Fluorescent Organogels

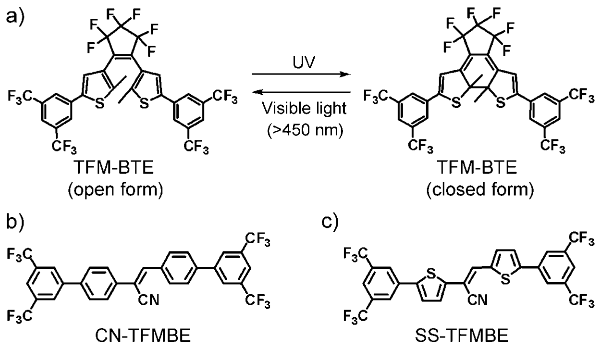
DOI: 10.1002/anie.200902777

Dual-Mode Switching in Highly Fluorescent Organogels: Binary Logic Gates with Optical/Thermal Inputs**

*Jong Won Chung, Seong-Jun Yoon, Seon-Jeong Lim, Byeong-Kwan An, and Soo Young Park**

Gels prepared from π-conjugated low-molecular-mass organogelators (LMOGs) have shown that the properties can be tailored and functionalized by incorporating stimuli-responsive units, for example, temperature-sensitive and photoactive units, as a part of the gelator molecule. These stimuli-responsive organogels,[1–3] alternatively called "smart" or "intelligent" gels, show reversible changes in morphology and/or physical properties in response to various external stimuli.[3–9] In particular, photoactive smart gels comprising π-conjugated LMOGs have been actively explored for various applications.[10–17] With the aim of developing fluorescent optical memory devices or logic gates containing LMOGs, efficient fluorescence-switching organogel systems activated by a single external stimulus have already been demonstrated.[12,18] However, no reliable multistimulus logic-gate switching has been achieved so far.[19] In the present work, we sought to obtain a highly efficient dual-mode (photo and thermal) fluorescence switching in a LMOG system, thus enabling logic-gate operation. The behavior of this organogel system can be described by a binary logic gate exhibiting fluorescence emission as the optical output as a response to the dual inputs of UV irradiation and thermal heating.

Among many fluorescent LMOGs reported so far,[10–12,20–22] 1-cyano-*trans*-1,2-bis[3′,5′-bis(trifluoromethyl)-biphenyl]ethylene (CN-TFMBE, Scheme 1 b) is the only candidate gelator for the realization of dual-mode logic gates, because it features a perfect "thermal switching" of the fluorescence emission between the sol and gel states.[22] This special LMOG is practically nonfluorescent in the molecular sol state but is switched on in the gel state, thereby showing an over 100-fold enhancement in the fluorescence intensity (this phenomenon has therefore been named aggregation-induced enhanced emission (AIEE)[23–26]). To achieve dual-mode logic-gate switching of the LMOG fluorescence, we combined "photo switching" properties with this AIEE turn-on fluorescent gelator by adding a photochromic compound. Herein, we report the design and synthesis of a novel 1,2-bis(thienyl)ethene (BTE) derivative[27–32] containing a trifluoromethyl (CF_3) moiety to improve its compatibility with the fluorescent gelator (CN-TFMBE), and thus facilitate intermolecular energy transfer between the organogelator and the BTE in simple mixed organogel systems.



Scheme 1. a) Chemical structure and photochromic reaction of TFM-BTE. b,c) Chemical structures of the fluorescent LMOGs CN-TFMBE (b) and SS-TFMBE (c).

Scheme 1 illustrates the chemical structure—and its photochromic switching—of a CF_3-containing BTE, namely, 3,3′-(perfluorocyclopent-1-ene-1,2-diyl)bis{5-[3,5-bis(trifluoromethyl)phenyl]-2-methylthiophene} (TFM-BTE). TFM-BTE was newly synthesized in this work (see the Supporting Information), while AIEE organogelators (CN-TFMBE and SS-TFMBE, see Scheme 1) were synthesized according to previously reported procedures.[22,33] TFM-BTE compounds were fully characterized by ^1H NMR and FTIR spectroscopy, mass spectrometry, and elemental analysis (see the Supporting Information).

As reported earlier in more detail, the organogelators CN-TFMBE and SS-TFMBE were found to exhibit an excellent self-assembly capability with extremely bright fluorescence emission in the gel state because of their characteristic AIEE properties.[22,33] Therefore, in this work we mainly focused on evaluating the photochromic properties and the compatibility of TFM-BTE with these AIEE organogelators.

TFM-BTE was found to exhibit reversible and bistable photochromism. Irradiation of a solution of TFM-BTE with 300 nm UV light led to the generation of a new absorption band at around 580 nm. Thus, the colorless TFM-BTE solution turned blue. However, subsequent irradiation by visible light ($\lambda > 450$ nm) restored the original absorption spectrum of the initial open-form TFM-BTE (see Figure 1 a). The ring-closing and ring-opening quantum yields of TFM-BTE in tetrahydrofuran were evaluated as 0.51 ($\Phi_{PC}^{O\to C}$) and 0.010 ($\Phi_{PC}^{C\to O}$), respectively, according to the literature proce-

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[*] J. W. Chung, S.-J. Yoon, S.-J. Lim, Dr. B.-K. An, Prof. Dr. S. Y. Park
Center for Supramolecular Optoelectronic Materials and
Department of Materials Science and Engineering
Seoul National University
San 56-1, Shilim-dong, Kwanak-ku, Seoul 151-744 (Korea)
Fax: (+82) 2-886-8331
E-mail: parksy@snu.ac.kr

[**] This work was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science, and Technology (CRI; RIAMI-AM0209(0417-20090011)).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200902777.

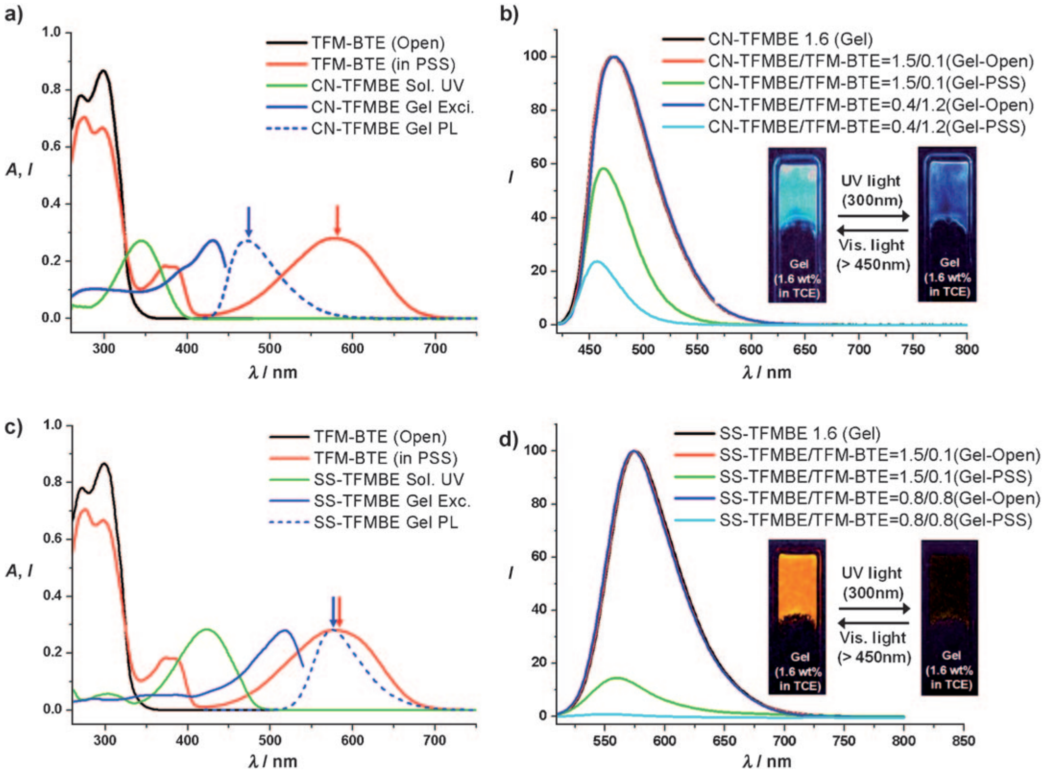

Figure 1. UV/Vis absorption and photoluminescence (PL) spectra of the open-form TFM-BTE and the photostationary state (PSS) with the AIEE organogelator. a,c) UV/Vis absorption spectra of TFM-BTE, CN-TFMBE, and SS-TFMBE. The arrows indicate the emission band of the AIEE gelator (blue arrow) and absorption band of TFM-BTE (red arrow). b,d) PL spectral changes observed upon the photochromic reaction of TFM-BTE with the CN-TFMBE and SS-TFMBE organogel systems, respectively. The insets show fluorescence switching in the gel state (1.6 wt% in TCE).

dure.[34–36] The photochromic conversion of TFM-BTE was significant, thus indicating that it is suitable for use as a switch unit.

First, the CN-TFMBE/TFM-BTE mixed organogel system was prepared by means of gentle heating at 60 °C to obtain a homogeneous mixture comprising 0 to 75 % (total content: 1.6 wt %) of TFM-BTE in 1,1,2,2,-tetrachloroethane (TCE). Then, the mixture was cooled slowly to room temperature. The upper limit of the TFM-BTE composition was set to 75 % because the minimum gelator content of CN-TFMBE was 0.4 wt % in the TCE solvent.

Fluorescence switching in the CN-TFMBE/TFM-BTE mixed organogel system was characterized as shown in Figure 1 b. The inset of Figure 1 b shows the reversible fluorescence on/off switching in the CN-TFMBE/TFM-BTE system after irradiation, even though the degree of fluorescence quenching is rather unsatisfactory. Figure 1 b shows the actual fluorescence spectral changes of the CN-TFMBE/TFM-BTE organogel before and after irradiation at different composition ratios. It is clearly seen that the CN-TFMBE/TFM-BTE organogel initially exhibits a strong fluorescence emission as a result of the characteristic AIEE effect. Upon irradiation with 300 nm UV light, however, the photochromic TFM-BTE molecule is transformed from the open- to the closed-ring form, and the fluorescence quenching is affected by intermolecular energy transfer (most likely by a Förster resonance energy-transfer mechanism) from CN-TFMBE to closed-form TFM-BTE. On the other hand, irradiation at wavelengths greater than 450 nm regenerated the open form and restored the original emission spectrum.

Although the fluorescence on/off switching in this fluorescent organogel system is obvious, it is noted that the fluorescence emission of the CN-TFMBE/TFM-BTE organogel system could not be completely quenched by irradiation with UV light. This finding is attributed to the limited overlap between the emission band of CN-TFMBE (blue arrow in Figure 1 a, $\lambda_{max} = 470$ nm) and the absorption band of the closed-ring form of TFM-BTE (red arrow in Figure 1 a, $\lambda_{max} = 577$ nm), which largely restricted the on/off fluorescence contrast ratio (on/off = 6:1; see Figure 1 b). Therefore, it is apparent that the ideal fluorescent gelator for the TFM-BTE switch should have a maximum emission wavelength at around 580 nm to fully exploit its energy-transfer efficiency to the closed-form TFM-BTE in the 300 nm photostationary state (PSS).

To meet this requirement, we designed and synthesized another AIEE gelator, namely, (*E*)-2,3-bis{5-[3,5-bis(trifluoromethyl)phenyl]thiophen-2-yl}acrylonitrile (SS-TFMBE, Scheme 1 c),[33] which is a CN-TFMBE derivative containing a thiophene moiety to attain a red-shifted fluorescence emission ($\lambda_{PLmax} = 575$ nm) in the gel state. In fact, as shown in Figure 1 c, the emission spectrum of SS-TFMBE completely overlaps with the absorption spectrum of closed-form TFM-BTE (see blue and red arrows in Figure 1 c). The SS-TFMBE/TFM-BTE mixed organogel system was prepared according to the same procedure followed to obtain the CN-TFMBE/TFM-BTE gel system to yield a 1.6 wt % TCE solution, but the composition varied only within 0 to 50 % of TFM-BTE. This is because the minimum gelator content of SS-TFMBE was 0.8 wt % in the TCE.

As expected from the favorable spectral overlap, it was observed that the integrated fluorescence intensity of the gel system in the 300 nm PSS was significantly reduced to 0.6 % that of the initial gel state with open-form TFM-BTE (on/off

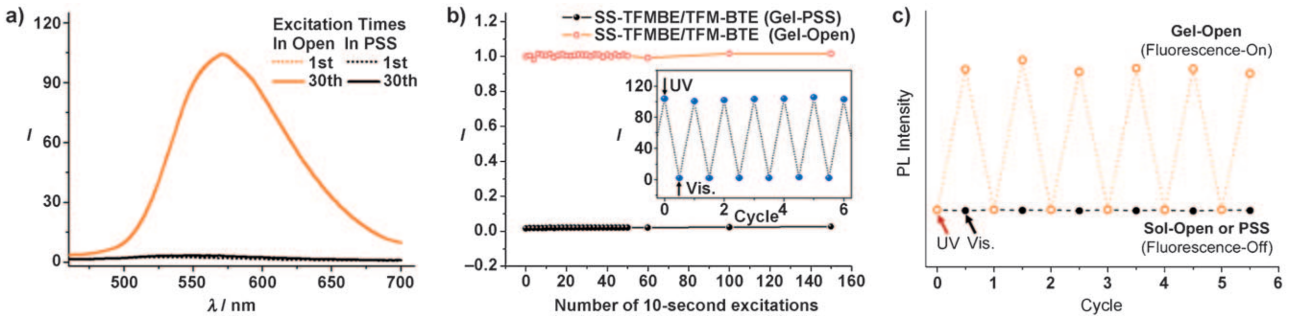

Figure 2. a,b) Nondestructive readout capabilities of the SS-TFMBE/TFM-BTE gel in the open-form state (orange lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}) and in the 300 nm PSS (black lines, $\lambda_{ex} = 415$ nm, 200 μW cm^{-2}). The inset in (b) shows the photochromic modulation of the AIEE fluorescence in the SS-TFMBE/TFM-BTE organogel system. c) Binary logic control between the SS-TFBME/TFM-BTE sol and gel states. Gel state with open-form TFM-BTE (upper orange circles), sol state with open-form TFM-BTE (lower orange circles), and PSS (black circles).

fluorescence switching ratio > 166, see Figure 1 d). It is clear that this very high contrast fluorescence switching is attributable to the highly efficient intermolecular energy transfer between SS-TFMBE and the closed-ring form of TFM-BTE. Figure 2 a shows on/off PL spectra of the SS-TFMBE/TFM-BTE organogel system in the open form and in the 300 nm PSS of TFM-BTE. The repeated switching behavior (at $\lambda_{max} = 575$ nm) with alternate UV and visible-light irradiation is shown in the inset of Figure 2 b. Notably, the switching behavior is reproducible and reversible. When the SS-TFMBE/TFM-BTE organogel was irradiated with the relatively weak 415 nm light for the fluorescence readout, the activated "turn-on" state was continuously preserved ("nonvolatile" memory characteristics), regardless of the excitation number (see Figure 2 b). Such a nondestructive readout capability is attributed to the characteristics of the optical-window region where the absorbance values of both open- and closed-form TFM-BTE vanish, while the excitation of fluorescence is highly effective (410–432 nm region, see Figure 1 c).[37]

It was also found that the highly fluorescent SS-TFMBE/TFM-BTE organogel system showed on/off modulation not only through light-driven photochromic isomerization but also through a thermally driven gel-to-sol phase transition, similar to an "OR" algorithm: thermal fluorescence switching was effected for open-form TFM-BTE while both the gel and sol states were nonfluorescent in closed-form TFM-BTE (see Figure 3). Such a unique response of the SS-TFMBE/TFM-BTE organogel system can be appropriately described by a binary OR logic gate with fluorescence quenching as the optical output in response to two inputs of "UV light" and "heat" based on the truth table shown in Figure S1 in the Supporting Information. We believe that this is the first demonstration of high-contrast reversible fluorescence switching showing binary logic operation in an organogel system. Although Tian and co-workers have previously reported an organogel system containing a fluorescent photochromic compound, the level of fluorescence-intensity modulation in the gel state was insufficient for achieving an efficient logic operation.[19]

We have further found that such unique fluorescence-switching behavior is suitable for achieving high-density optical logic memory storage. Figure 4 shows the operation procedures for recording and erasing fluorescence images in the SS-TFMBE/TFM-BTE gel system. We start from the nonfluorescent gel state (that is, the PSS state, Figure 4 d), which can be conveniently generated, irrespective of the previous treatment history, by exposing the sample either to UV light or to thermal heating. By irradiation of visible light through a mask containing the letters "AIEE", we were able to obtain a high-contrast fluorescence image of the AIEE letters (positive-tone letters, see Figure 4 a). The fluorescence

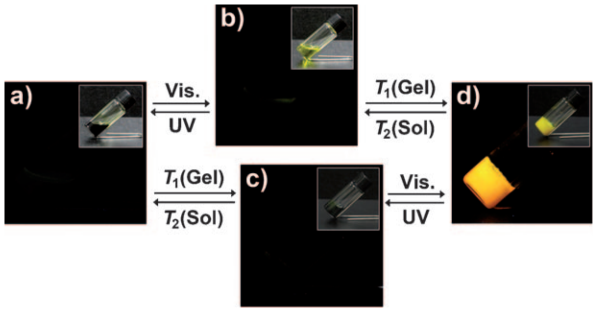

Figure 3. The fluorescence image as output of the two-input logic gate based on the SS-TFMBE/TFM-BTE organogel. Output fluorescence image of the organogel under the cooperative effect of light and heat as input: a) sol/closed form (1, 1), b) sol/open form (0, 1), c) gel/closed form (1, 0), d) gel/open form (0, 0). The inset shows an image under room light.

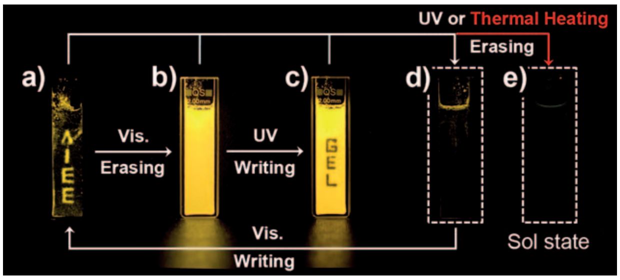

Figure 4. Reversible fluorescence image of the SS-TFMBE/TFM-BTE organogel system in a quartz cell ($\lambda_{ex} = 365$ nm). a) Writing, b) erasing, c) rewriting, d) re-erasing, and e) erasing by heat–sol state. The dark region represents the irradiated area (with 300 nm UV light). White dashed lines are shown around d) and e) for clarity.

image of Figure 4 a could be erased either to the nonfluorescent form (Figure 4 e) by a thermal route or to the fluorescent form (Figure 4 b) by nonlocal irradiation with visible light. By exposing the fluorescent gel to 300 nm UV light through a mask with the letters "GEL", a fluorescence image of the word GEL (negative-tone letters, see Figure 4 c) could be inscribed. Therefore, we have successfully demonstrated a write–erase–rewrite cycle and nondestructive read-out of a fluorescence optical recording based on a binary "OR" gate operation.

Finally, we investigated the compatibility effect of the SS-TFMBE gelator and the photochromic unit on the endurance of the recorded fluorescence image. The long-term stability of fluorescence-off images was compared over several hours for patterned images obtained in 0.8 wt % SS-TFMBE with 0.8 wt % of either TFM-BTE or 1,2-bis(2′-menthyl-5′-phenyl-3′-thenyl)perfluorocyclopentene (BP-BTE)[34,37] (without a CF_3 group, which is considered to be less compatible with SS-TFMBE) in TCE. The two samples were identically photopatterned with UV light—using a photomask to generate an image—and the fading and spreading of the fluorescence images were monitored over 30 min (see the Supporting Information). Closed-form TFM-BTE in the organogel maintained the same original spatial location, which implies a compatibility of TFM-BTE and SS-TFMBE, most likely through C–F···F–C and/or C–F···π interactions.[38,39] In contrast, it was observed that the fluorescence image of the SS-TFMBE/BP-BTE organogel gradually faded and spread with time (see Figure S2 in the Supporting Information).

In summary, we have constructed a fluorescent organogel-based supramolecular binary "OR" logic gate from an AIEE organogelator and a photochromic compound. This logic-gate system demonstrated high-contrast stimuli-responsive fluorescence modulation (with a fluorescence-switching ratio above 166) and also allowed us to address the fluorescence image with light. We believe that this switchable fluorescent organogel system is a promising candidate for erasable optical data storage. We are currently working on smarter systems that integrate multiswitchable functions into a single organogelator molecule.

Experimental Section

The starting materials were purchased from Alfa Aesar Co. and Sigma–Aldrich Chemical Co. and used without further purification, unless otherwise stated. The synthetic routes and characterization of TFM-BTE are described in the Supporting Information. UV/Vis absorption spectra were recorded on a Shimadzu UV-1650 PC spectrometer using samples in solution. Fluorescence spectra were recorded on a Shimadzu RF 5301 PC fluorescence spectrometer with samples in the solution or gel states. The ^{1}H NMR spectra used in the characterization of the products were recorded with a DPX Bruker 300 (300 MHz) spectrometer. The proton (0.1 ppm) chemical shifts were measured with respect to internal tetramethylsilane (TMS) at the probe temperature in $CDCl_3$. Thin-layer chromatography analyses were carried out on aluminum sheets coated with silica gel 60 (Merck 5554). Column chromatography was performed on Merck silica gel 60. Mass spectra were measured with a JEOL JMS AX505WA mass spectrometer. Elemental analysis was carried out with a CE Instruments EA110 elemental analyzer. High-performance liquid chromatography measurements were carried out using a Shimadzu LC-20AD chromatograph with an injection volume of 1 μm. The fluorescence images were obtained with a digital camera (Canon PowerShot G6) under illumination at 365 nm.

Received: May 25, 2009

Keywords: aggregation · fluorescence · organogels · photochromism · self-assembly

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