zhou, Y. Zou, M. Zhang, X. Yu, S. Zhang, T. Yi, C. Huang, Langmuir 2011, 27, 5090; d) K. Rameshbabu, L. Zou, C. Kim, A. Urbas, Q. Li, J. Mater. Chem. 2011, 21, 15673; e) V. C. Edelsztein, E. A. Jares-Erijman, K. Müllen, P. H. Di Chenna, C. C. Spagnuolo, J. Mater. Chem. 2012, 22, 21857; f) S. Yagai, K. Ishiwatari, X. Lin, T. Karatsu, A. Kitamura, S. Uemura, Chem. Eur. J. 2013, 19, 6971; g) L. C. Schmidt, V. C. Edelsztein, C. C. Spagnuolo, P. H. Di Chenna, R. E. Galian, J. Mater. Chem. C 2016, 4, 7035; h) J. T. van Herpt, J. Areephong, M. C. Stuart, W. R. Browne, B. L. Feringa, Chem. Eur. J. 2014, 20, 1737; i) S. Yagai, K. Ohta, M. Gushiken, K. Iwai, A. Asano, S. Seki, Y. Kikkawa, M. Morimoto, A. Kitamura, T. Karatsu, Chem. Eur. J. 2012, 18, 2244.
- [5] J. W. Chung, S. J. Yoon, S. J. Lim, B. K. An, S. Y. Park, Angew. Chem., Int. Ed. 2009, 48, 7030.
- [6] Q. Chen, Y. Feng, D. Zhang, G. Zhang, Q. Fan, S. Sun, D. Zhu, Adv. Funct. Mater. 2010, 20, 36.
- [7] a) S. K. Samanta, S. Bhattacharya, *Chem. Commun.* 2013, 49, 1425;
 b) A. Bobrovsky, V. Shibaev, V. Hamplová, V. Novotna, M. Kašpar, *RSC Adv.* 2015, 5, 56891; c) L. Shi, X. Ran, Y. Li, Q. Li, W. Qiu, L. Guo, *RSC Adv.* 2015, 5, 38283.
- [8] Q. Chen, D. Zhang, G. Zhang, X. Yang, Y. Feng, Q. Fan, D. Zhu, Adv. Funct. Mater. 2010, 20, 3244.
- [9] S.-Z. Pu, Q. Sun, C.-B. Fan, R.-J. Wang, G. Liu, J. Mater. Chem. C 2016, 4, 3075.
- [10] a) Y. C. Jeong, S. I. Yang, K. H. Ahn, E. Kim, *Chem. Commun.* 2005, 2503; b) Y.-C. Jeong, S. I. Yang, E. Kim, K.-H. Ahn, *Tetrahedron* 2006, 62, 5855.
- [11] K. Uno, H. Niikura, M. Morimoto, Y. Ishibashi, H. Miyasaka, M. Irie, J. Am. Chem. Soc. 2011, 133, 13558.
- [12] a) B. Roubinet, M. L. Bossi, P. Alt, M. Leutenegger, H. Shojaei, S. Schnorrenberg, S. Nizamov, M. Irie, V. N. Belov, S. W. Hell, Angew. Chem., Int. Ed. 2016, 55, 15429; b) Y. Arai, S. Ito, H. Fujita, Y. Yoneda, T. Kaji, S. Takei, R. Kashihara, M. Morimoto, M. Irie, H. Miyasaka, Chem. Commun. 2017, 53, 4066; c) B. Roubinet, M. Weber, H. Shojaei, M. Bates, M. L. Bossi, V. N. Belov, M. Irie, S. W. Hell, J. Am. Chem. Soc. 2017, 139, 6611.
- [13] S. Pu, M. Li, C. Fan, G. Liu, L. Shen, J. Mol. Struct. 2009, 919, 100.
- [14] T. Yamaguchi, M. Irie, J. Photochem. Photobiol., A **2006**, 178, 162.
- [15] M. Irie, T. Lifka, S. Kobatake, N. Kato, J. Am. Chem. Soc. 2000, 122, 4871.
- [16] B.-K. An, D.-S. Lee, J.-S. Lee, Y.-S. Park, H.-S. Song, S. Y. Park, J. Am. Chem. Soc. 2004, 126, 10232.
- [17] B.-K. An, S. H. Gihm, J. W. Chung, C. R. Park, S.-K Kwon, S. Y. Park, J. Am. Chem. Soc. 2009, 131, 3950.
- [18] J. R. Lakowicz, Principles of Fluorescence Spectroscopy, 3rd ed., Springer, New York 2006, p. 443.
- [19] B.-K. An, J. Gierschner, S. Y. Park, Acc. Chem. Res. 2012, 45, 544.
- [20] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian Inc, Wallingford, CT 2013.
- [21] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.