Reversible Quadruple Switching with Optical, Chiroptical, Helicity, and Macropattern in Self-Assembled Spiropyran Gels

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Enantiomeric glutamate gelators containing a spiropyran moiety are designed and found to self-assemble into a nanohelix through gelation. Upon alternating UV and visible light irradiation, the spiropyran experiences a reversible change between a blue zwitterionic merocyanine state and a colorless closed ring state spiropyran in supramolecular gels. This photochromic switch causes a series of subsequent changes in the optical, chiroptical, morphological properties from supramolecular to macroscopic levels. While the solution of the gelator molecules does not show any circular dichroism (CD) signal in the region of 250–700 nm due to the fact that the chromophore is far from the chiral center, the gel shows chiroptical signals such as CD and circularly polarized luminescence (CPL) because of the chirality transfer by the self-assembly. These signals are reversible upon alternating UV/vis irradiation. Therefore, a quadruple optical and chiroptical switch is developed successfully. During such process, the self-assembled nanostructures from the enantiomeric supramolecular gels also undergo a reversible change between helices and fibers under the alternating UV and visible light trigger. Furthermore, a rewritable material fabricated from their xerogels on a glass is developed. Such rewritable material can be efficiently printed over 30 cycles without significant loss in contrast and resolution using UV and visible light.

1. Introduction

Currently, light-triggered dynamic chiroptical switching between different states in molecules and materials is attracting great interest.[1] On one hand, from the view of photoresponsive recoding materials, simultaneous realization of both the optical and chiroptical signals can add extra storage density. On the other hand, the chiroptical materials are found to exhibit many applications such as molecular information processing, data storage, or probes for the detection of chirality,[2] In particular, developing materials exhibiting circularly polarized luminescence (CPL) has drawn more and more attention, not only for understanding the mysteries of homochirality, but also due to the important potential applications of CPL materials. For example, the devices displaying CPL may be a powerful method for addressing encoded information (cryptography) or for preparing 3D displays.[3]

Generally, there are basically three kinds of chiroptical information related to the materials, i.e., the optical rotation (OR), circular dichroism (CD) and CPL, which are characterized by differences between left- and right-handed circularly polarized light transmission, absorption and emission, respectively. In developing the chiroptical materials, chiral molecules are generally required. Two kinds of well-known molecules are widely used as the chiroptical switches, which are sterically overcrowded unsymmetrical thioxanthenes or analogue and the helicene.[4] An alternative way in fabricating chiroptical materials is to covalently attach the chiral moiety into the chromophore. Unfortunately, in this latter case, the molecules do not always show the chiral signals due to the deviation of the chiral moiety from the chromophores. To address this challenge, the supramolecular self-assembly provides an efficient way to transfer to the molecular chirality to the supramolecular system and both chiral and achiral molecules can be involved to construct the chiroptical systems.[5] Thus, dynamic chiroptical switching is changing from the molecular level to supramolecular and nanoscale level. So far, a large number of chiroptical switches have been developed.[1,6] However, many of them are limited to the switch by using the individual CD or CPL signals. Here, we provided the example showing quadruple reversible switches based on the chiroptical signals in CD, CPL and even their chiral nanostructures besides the optical reversibility. In addition, such chiroptical switch is stable and can be repeated many times.

Figure 1 shows the spiropyran based gelators, which are composed of the spiropyran moiety and the dialkyl glutamides. Both of these compounds form a pair of enantiomers and are

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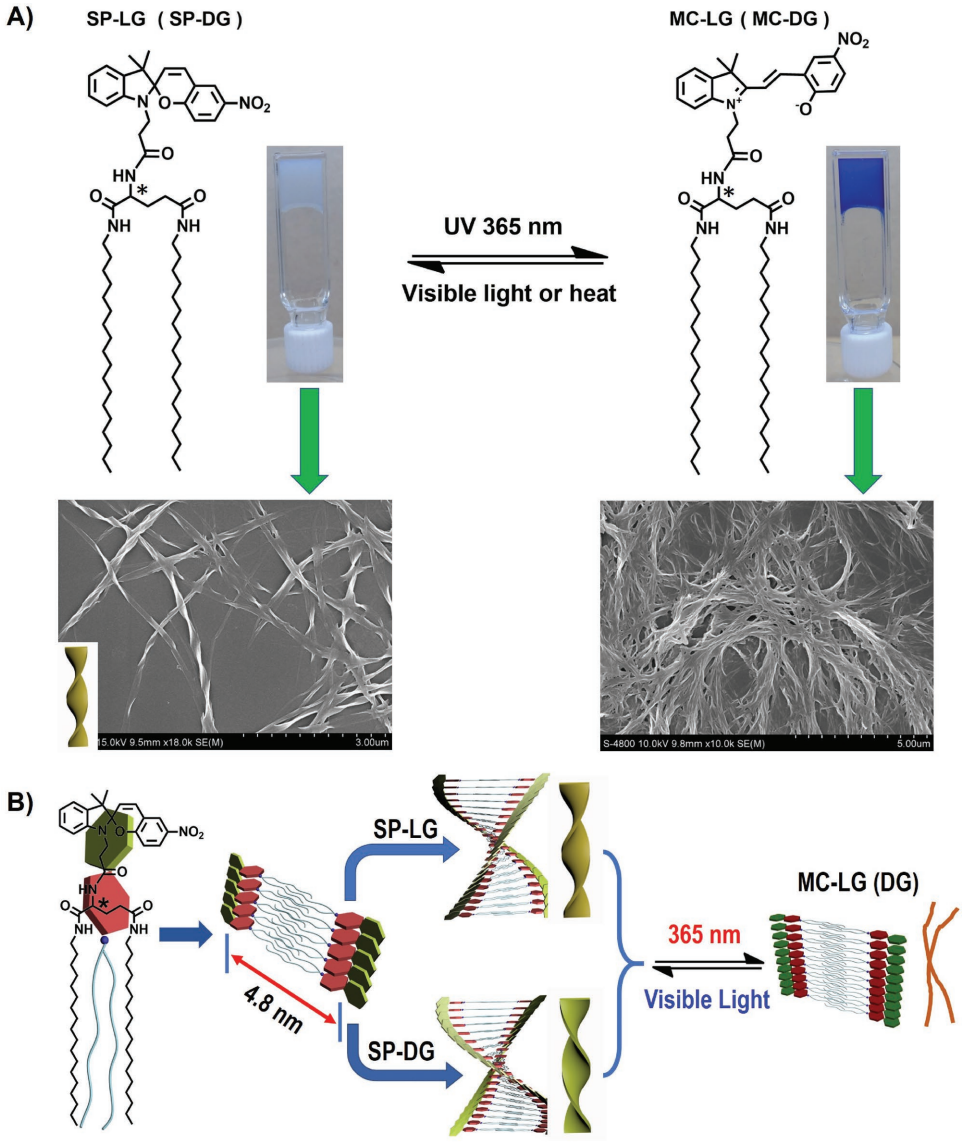

Figure 1. A) Molecular structure of the enantiomeric glutamate derivatives containing spiropyran moiety. And the schematic reversible transformation between a blue zwitterionic MC form and colorless closed ring state in supramolecular gels upon alternating UV and visible light irradiation. The SEM images of SP-LG xerogels before (left) and after (right) UV irradiation. B) The schematic reversible transform from the *P*- and *M*-helices assembled in the SP-LG and SP-DG gels to nanofibers in the MC-LG and MC-DG gels upon alternating UV/vis irradiation.

abbreviated as SP-LG or SP-DG, where L and D refer to the compounds derived from the L- and D-glutamic acid, respectively. Spiropyran and its chemical derivatives are known as the most widely studied photochromic compounds besides the well-known fulgides, diarylethenes, and azobenzenes.[7] The closed form of spiropyran would be transformed into the open (merocyanine, MC) form under UV light irradiation.[8] Back-conversion from the MC form to the spiro mode is accelerated by excitation in the visible band or heating.[9] By attaching the chiral groups covalently to the spiropyran moiety, it is expected that the chiroptical properties can be endowed into the system. However, the phototriggered chiroptical switch based on spiropyran moiety was scarcely presented although the photochromic switches have been reported extensively. Only a few efforts have been contributed for such investigation. For example, Angiolini et al. tried to bond the spiropyran chromophore covalently to a polymer bearing the optically active L-lactic acid in the side chain or to binaphthalene moiety.[10] In such instances, they found that the photoisomerization of the spiropyran group caused changes in the chiral signals, which allowed the system to behave as a chiroptical switch. We reported a co-gel system containing an amphiphilic achiral spiropyran and a chiral gelator, which could be served as a chiroptical logic circuit using UV irradiation and acid stimuli.[11] In order to develop a complete light-driven multichiroptical switches, herein, we designed two enantiomeric spiropyran-conjugated L(D)-glutamate gelators (SP-LG and SP-DG) and investigated their self-assembly as well as the chiroptical properties.

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2. Results and Discussion

2.1. Gel Formation and Reversible Switching of Micromorphology

It was found that both SP-LG and SP-DG could immobilize many kinds of organic solvents in a relative low critical gelation concentration (CGC), as shown in Table S1 (Supporting Information), suggesting the good capacity for the formation of organogels from these compounds. Interestingly, all the gels were found to be photochromic. For example, in ethyl acetate, the off-white supramolecular gels from closed SP-LG or SP-DG compounds were readily responsive to form the blue open merocyanine (MC-LG or MC-DG) upon UV light irradiation (Figure 1A). When the UV light was removed, the open merocyanine structure would recover its original closed spiropyran gradually. In this process, if the additional visible light was employed, the recovery would be accelerated.

Interestingly, the nano/microstructures of SP-LG or SP-DG gels were also reversible by the stimuli from UV and visible light alternately. In ethyl acetate, the SP-LG gels always self-assembled into *P*- helices as shown in Figure 1A. Accordingly, the *M*-helices could always be observed in SP-DG gels (Figure S1, Supporting Information). The similar width and pitch in both enantiomeric gels were ≈300 and 800 nm, respectively. Under UV irradiation, the *P*- or *M*-helices changed into disordered nano fibers without clear expression of helicities. Subsequent irradiation of visible light would recover the original helices. Thus, through irradiation of alternating UV and visible light, a regulation of reversible switch of nano structures was achieved.

In order to understand the packing in the organogels, we have measured the X-ray diffraction (XRD) patterns for the xerogels, as shown in Figure S2 (Supporting Information). In the case of SP-LG xerogels (Figure S2a, Supporting Information), the XRD patterns revealed that three peaks appeared at 2θ values of 1.84°, 3.68°, and 5.52°, respectively. According to Bragg equation $2d\sin\theta = n\lambda$, these three peaks suggested 4.80, 2.40, and 1.60 nm, which corresponded to the 001, 002, and 003 diffractions. Thus, the *d* spacing was about 4.80 nm. This value was larger than the extended length of an SP-LG molecule (3.1 nm from CPK space-filling model), but smaller than twice that of the molecular length. Thus, it was suggested that the SP-LG molecules self-assembled into a bilayer structure with the alkyl chains tilted, while the amide moieties organized into a well-defined arrangement through strong hydrogen-bonding interactions and the aromatic chromophore exhibited π–π stacking. As a result, the gelators formed a bilayer structure as the basic unit and then the multilayered bilayers formed the helices and nanofibers, as shown in Figure 1B.[12] The π–π stacking of aromatic chromophore could be confirmed by the UV–vis spectral measurements, as will be discussed in the following section. For the MC-LG xerogels, which were obtained from SP-LG gels after successive irradiation of UV light (365 nm) for 8 min (Figure S2b, Supporting Information), a peak at 2θ value of 1.84° was observed, which corresponded to a *d* space of 4.80 nm. Although these xerogels showed only one peak, from the structural similarity, it can be suggested that the MC-LG also formed a bilayer as the basic unit. The disappearance of the 002 and 003 peaks suggested that the packing of the MC-LG gel was not as good as that of SP-LG gels. Similar results were obtained from the investigation of SP-DG gels. Based on these observations, we speculated the formation of chiral helices are mainly due to the tetrahedron configuration of closed form from spiropyran, in which two aromatic rings were distorted and not situated in the same plane. In gels, the π–π stacking of above aromatic rings, together with other noncovalent bond interactions, would lead the gelator molecules to distortion easily. As a result, chiral helices were observed. However, after UV irradiation, two aromatic rings of MC forms are located in the same plane due to the large conjugated π-bond interaction. Therefore, the distortion might become weaker. As a result, the gelator molecules self-assembled into nanofibers. The schematic illustration on the formation of the nanohelices was presented in Figure 1B. In addition, the similar mirror-imaged helical structure were also observed in the SP-L(D)G organogels form some other solvents with medium polarity, such as tetrahydrofuran, *n*-butanol, and 1,4-dioxane (Figure S3, Supporting Information). This confirmed the self-assembly mechanism in the gels from these solvents with medium polarity is similar.

2.2. Optical Switch by UV–Vis Absorption

The optical or photochromic properties were investigated by UV–vis spectra. **Figure 2**A showed the UV–vis absorption of both organogel and solution of SP-LG from ethyl acetate before and after UV irradiation of 365 nm. As shown in Figure 2A-a, the colorless SP-LG solution displayed an absorption band at 332 nm before UV irradiation, which was ascribed to the internal charge-transfer transition of the closed spiropyran system.[10] However, in SP-LG organogel, this absorption would take a red shift to 345 nm (Figure 2A-c). This suggested that J- like aggregates were formed in SP-LG organogel, where the chromophores stacked in a head-to-tail way. Following UV irradiation of 365 nm for 8 min, both the SP-LG solution and organogel became blue and accompanied by a remarkable increase of the absorption in the region of 500–650 nm, implying that the closed-ring state SP was photoconverted to the blue MC open form. In the case of SP-LG solution after UV irradiation (Figure 2A-b), the absorption peak appeared around 553 nm, which was attributed to the absorption from the free MC forms.[11] However, upon UV irradiation, the SP-LG organogel exhibited absorption band at 577 nm (Figure 2A-d), which showed a red shift of about 24 nm to that in solution. This also indicated that the π–π stacking of chromophores formed in the organogel.[13] In addition, the intensity of the absorption at 577 nm in the organogel would reach the maximum as the irradiation time exceed 8 min. Thereafter, after removing UV irradiation, the blue gels were exposed to the natural condition, this broad absorption disappeared gradually due to the transformation of MC into the closed SP form as expected. We detected such variation and plotted in Figure 2B. It could be seen that the MC form would change into closed form completely after 2 h. The visible light could accelerate the conversion. From these observations, it could be concluded that the closed form of spiropyran is more stable while the open MC form can be negligible in the natural condition. Thus, in the gels, the open MC-L(D)G obtained upon UV irradiation could be converted to

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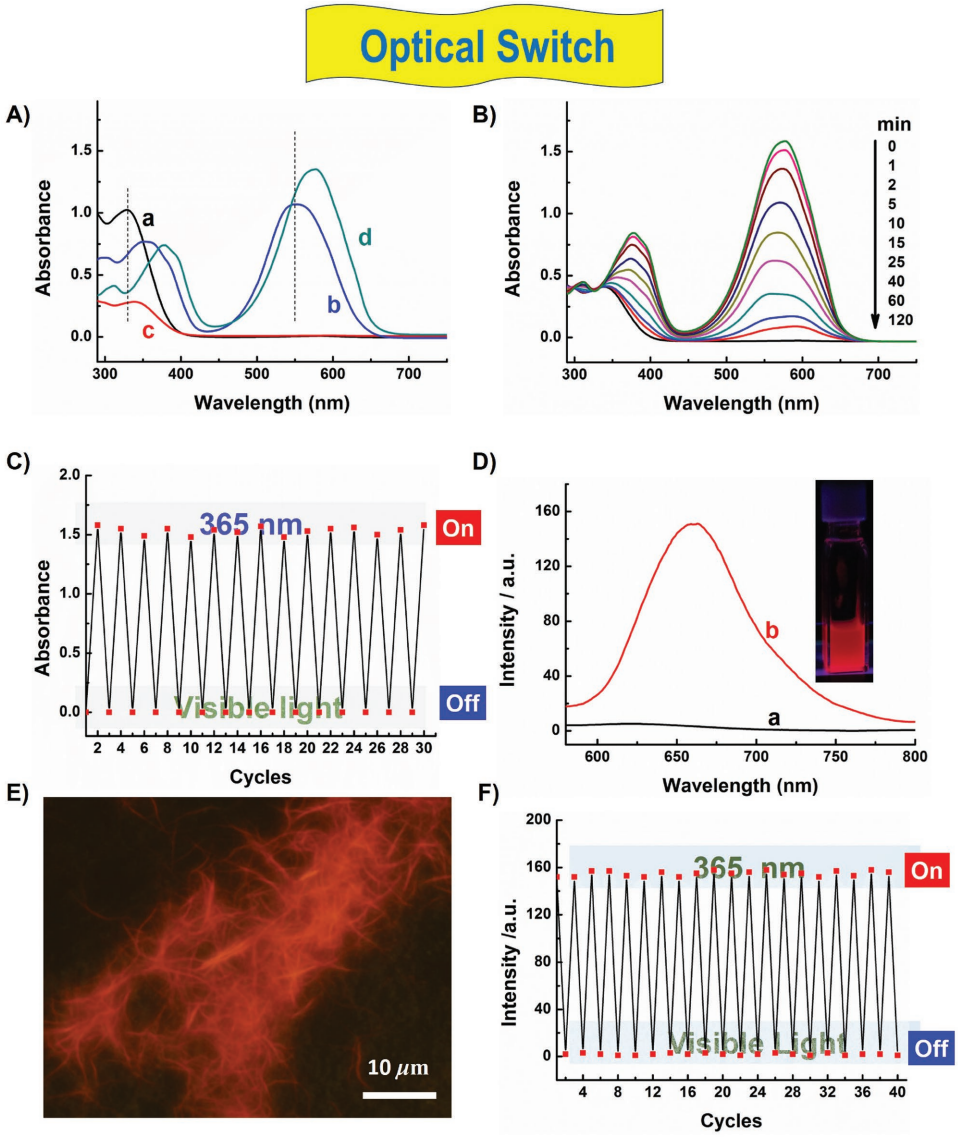

Figure 2. A) Absorption spectra of SP-LG in ethyl acetate solution a) before and b) after UV irradiation and in ethyl acetate organogels c) before and d) after UV irradiation for 8 min. B) Absorption spectra of blue MC-LG gels under the natural condition for a certain time. C) The reversible switch of the absorption intensity of SP-LG gels at 577 nm by alternating UV and visible light irradiation. The reversible cycles could be repeated as many as 50 times. D) Fluorescence spectra of SP-LG gels a) before and b) after UV irradiation for 8 min, the excitation wavelength was 560 nm. The insets showed the photo of SP-LG gels under UV (365 nm) light illumination. E) Confocal laser scanning microscopy (CLSM) images of SP-LG xerogels after irradiation by UV light (365 nm) for 8 min, the excitation wavelength was 560 nm. F) The reversible switch of the fluorescence intensity of SP-LG gels at 662 nm by alternating UV and visible light irradiation.

the closed SP-L(D)G completely. Here, a traditional light-triggered photochromic switch was obtained both in solution and gels. In the case of SP-DG, similar phenomena were observed, which was displayed in Figures S4 and S5 (Supporting Information).

2.3. Optical Switch by Fluorescence

Interestingly, when excited by 560 nm laser light, the closed off-white SP-LG gels showed almost no luminescence as shown in Figure 2D. However, the open blue MC-LG gels, which were obtained from SP-LG gels after UV irradiation (365 nm) for 8 min, emitted strong red light near 662 nm by the same excitation wavelength. Similar phenomena were obtained in the observation of luminescence from its xerogels. After UV irradiation, the xerogel also showed strong red fluorescence as indicated by the confocal laser scanning microscopy (CLSM) image (Figure 2E), where red fibers were observed. Therefore, the strong red fluorescence of MC-LG gels can be switched off by additional visible light irradiation due to the conversion of the MC form into the closed form of SP. In this way, the reversible regulation of fluorescence from supramolecular gels by alternating UV and visible light irradiation was obtained as shown

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in Figure 2F, where the changes of the fluorescence intensity at 662 nm were investigated. As a result, a reversible fluorescence switch was developed by elicitation of alternating UV and visible light. The SP-DG gels and their xerogels showed the same results as SP-LG, which were displayed in Figures S6 and S7 (Supporting Information).

2.4. Chiroptical Switch by CD

The enantiomeric SP-LG and SP-DG gelator molecules have the chiral center localized in the glutamic moiety. While in the molecular state, for example in solution, such localized chirality cannot be transferred to the chromophore. As a result, no CD signal was detected in the absorption region of 250–700 nm. However, this molecular chirality could be transferred to the chromophore of spiropyran as supramolecular chirality upon gelation. **Figure 3**A showed the CD spectra of SP-LG and SP-DG gels from ethyl acetate before and after UV irradiation. Before UV irradiation, a positive signal centered at 410 nm in SP-LG gels was observed due to the self-assembly (Figure 3A-a). In the case of SP-DG gels, the mirror-imaged CD spectrum (Figure 3A-b) could always be obtained. This confirmed that the supramolecular chirality was due to the chirality transfer. Under exposure to UV light, strong CD signals in visible region appeared. As shown in Figure 3A-c, two new positive signals from SP-LG gels appeared at 616 and 661 nm, respectively. Accordingly, the mirror-imaged CD signals exhibited in SP-DG gels (Figure 3A-d). It seemed that the CD band at 662 nm was derived from the UV-absorption. However, to our curiosity, the absorption of the same gels detected in CD measurement was a little different from that of the UV–vis spectra investigation. As shown in Figure S9 (Supporting Information), not a single peak at 577 nm (Figure 2A) but two absorption at 577 and 626 nm occurred when irradiated by UV light. In addition, such phenomena were investigated in all gels from various solvents, such as cyclohexane and DMF in Figures S10 and S11 (Supporting Information). To sum up, the CD detection was always in good accordance with the observation of UV spectra no matter before and after UV irradiation. Moreover, the CD signals from MC-LG and MC-DG gels in the region of 550–750 nm would disappear completely in the natural condition or upon visible light irradiation for a certain time, which further confirmed that the closed form of spiropyran is more stable in the natural condition. Therefore, like the UV absorption and fluorescent emission, the CD signals from SP-LG and SP-DG gels could also be switched as on-off by alternating UV and visible light. Thus, as shown in Figure 3B, the chiroptical switch was obtained.

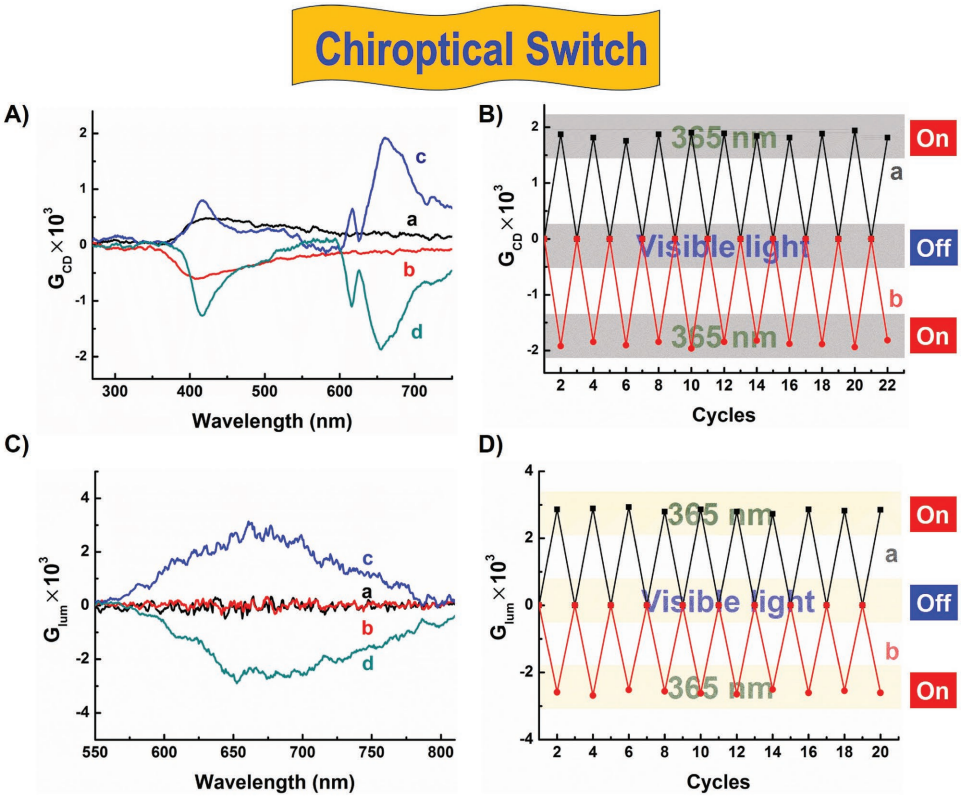

Figure 3. A) CD spectra of a) SP-LG and b) SP-DG gels before UV irradiation and those of c) MC-LG and d) MC-DG gels after UV irradiation for 8 min. B) Corresponding reversible switch of the G value at 662 nm of enantiomeric gels by the stimuli of alternating UV and visible light. C) CPL of a) SP-LG and b) SP-DG gels before UV irradiation and those of c) MC-LG and d) MC-DG gels after UV irradiation for 8 min. D) Corresponding reversible switch of the CPL intensity at 675 nm of enantiomeric gels by the stimuli of alternating UV and visible light irradiation.

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2.5. Chiroptical Switch by CPL

The supramolecular gels having CPL property are attracting current interest.[14] Generally, it is necessary the gel possesses both chirality and luminescence for obtaining CPL gels. Since the solution of these compounds showed no CD signals, they showed no CPL. On the other hand, the closed SP-LG and SP-DG showed no luminescence. Thus, no CPL in gels was detected as shown in Figure 3C-a,b. However, the MC-LG and MC-DG gels obtained from SP-LG and SP-DG gels under exposure to UV light exhibited both CD and fluorescenece, which gave rise to the obvious CPL properties (Figure 3C-c,d). Under irradiation of visible light, such CPL signals disappeared along with the transformation from MC forms to original closed SP modes. Consequently, the chiroptical CPL switches were obtained from the supramolecular gels by alternating UV and visible light, which were illustrated in Figure 3D. Such cycle can also be repeated many times. In addition, both MC-LG and MC-DG gels showed the mirror-CPL.

2.6. Soft Recoding and Rewritable Printing

The reversible process of the gels can be further extended to the soft recoding and rewritable printing by light. The MC form in gels is more stable than that in solution, which facilitates the development of soft materials for information storage. As illustrated in **Figure 4**A, the off-white gel from spiropyran derivatives in quartz cell was covered with a photomask containing the characters "GEL" and these characters became apparent after exposure to UV light for 2 min. This pattern is relatively stable and could be exhibited for ≈2 h in the natural condition as above-mentioned. To erase the written data and regenerate the original gel state rapidly, the gels should be either illuminated by visible light for 5 min or heated at 50 °C for 3 min.

Moreover, it was found that the xerogels on a glass (15×20 cm^2) could also be rewritten by letters and all kinds of patterns upon UV light irradiation for 8 min through a photomask, which was preproduced by ink-jet printing on a plastic transparency, as shown in Figure 4B. Such written patterns on xerogels were much more stable than those on gels, which could be investigated even for four days under the natural condition. To erase the written data, the written patterns should be exposed to visible light over 40 min, which was much longer than that for gels. Or else, the prints could be erased completely at 80 °C for 30 min. In addition, such rewritable material can be efficiently printed over 30 cycles without significant loss in contrast and resolution using ultraviolet and visible light.

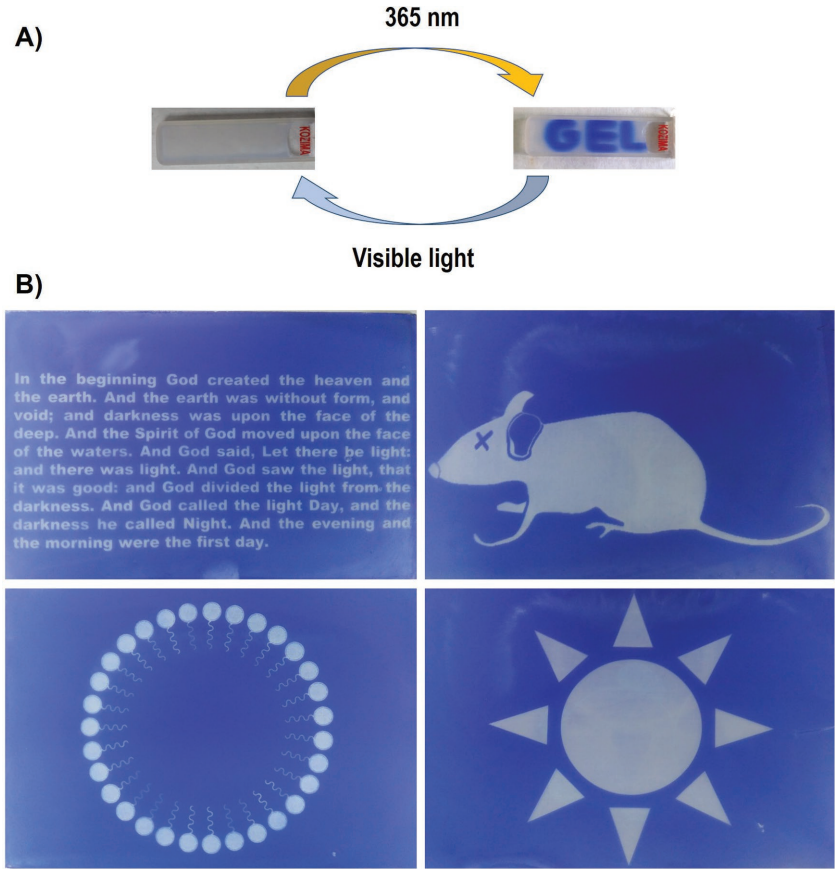

Figure 4. A) Illustration of the recording of "GEL" characters on SP-LG gels by exposure to UV light (365 nm) for 2 min, and erasing the recorded pattern by exposure to the natural condition for 2 h or under the irradiation of visible light for 5 min. B) The printing letters and complex patterns from the rewritable SP-LG xerogels on a glass (15×20 cm^2) using photomask upon UV light irradiation. The quotation in panel (B) is from the Bible.

3. Conclusion

We designed and prepared two enantiomeric super glutamate gelators containing spiropyran moiety. It was found that these two enantiomeric gelators could immobilize all tested solvent. Moreover, by the stimuli of alternating UV and visible light, the UV–vis absorption, fluorescence, CD signal, and CPL of the enantiomeric supramolecular gels exhibited on–off properties. Therefore, a reversible quadruple optical and chiroptical switch was developed successfully. During such process, the self-assembled nanostructures from the enantiomeric supramolecular gels also underwent a reversible change between helices and fibers under the alternating UV and visible light trigger. Furthermore, a rewritable material fabricated from their xerogels on a glass was developed. Such rewritable material can be efficiently printed over 30 cycles without significant loss in contrast and resolution using ultraviolet and visible light.

4. Experimental Section

Materials: All starting materials were obtained from commercial suppliers and used as received. The solvents used were dried and

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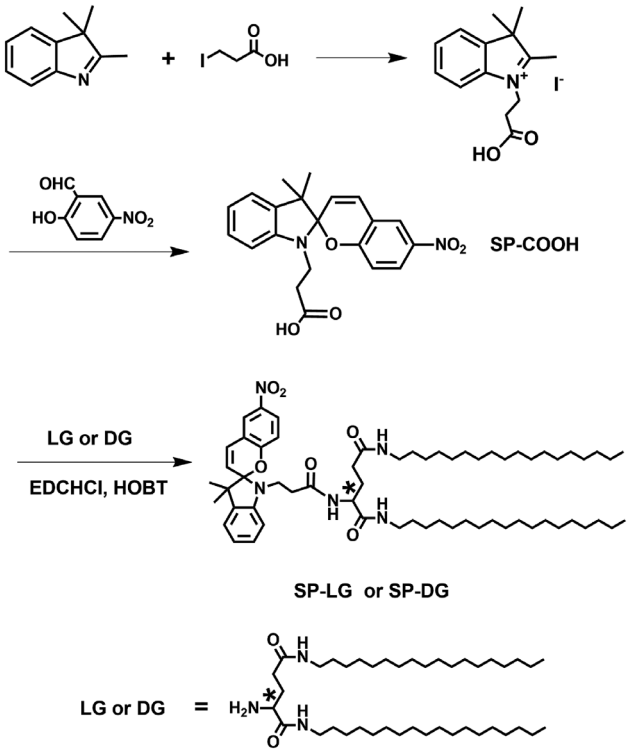

Scheme 1. Synthetic route for enantiomeric SP-LG and SP-DG gelator molecules.

purified by standard methods prior to use. ^{1}H NMR spectra were obtained on an ARX400 (Bruker) NMR spectrometer in DMSO-d_6 or $CDCl_3$ with TMS as an internal standard. MS spectra were determined with BEFLEX III for MALDI-TOF mass spectrometer. Elemental analyses were performed on a Carlo-Erba-1106 instrument. The synthetic route for SP-LG and SP-DG was exhibited in **Scheme 1** as following.

Synthesis of Carboxyl-Containing Spiropyran (SP-COOH): The synthetic method was modified from previous report.[15] The main procedures were as follows: All the reactions should be performed in the dark. 3.18 g of 2,3,3-trimethylindolenine (20 mmol) and 4.0 g of 3-iodopropanoic acid (20 mmol) were mixed in a sealed round bottom flask. Then, the reaction mixture was stirred vigorously under nitrogen at the temperature of 85 °C for 2 h. After cooling to room temperature, the residue was dissolved in 500 mL of water and washed with chloroform (3 × 100 mL). The organic layer was removed, while the aqueous phase was evaporated to give 5.4 g of pure l-(*b*-carboxyethyl)-2,3,3-trimethylindolenine iodide (yield: 75%), which was not further purified for next step.

3.6 g of l-(*b*-carboxyethyl)-2,3,3-trimethylindolenine iodide (10 mmol), 1.67 g of 5-nitrosalicylaldehyde (10 mmol), and 1 mL of piperidine were dissolved in 50 mL of 2-butanone and then heated to reflux under nitrogen for 4 h. After cooling to room temperature, the yellowish crude product was filtered, dried under vacuum, and then recrystallized from acetone (2 × 100 mL) to harvest 2.67 g of pure SP-COOH (yield: 70%). mp: 206 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 1.08 (s, 3H), 1.19 (s, 3H), 2.45–2.55 (m, 2H), 3.45–3.55 (m, 2H), 5.95 (d, J = 10.4 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 7.11–7.15 (m, 2H), 7.20–7.23 (d, J = 10.4 Hz, 2H), 7.99–8.02 (m, 1H), 8.22 (d, J = 2.8 Hz, 2H), 12.2 (s, 1H). Anal. calcd for $C_{21}H_{20}N_2O_5$: C 66.31, H 5.30, N 7.36; found: C 66.52, H 5.35, N 7.32.

Synthesis of Target Compound SP-LG: 0.38 g of SP-COOH (1 mmol) and 0.65 g of *N*,*N*′-Bisoctadecyl-L-aminoglutamicdiamide (LG), which were synthesized according to our previous works,[16] were dissolved in 150 mL of dichloromethane. Then, 0.29 g of 1-ethyl-3-(3-dimethyllaminopropyl)carbodiimide hydrochloride (EDC·HCl, 1.5 mmol) and 0.20 g of 1-hydroxybenzotrizole (HOBT, 1.5 mmol) were added. The mixture was stirred at room temperature for 72 h. After removal of the solvents, the remained substance was dissolved in 100 mL of tetrahydrofuran and then poured into the 1000 mL of 0.5% Na_2CO_3 aqueous solution. The solid was collected by filtration, dried in vacuum, and then recrystallized from the mixed solvent of CH_2Cl_2 and EtOH (1:4, v/v, 3 × 100 mL) to afford 0.86 g of pure purplish product, SP-LG (yield: 85%). mp: 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.90 (t, J = 6.0 Hz, 6H), 1.15–1.38 (m, 66H), 1.42–1.50 (m, 4H), 1.87–2.00 (m, 2H), 2.17–2.36 (m, 2H), 2.45–2.59 (m, 2H), 3.11–3.20 (m, 4H), 3.51–3.69 (m, 2H), 4.25–4.29 (t, J = 6.8 Hz, 1H), 5.95 (m, 2H), 6.68–6.72 (t, J = 6.8 Hz, 1H), 6.77–6.80 (m, 1H), 6.85–6.95 (m, 2H), 7.09 (d, J = 6.8 Hz, 1H), 7.18–7.22 (m, 2H), 8.01–8.04 (m, 2H). MALDI-TOF-MS: calcd for $C_{62}H_{101}N_5O_6$: 1012.5. Found: 1034.9 [M^+ + Na]. Anal. calcd for $C_{62}H_{101}N_5O_6$: C 73.55, H 10.05, N 6.92; found: C 73.45, H 10.16, N 7.07.

Synthesis of Target Compound SP-DG: 0.38 g of SP-COOH (1 mmol) and 0.65 g of *N*,*N*′-Bisoctadecyl-D-aminoglutamicdiamide (DG) were dissolved in 150 mL of dichloromethane. Then, 0.29 g of EDC·HCl (1.5 mmol) and 0.20 g of HOBT (1.5 mmol) were added. The mixture was stirred at room temperature for 72 h. After removal of the solvents, the remaining substance was dissolved in 100 mL of tetrahydrofuran and then poured into the 1000 mL of 0.5% Na_2CO_3 aqueous solution. The solid was collected by filtration, dried in vacuum, an then recrystallized from the mixed solvent of CH_2Cl_2 and EtOH (1:4, v/v, 3 × 100 mL) to afford 0.77 g of pure purplish product, SP-DG (yield: 76%). mp: 116–117 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.90 (t, J = 6.0 Hz, 6H), 1.15–1.38 (m, 66H), 1.42–1.50 (m, 4H), 1.87–2.00 (m, 2H), 2.17–2.36 (m, 2H), 2.45–2.59 (m, 2H), 3.11–3.20 (m, 4H), 3.51–3.69 (m, 2H), 4.25–4.29 (t, J = 6.8 Hz, 1H), 5.95 (m, 2H), 6.68–6.72 (t, J = 6.8 Hz, 1H), 6.77–6.80 (m, 1H), 6.85–6.95 (m, 2H), 7.09 (d, J = 6.8 Hz, 1H), 7.18–7.22 (m, 2H), 8.01–8.04 (m, 2H). MALDI-TOF-MS: calcd for $C_{62}H_{101}N_5O_6$: 1012.5. Found: 1034.9 [M^+ + Na]. Anal. calcd for $C_{62}H_{101}N_5O_6$: C 73.55, H 10.05, N 6.92; found: C 73.29, H 10.02, N 7.15.

Gel Formation: The preparation of supramolecular gels was under ambient temperature and visible light conditions (λ > 500 nm). A weighed sample of SP-LG or SP-DG gelator was mixed with a solvent (1 mL) in a septum-capped vial and heated until the solid was dissolved. Then the sample vial was cooled to room temperature. If no flow was observed when inverting the vial, a stable gel was formed. The CGC of the gelators was determined by measuring the minimum amount of gelator required for the formation of a stable gel at room temperature. For the experimental measurement of all kinds of optical properties, the gels containing 4 mg of SP-LG or SP-DG from ethyl acetate were employed all the while. The obtained supramolecular gels from SP-LG or SP-DG gelators are off-white, which would become blue after irradiation with UV light (365 nm) for 8 min. The light source used for the UV-induced opening process (SP→ MC) was UV lamp (λ = 365 nm, 40 W) and the distance of UV source–sample used in the irradiation experiments was 10 cm with a light intensity of 280 mW cm^{-2} in the dark. Natural condition (ambient temperature and visible light conditions) or a visible lamp with intensity of 520 mW cm^{-2} was employed for the recovery of the gels. After exposure to natural environment for 2 h or irradiation with visible light for 5 min, the blue gels faded to original off-white color.

Characterization: The supramolecular gels of SP-LG and SP-DG compounds were cast onto single-crystal silica plates, the solvent was evaporated under the ambient conditions and visible light, and then vacuum-dried, while the silica plates fabricated with MC-LG and MC-DG gels were dried under UV irradiation all the while. The sample surface was coated with Pt, which were recorded on a Hitachi S-4800 FE-SEM microscope, operating at accelerating voltages of 10 kV. Glass-sustained xerogel films were used for XRD measurements on a Rigaku D/Max-2500 X-ray diffractometer (Japan) with CuKa radiation (λ = 1.5406 Å), which was operated at 45 kV, 100 mA. UV and CD spectra were obtained on JASCO UV-550 and JASCO J-810 CD spectrophotometers, respectively. The CLSM system, FV-1000-IX81 Olympus (Japan), was employed. Fluorescence spectra were measured with a Hitachi F-4500 spectrophotometer. CPL measurements were performed with a JASCO CPL-200 spectrometer.

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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

chiroptical switches, helices, optical switches, rewritable materials, supramolecular chirality

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