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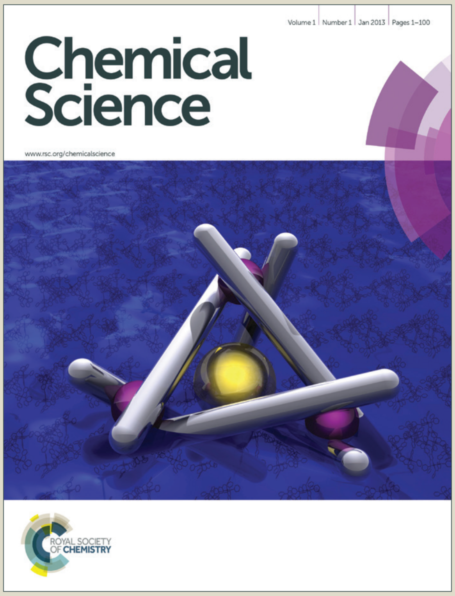

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ARTICLE TYPE

Photoisomerization-Induced Gel-to-Sol Transition and Concomitant Fluorescence Switching in a Transparent Supramolecular Gel of Cyanostilbene Derivative

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We report a transparent and fluorescent gel by using a cyanostilbene-containing aggregation-induced enhanced emission (AIEE) material (compound **1**) which incorporates bulky and flexible spacers via amide group. The photoinduced morphological change (gel-to-sol) upon the photoisomerization of **1** was successfully demonstrated, which accompanied the fluorescence color switching from its aggregate emission (490 nm) to the monomer emission (465 nm). It is to be noted that our innovative system is to induce both the gel-to-sol transition and the fluorescence color driven by the photoisomerization of the cyanostilbene moiety.

Introduction

Stimuli-responsive supramolecular materials have received a great deal of attention due to their fundamental interests and practical applications in which their physical properties or functions are controlled by various stimuli such as temperature, light, pH, mechanical force, chemicals, and electric field.[1] Among them, azobenzene materials have been widely and intensively explored because of their utilities as photo-responsive materials for surface relief grating (SRG), optical data storage and resonance filters, and optical switches.[2] Recently, much attention has been focused on the photomechanical effect of the azobenzene in supramolecular system like gel, liquid crystal, polymer, and nanostructures (nanoparticle, nanovesicle, and nano/microwire), thereby controlling morphology (gel-to-sol and LC-to-isotropic), size (expansion and shrinking) and shape (curling, bending and stretching).[3] Such photomechanical effects are usually rationalized to originate from reversible trans-cis photoisomerization of the azobenzene unit. For some cases, the molecular environment providing a sufficient space for photoisomerization is necessary to allow the switching event to take place. For other cases, the interaction of the azobenzene with polarized light is also essential to induce anisotropic molecular orientation. Among the azobenzene-containing supramolecular gels, the photoinduced morphological transition from gel to sol state was successfully demonstrated in some specific examples that could offer appropriate local space to facilitate the photoisomerization of the azobenzene unit, in spite of the large steric hindrance in 3-dimensional networks of the gel state constructed by noncovalent secondary interactions like π-π interaction of azobenzene unit, hydrogen bonding, electrostatic, van der Waals interaction etc.[3a-g] However, it still remains a challenge to demonstrate a photoisomerization-induced morphological change with concomitant fluorescence switching, which must be achieved with fluorescent photoisomerizable materials like stilbene and cyanostilbene derivatives. In fact, those candidate materials are well known to intrinsically have attractive dual functions of fluorescence and photoisomerization whereas the azobenzene materials are commonly non-fluorescent. Thus, it is highly demanded to investigate a photomechanical effect in stilbene and cyanostilbene-based organogel. To this end, only one paper has been reported, very recently, for stilbene-containing gel, which described photoinduced gel-to-sol transition but with rather trivial modulation in fluorescence color simply reducing the fluorescence intensity by about one-third.[4] On the other hand, cyanostilbene-type gels still remain unexplored to date.[5]

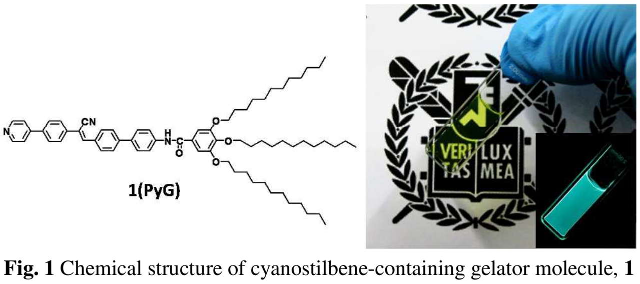

Fig. 1 Chemical structure of cyanostilbene-containing gelator molecule, **1** (PyG) and photo image of its transparent gel in cyclohexane (1 wt%) under room light. Inset shows the fluorescence photo image of the gel under UV light.

So far, we have reported highly fluorescent supramolecular self-assembly system forming various types of nanostructures (nanoparticles, nanowires, nanofabrics, 3D organogel networks and coaxial nanocables) that were directed by a precise control of intermolecular interaction in a cyanostilbene scaffold.[6] Most peculiarly, the elastic twist characteristic of cyanostilbene-based backbone was associated with a unique aggregation-induced enhanced emission (AIEE) behavior; it is virtually non-fluorescent in the monomer state in solution but becomes highly fluorescent upon self-assembly into supramolecular aggregates.[6c] Moreover, we have recently elucidated the photoisomerization behavior of AIEE type molecule in solution and in solid state which surprisingly accompanied fluorescence on/off switching.[7] In addition, we could fabricate a highly fluorescent SRG of the liquid crystalline cyanostilbene derivative, which is based on the crystallization-induced mass flow via photo-triggered phase transition.[8] Therefore, these new findings motivated us to exploit the photomechanical feature of the fluorescent AIEE supramolecular gels or nanostructures. However, most of our fluorescent AIEE gels reported earlier were highly crystalline and non-transparent due to a tight and close packing of AIEE molecules, which practically hampered photoisomerization process.[6b,c,g,h] In this work, we report a transparent and fluorescent gel by using newly designed cyanostilbene-containing AIEE compound **1** with bulky and flexible spacers via amide group (see Fig. 1), which successfully demonstrates its photoinduced morphological change (gel-to-sol) upon the photoisomerization, accompanying a unique fluorescence color switching (greenish blue-to-blue).

Results and discussion

Fig. 1 depicts the molecular structure of compound **1** and its formation of the transparent organogel in cyclohexane (1 wt%). T_{gel} of the gel is determined to be ~61 ^{o}C by the ball dropping method. The formed gel shows yellow color to the naked eye with excellent optical transparency and a strong greenish blue AIEE fluorescence (*vide infra*). Such a transparent feature without scattering is quite different from the conventional AIEE crystalline gel previously reported.[6b,c,g,h] We presumed it must be closely related to the morphology of the self-assembled gel. As shown in Fig. 2, the SEM image of the dried gel appears much like the amorphous-like surface at the micrometer level.[6f,9] However, the more magnified image (inset in Fig. 2a) shows the wrinkled matrix morphology that is composed of the nanowire bundles with ultra-fine structures at the nanometer level (See AFM image in Fig. 2b)~~.~~In the XRD pattern, unlike the sharp and strong peaks as usually shown in crystalline structures, a broad and weak peak is observed, corresponding to the d-spacing of 42.42 Å in the small angle region. (See Fig. 3a) This spacing is consistent with the molecular length of compound **1**. In the wide angle region, the relatively strong diffraction centered at $2\theta = \sim 20$ °, corresponding to the d-spacing of 4.5 Å, is observed with a halo diffraction. This is typically attributed to the intermolecular hydrogen bonds between amide moieties in the self-assembled gel.[10] Taken all together, the transparent gel characteristics is mainly attributed to the amorphous-like nano-sized hierarchical structure of the self-assembled gel. To have all these experimental results consistent and acceptable, we propose the schematic arrangement of one-dimensional self-assembly of compound **1** in the gel state; compound **1** is interconnected via hydrogen bonding between amide groups at the center along the fiber axis, whereas the peripheral rigid cyanostilbene aromatics and flexible alkyl chains are randomly located in a hierarchical arrangement while being tethered to amide at the center. (See schematic illustration in Fig. 4). Such geometry may induce weak interaction between those rigid cyanostilbene aromatics in aggregates. That is, this organization is considered to be far from the perfect crystalline orientation with strong π-π interaction which has been commonly shown in highly crystalline 1D nanowire of the conventional AIEE molecules based on rigid aromatic backbone without flexible alkyl chains.[6b,c,g,h] Thus, this proposed arrangement would be anticipated to offer local free space in the gel networks and facilitate their photoisomerization process.

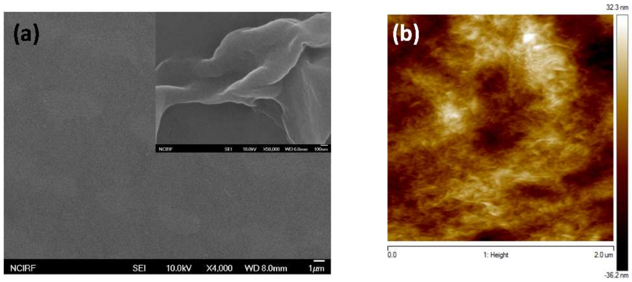

Fig. 2 (a) SEM image of the dried gel (from 1 wt% in cyclohexane) with its magnified image (inset), and (b) its AFM image.

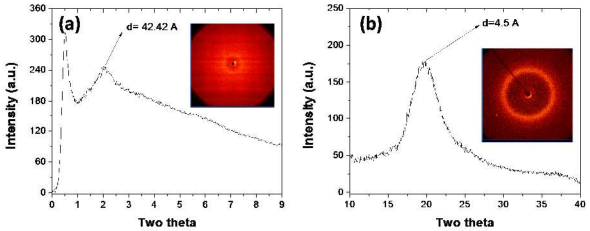

Fig. 3 (a) Small-angle X-ray diffraction pattern and (b) wide-angle X-ray diffraction pattern of the dried gel (from 1 wt% in cyclohexane) with their oriented pattern images, respectively (inset).

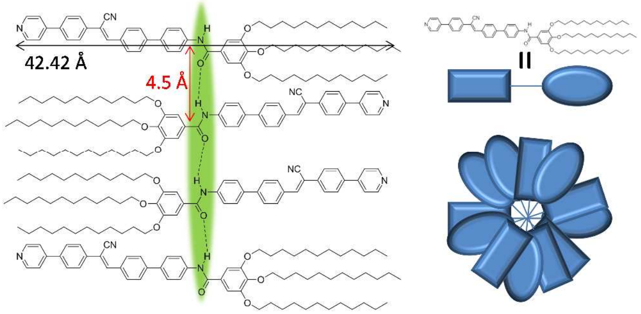

Fig. 4 Proposed schematic representation of the molecular arrangement in the gel.

To get more insight into photoinduced trans-cis isomerization, we have studied the evolution of UV-Vis absorption spectra of pure **1**-trans and **1**-cis isomers in solution as a function of UV light irradiation time. Pure **1**-cis is obtained by purification using the column chromatography from the photostationary-state mixtures after UV light irradiation of **1**-trans. (See details in Supplementary Information) As shown in Fig. 5, the absorption maximum of the pure **1**-trans is observed at 363 nm while that of the pure **1**-cis is distinctively shifted to the blue by 15 nm. This optical behavior is consistent with the results of the density functional theory (DFT) computational studies of trans and cis isomers of **1**. (See Fig. S1 and S2) Due to the bent configuration, the conjugation length of **1**-cis is smaller than that of **1**-trans, resulting in a blue-shifted absorption band. For both isomers, however, most of the electron populations in HOMO are well distributed at amine-substituted biphenyl while those in LUMO are crowded at near electron-accepting cyanostilbene moiety. Thus, it caused a small spectral difference in absorption maximum between those isomers despite the bent configuration of **1**-cis. Solution of each isomer was exposed to UV light using 365 nm-handheld UV lamp (~1 mW•cm^{-2}) to monitor the evolution of absorption bands along with the photoisomerization process. For **1**-trans, the main absorption band at 363 nm decreased gradually with illumination time while the short-wavelength band centered at 270 nm increased with one isosbestic point at 335 nm. For **1**-cis, just the opposite change was observed to give the same photostationary state (PSS) spectrum as **1**-trans, after sufficiently prolonged irradiation time. At the PSS, the ratio of the trans to cis isomers were estimated to be 1 : 1.5 (See Fig. S3 in Supplementary Information), thus indicating that the trans-cis photoisomerization of the cyanostilbene is well-defined and well-operating similar to that of pseudo-stilbene derivatives.[7,8,11] Although **1**-trans in solution emits a blue fluorescence at 463 nm, it is very weak and virtually non-fluorescent to the naked eye as its photoluminescence quantum yield (PLQY) is very low (0.003). (See Fig. 5b) **1**-Cis is even less fluorescent than **1**-trans in solution as shown in Fig. 5b. On the other hand, **1**-trans in the powder state is highly fluorescent revealing its AIEE behavior, while **1**-cis is non-fluorescent in the powder state as well (see Fig. 5c). Upon UV irradiation on **1**-cis powder, however, it starts to fluoresce. Quite interestingly, it is gradually enhanced to exhibit a bluish green color characteristic of the emission color of the **1**-trans powder. This is attributed to the cis-to-trans photoisomerization at the surface of **1**-cis powder, as was similarly observed in other AIEE compound.[7] As shown in Fig. S4 in supplementary information, the blue emission of non-aggregated **1**-trans is found at 469 nm (absolute PLQY = 0.065) in low concentration (2 wt%)-doped PMMA film (as solid solution), whereas the bluish green emission of aggregated **1**-trans is found at 500 nm (Absolute PLQY = 0.270) in high concentration (23.3 wt%)-doped PMMA film. Thus, it is reasonable that the generated bluish green emission in Fig. 5c can be assigned as the aggregate emission of **1**-trans. This assignment is consistently supported by the observation of 496 nm fluorescence of the **1**-trans nanoparticle (in THF : H_2O = 20 : 80).[12] (See Fig. S5 and Table S1 in supplementary information)

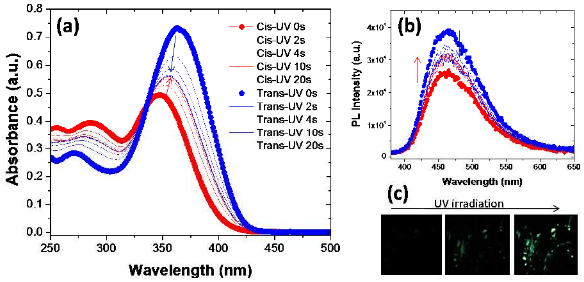

Fig. 5 (a) UV-visible absorption spectrum changes of **1**-trans and **1**-cis in chloroform (2×10^{-5} mol·L^{-1}) by increasing the illumination time of 365 nm light, respectively. Blue-line is trans-isomer (circle: initial) and red-line is cis-isomer (circle: initial). The arrow indicates the irradiation time increases from 0 to 20 Sec. (b) their corresponding emission spectra in the same condition (excited at each absorption maxima), and (c) the fluorescence photo image of the **1**-cis in powder as the UV light irradiation time increases.

To investigate the photoresponsive effect of the gel, the cyclohexane gel (0.25 wt%) of **1**-trans was irradiated with a blue LED (emission wavelength = 460 (±10) nm, power = ~10 mW). As shown in Fig. 6a, the aggregates in the gel state can absorb a considerable light at 460 nm, contrary to the solution state absorption (see Fig. 5a). Upon the light irradiation, the collapse of the gel began in 5 min. The gel was totally changed into the viscous sol state within ~15 min. Correspondingly, yellow color of the gel became colorless in the sol since the absorption band is significantly blue shifted. (See Fig. 6a, inset) Similarly, the emission is shifted to the blue as the irradiation time increases. (See Fig. S6) As a result of the light irradiation, therefore, it is unambiguous that the photoinduced gel-to-sol transition occurred successfully in cyanostilbene-containing materials. The main driving force for this morphological change is attributed to the trans-cis photoisomerization of the cyanostilbene moiety in the gel networks. This is additionally evidenced by monitoring the MALDI-TOF and the ^{1}H NMR spectroscopy (See Fig. S7 and S8 in supplementary information) that provided clear insights into the photoisomerization. The MALDI-TOF results of compound **1** before and after irradiation were identical with the same molecular weight, implying a formation of the photoisomers without any other photoproducts like [2+2] photodimer.[13] From the results of the ^{1}H NMR spectroscopy in Fig. S8 (Blue LED irradiation for 5 and 15 min), the two specific protons centered at ~8.70 and 7.05 ppm are generated in the cis form as being distinguished from those of the trans form, corresponding to H_a (from pyridine ring) and H_b (from tridodecyloxy-substitued benzene), respectively. From those peaks in partial ^{1}H NMR, the ratio of the trans to the cis isomers could be determined as a function of the light irradiation time. As the irradiation time increases, it was found that the trans form decreases whereas the cis form increases up to 84%. When the blue light (for 15 min) was used, the ratio of the trans to the cis in gel was 1 : 5.25 which is much smaller than that (1 : 1.5) in solution state under UV light irradiation. It should be importantly noted that the gel-to-sol transition did not happen by shining UV light even for several hours, while it proceeded rapidly with 460 nm blue LED. Since the spectral separation in the absorption band of the trans in the gel aggregate and of the cis in the sol state is so large as shown in Fig. 6a and Fig. 5a, respectively, 465 nm blue light irradiation is exclusively absorbed by the trans isomer giving rise to the higher trans-to-cis conversion ratio which efficiently triggers gel-to-sol transition.

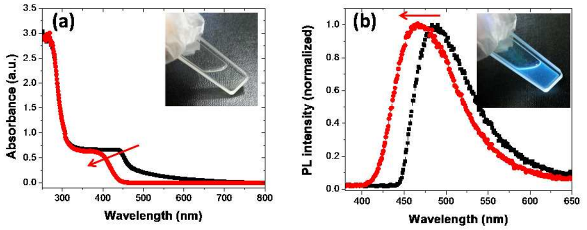

Fig. 6 (a) UV-visible absorption spectra and (b) emission spectra of the gel (0.25 wt%) in cyclohexane before (black) and after (red) the blue light irradiation. Each inset shows the photo image of the sol state after the 465 nm light irradiation under room light (left) and UV light (right), respectively. The corresponding photo images of the gel state were shown in Fig. 1.

Fig. 6b shows the fluorescence change of the gel after the light irradiation. The bluish green emission of the gel at 490 nm is switched into the blue emission of the sol at 463 nm. As discussed above, the gel emission at 490 nm can be assigned as the aggregate emission of the **1**-trans. In contrast, the sol emission at 463 nm is similar to the monomer emission (at 463 in solution and at 469 nm in solid solution) of the **1**-trans. It is noted that the 1-trans (0.25 wt% in cychlohexane) in both the gel and sol states is at higher concentration state (~1.9 x 10^{-3} M), which is a different environment from the dilute chloroform solution state (~2 x 10^{-5} M, 0.0026 wt%), giving rise to a different AIEE behavior. The time-resolved fluorescence indicated that the average fluorescence lifetime became distinctively longer in gel state (τ_{avg}=4.29 ns) than that in sol state (τ_{avg}=1.16 ns). (See Fig. 7a) The fluorescence lifetimes are determined by three component exponential fitting as follows; τ_1=0.33 (55.49), τ_2=2.64 (28.91) and τ_3=6.31 ns (15.61%) for the gel. These multiple decay components were similar to those in high concentration-doped PMMA film, implying that various molecular environments are present upon aggregation. (See Table S1) In contrast, it was shown that a long decay component decreases profoundly in sol state (from the fitting results, τ_1=0.43 (61.48), τ_2=1.32 (37.71) and τ_3=4.42 ns (0.81%)), upon disintegration of the gel aggregates. As a result of the light irradiation, the **1**-trans aggregates organized in the gel began to isomerize into the **1**-cis, thereby perturbing the proposed organization and inducing a disruption of the gel. As indicated by NMR study, 16% of trans and 84% of cis molecules are present in the viscous sol state after prolonged 465 nm irradiation. After all, those remaining 1-trans caused a blue fluorescence at 463 nm as monomer emission in the sol state because the **1**-cis was found to be non-fluorescent as explained earlier. It is noted again that the photoinduced gel-to-sol transition in a cyanostilbene-containing gel was demonstrated, accompanying the fluorescence color switching from the aggregate emission (490 nm) to the monomer emission (465 nm) of **1**-trans. The absolute fluorescence quantum yield of gel and sol state corresponds to be 0.12 and 0.10, respectively. As a result, our innovative system is to induce both the gel-to-sol transition and the fluorescence color driven by the photoisomerization of the cyanostilbene moiety Based on such perspective, we were prompted to explore its potential application to the fluorescence photopatterning.

The negative-photomasked 465 nm irradiation experiment was performed in the gel state as shown in Fig. 7b. The emblem of our university was readily inscribed into the gel. In the irradiated region, yellow color became colorless at room light. At the same time, a bluish green fluorescence was also switched into a blue fluorescence. (See the photo image under the UV light excitation in Fig. 7b, right) In a similar manner, the fluorescent photopattern could be simply recorded in PMMA film doped with high concentration of the compound **1**, exhibiting an apparent dual emission color (See Fig. 7c).

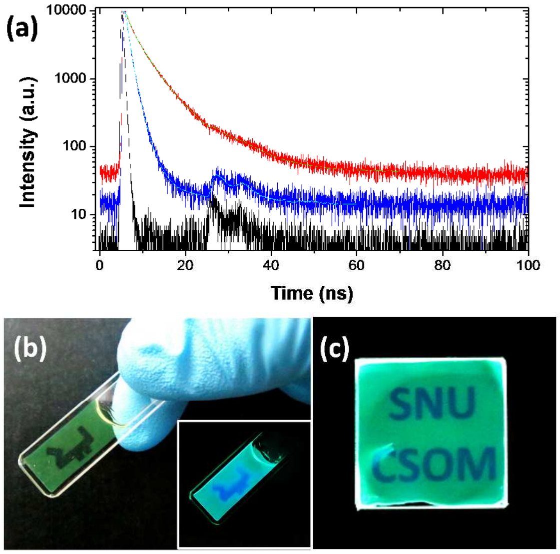

Fig. 7 (a) Fluorescence kinetic profiles of the gel state (red line) and the sol state (blue line) (prepared from Fig. 6) with the IRF (instrument response function) (black line). The sample was excited at 377 nm and monitored at 490 nm and 463 nm for the gel and the sol, respectively. The lines (green and sky blue color) are convoluted fits for the profiles. (b) Photograph of a photopatterning image in the gel state with the specific emblem, under room light. Its fluorescence image was shown in inset. (c) Fluorescence image of the photopatterned thin film of compound **1** (23.3 wt%) in PMMA.

Conclusions

In conclusion, we have prepared a transparent and fluorescent gel bearing a cyanostilbene moiety. We successfully demonstrated the photoinduced gel-to-sol transition in our fluorescent gel upon 465 nm-light irradiation. In addition, this transition accompanied the concomitant fluorescence color switching between the aggregates and monomer of **1**-trans. This innovative approach on the principle of the photoinduced isomerization in cyanostilbene-based materials can be useful for developing a facile fabrication of the fluorescence photopatterning, which has great potential in practical applications. Furthermore, this work is believed to open the door to new class of smart materials with dual response of mechanical and fluorescent modulation at the same time triggered by the photoisomerization.

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† Electronic Supplementary Information (ESI) available: Details of experimental for synthesis and measurements, and additional supplementary data (Fig. S1-S8, Scheme S1 and Table S1). See DOI: 10.1039/b000000x/

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12. Its emission in nanoparticle was enhanced from the THF solution by approximately 11.5 times which is not high as compared with those (>100 times) reported in crystalline AIEE molecules based on tight and rigid molecular packing. It implies that less ordered structure upon aggregation was formed probably due to the peripheral flexible alkyl chains, like the gel state.

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