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Fluorescence Regulating and Photoresponsivity in AIEE Supramolecular Gels Based on a Cyanostilbene Modified Benzene-1,3,5-tricarboxamide Derivative

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Abstract: Supramolecular interactions play an important role in regulating the optical properties of molecular materials. Different arrangements for identical molecule afford a more straightforward insight into the contributions of supramolecular interactions. Herein, a novel gelator, BTTPA, composed of a benzene-1,3,5tricarboxamide (BTA) central unit functionalized by three cyanostilbenes is designed, which forms two kinds of gels in DMSO/water mixtures. Depending on the water volume content, the gels exhibit quite different aggregation-induced emission enhancement (AIEE) properties with one emitting a green emission (G-gel), while the other emits a blue emission (B-gel). The main reason for this observation is that water affects H-bonding and $\pi\text{-}\pi$ interactions, further resulting in disparate packing modes of gelators. In addition, only G-gel displays gel-to-sol transition accompanied with fluorescence switching according to the trans-cis photoisomerization of cyanostilbene under UV light irradiation. B-gel fails to exhibit any gain due to its tight hexagonal packing arrangement. Such packing modes restricted the space in which molecules were located and inhibited the configuration transformation of cyanostilbene. These phenomena underline the incomparable status of packing modes and molecular configuration in regulating fluorescence properties and photoresponse behavior in organic solid-state luminescent materials.

stimulus like sound, temperature, light, solvent and so forth, which makes supramolecular gels have the potential to be smart materials.^[4] Therefore, to gain more knowledge of the nature in supramolecular gels and to develop functional luminescence regulating gel materials remain to be seen a crucial challenge.

Cyanostilbene could be supposed to be a good candidate to help us to face the challenge. Most cyanostilbene-based backbones could produce typical aggregation induced emission (AIE) or aggregation induced emission enhancement (AIEE) behavior.^[5] Videlicet, the emission of cyanostilbene derivatives is quite weak or none in dilute solution but becomes enhanced accompanied with aggregates or gels formation.^[6] Especially, the conformation and relative arrangement of cyanostilbene derivatives in aggregates are sensitive to environment owing to distorted structures of molecules. the Furthermore. cyanostilbene could undergo trans-cis photoisomerization under UV light irradiation.^[7] The transition of configuration can lead to the photomechanical effect like gel-to-sol or liquid crystal-toisotropic liquid transition, making the luminescence in selfassemblies changed as well.^[8] However, there was little known in photoresponsive gels containing cyanostilbene to data on account of the narrow space in which cyanostilbene situate.^[9]

1. Introduction

Organic solid-state luminescent materials have attracted considerable attentions because of their underlying applications in fluorescence sensors, Organic Light Emitting Diodes (OLEDs), bioimaging and so forth.^[1] Fluorescence properties such as emission color of materials are not only decided by covalent structures of molecules themselves but also by the effects of relative supramolecular interactions (H-bonding, π - π interactions, hydrophobic interactions, etc).^[2] That is to say the modulation of fluorescence properties can be achieved at the unimolecular level by controlling ordered molecular self-assemblies.^[3] Supramolecular gels are supposed to be formed by gelators linked with supramolecular interactions and solvents. Various supramolecular interactions here produce the possibility of forming different packing structures. Besides, the biggest advantage of supramolecular gels is their sensitivity to external

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Scheme 1. Molecular structure and detailed synthetic route of BTTPA.

With these considerations in mind, we designed a novel gelator (**BTTPA**) containing a benzene-1,3,5-tricarboxamide (BTA) central unit functionalized by three cyanostilbenes as shown in Scheme 1. BTA structure has a huge advantage in fabricating hierarchical supramolecular architectures owing to its unique structure-three amides attached to a benzene core. The three amide bonds provide not only strong threefold H-bonding but also a one-dimensional growth tendency.^[10] The AIE active cyanostilbene π -conjugated backbone was chosen because of the attractive dual advantages of remarkable fluorescent

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features and photoisomerization, which are very sensitive to the aggregation behaviors. We supposed that the synergy between H-bonding and π - π interactions could give rise to ordered selfassemblies and the effects could influence the packing modes of π-conjugated cyanostilbene, further leading to distinct fluorescence properties of the gels. As expected, BTTPA could form two kinds of gels in the mixture of dimethyl sulfoxide (DMSO) and water due to the different self-assembly behaviors. The gels have distinctly different emission behavior with one emitting green emission (G-gel), while the other emits blue emission (B-gel). In addition, only G-gel exhibits a gel-to-sol transformation accompanied with fluorescence diminishment according to the trans-cis photoisomerization of cyanostilbene moieties under UV light irradiation. But B-gel exhibits outstanding photostability. To make full use of this point, an interesting photoinduced confidentiality pattern is performed.

2. Results and Discussion

2.1. Synthesis

BTTPA was prepared by treating 1,3,5-benzenetricarboxylic acid chloride with 2-(4-aminophenyl)-3-phenylacrylonitrile (2). Compound 2 was obtained using a reduction reaction of 2-(4nitrophenyl)-3-phenylacrylonitrile (1). Compound 1 was synthesized by a knoevenagel condensation between benzaldehyde and 4-nitrophenylacetonitrile (Scheme 1). Experimental details and corresponding characterization data are given in the experimental section and supporting information. The final product was obtained in about 54% yield. ¹H, ¹³C NMR spectroscopic measurements, elemental analysis, and mass spectra were employed to confirm its structure (Figure S1, S2 and S8).

DMSO/water	Phase	DMSO/water	Phase
90/10	S	40/60	I.
85/15	G (9.53), G-gel	30/70	1
70/30	G _I , B-gel	20/80	- I
60/40	G _I , B-gel	10/90	I
50/50	G _t , B-gel		

Note: S, soluble; G, gel; I, insoluble; GI, gel (cannot dissolve completely when heated). Number in bracket is the critical gel concentration (CGC, mg mL⁻¹).

2.2. Gelation Properties

The gelation ability of **BTTPA** was systematically investigated at first. A traditional strategy by heating-and-cooling a mixture of the gelator and a selected solvent was performed. The gel formation was judged by the "inversion-vial" method, that is,

there is no liquid flow upon the inversion of the sealed glass vial when hot solution was cooled to room temperature. BTTPA can't form gel in any tested organic solvent and only dissloved in THF, DMF and DMSO (Table S1). Additionally, mixtures of good solvents with water were used to probe the gelation ability (Table 1, S2 and S3). However, the gel formation was only observed when water was added into DMSO solution containing BTTPA. Depending on the water content, two kinds of gels were obtained and could endure ambient conditions for several weeks (Table 1). At 15% water, BTTPA could form yellow gel with green emission (G-gel). When the water content increased to between 30% and 50%, white gel with blue emission was obtained (B-gel) (Figure 1). Detailed gelation test was given in the experimental section. In addition, corresponding actual morphologies of the microstructure of xerogels were shown by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Figure 1, S3). Both kinds of xerogels exhibited entangled network nanostructures consisting of nanofibers, implying that the gel formation was ascribed to the immobilization of solvent by the winding structure. Crooked and gracile fibers with diameters of 30-70 nanometers of the xerogel prepared from G-gel were observed. Nevertheless, fibers of xerogels prepared from B-gel were more straight and wide and the width was up to 200-300 nanometers, implying a more rigid structure.



Figure 1. SEM images of **BTTPA** self-assembled structures for G-gel and B-gel (in DMSO/water mixed solvents with different volume content), G-gel: (a) 85/15, B-gel: (b) 70/30 (c) 60/40 (d) 50/50; insets are the photographs of corresponding gels under ambient light (left) and under illumination at 365 nm (right).

To provide a more accurate standard of gelation judgment of the gels with different water content, rheology experiments were employed. As shown in Figure 2, both G-gel and B-gel exhibited a higher elastic storage modulus (G') and a lower loss modulus (G''), indicating the authenticity of gelation judgment again.^[4c,11] More interestingly, with the increase of water content from 15% to 50%, both G' and G'' increased significantly, implying that the

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enhanced mechanical properties of the gels with more water content. That means B-gel exhibited higher mechanical strength than G-gel. Furthermore, the recovery experiments of B-gel were also performed (Figure S4). When exerted a constant strain of 100% during one minute, the gel got destroyed (G' >G'). And the gel state would be recovered when the strain was decreased to 1% (G' >G''). The circulation could be repeated many times, indicating that the gel showed good thixotropic properties.^[12]



Figure 2. (a) Frequency dependence of G' and G'' for G-gel and B-gel (10 mg ml^{-1}) in DMSO/water mixed solvents with the strain at 1%. (b) Dynamic strain sweep measurement of G-gel and B-gel in DMSO/water mixed solvents with angular frequency at 10 rad s-1. Legends are same in (a) and (b).

2.3. AIEE Characteristics

As mentioned above, the gels emit strong fluorescence. Hence, the fluorescent characteristics of BTTPA were worth investigating. In pure DMSO, BTTPA had an emission peak at 430 nm with a bluish violet color, while the emission was too weak to be observed under UV light (Figure 3a, 3c). With the water content increasing, the intensity decreased gradually accompanied with a little bathochromic shift, which might caused by the twisted intramolecular charge transfer (TICT) effect.^[13] The intensity of the emission suddenly enhanced when the water content reached 40%. With the increase of water content, the intensity became larger and a sky blue fluorescence (λ = 480 nm) was observed. At 60% water, the intensity reached to maximum, which was almost 7.5-fold greater than that in DMSO solution. The enhanced emission could be contributed to the poor solubility of BTTPA in water compared to that in DMSO, indicating BTTPA exhibited typical AIEE characteristics. In terms of UV-Vis absorption, an absorption peak at 347 nm was observed in pure DMSO, which was attributed to π - π * transition absorption of cyanostilbene moieties.^[14] Along with the increase of water content, a wilder peak as well as level-off tails in the visible region were observed and the intensity of the main peak had a distinct decrease, revealing that BTTPA comes into aggregates definitely in the poor solvent of water (Figure 3b).^[15] The results further supported the AIEE characteristics of BTTPA.

2.4. Optical Properties in Gel State

In accord with the spectroscopic studies in solution, fluorescence properties in the gel state were also investigated in

detail. In the fluorescence spectra, G-gel (15% water) revealed a green emission at 511 nm (absolute PLQY = 5.3%), presenting a distinct bathochromic shift ($\Delta\lambda$ = 81 nm) and an increase in the intensity in contrast to the weak emission in solution (λ = 430 nm), implying the special packing modes of the gel (Figure S5a). As far as UV-Vis absorption spectra were concerned, a distinct tailing peak in the visible region appeared, suggesting the aggregation behaviors of BTTPA in the gel state (Figure S5b).^[15,16] Moreover, as is known that temperature could contribute to the dispergation of the gel owing to the nonaggregation behavior of molecules in a higher temperature.^[17] From the temperature-dependent fluorescence spectra (Figure 3d), a gradual decline of the intensity of emission peak was observed with the increase of temperature. Until the hot solution state was reached, the final fluorescence was almost gone, while the fluorescence would be restored accompanied with gel reformulation in a lower temperature, showing typical thermal-reversible AIEE gel characteristics. Therefore, a reversible emission transition between "On" and "Off" could be readily achieved by the variation temperature.



Figure 3. (a) Fluorescence (λ_{ex} = 345 nm) and (b) UV-Vis absorption spectra of **BTTPA** (10⁻⁵ M) in DMSO/water mixtures with different water volume fractions (from 0% to 90%). (c) Maximum fluorescence intensity of **BTTPA** (10⁻⁵ M) as a function of water content. (d) Temperature-dependent fluorescence spectrum of G-gel.

Modulating the water content, another kind of gel with disparate blue emission (B-gel) was formed and lost the thermalreversible characteristics. That means B-gel was insoluble when being heated. As to the fluorescence spectra (Figure 4a), B-gel (30%-50% water) exhibited a blue emission at 471 nm (absolute PLQY = 6.0%), expressing a big difference in comparison to G-gel (15% water) (λ = 511 nm) described previously ($\Delta\lambda$ = 40 nm). In terms of UV-Vis absorption spectra (Figure 4b), the absorption peak (λ = 345 nm) of G-gel was realized. But B-gel displayed a wider absorption peak and a distinct shoulder peak appeared at 404 nm. Particularly, with the increase of water content, the intensity of the shoulder peak increased as well, implying stronger π - π interactions of cyanostilbene moieties.^[4f] It

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is noticed that both green emission and blue emission of G-gel and B-gel could be sustained after solvent evaporation (in a xerogel state), respectively (Figure S6).



Figure 4. (a) Normalized fluorescence (λ_{ex} = 345 nm) and (b) UV-Vis absorption spectra of G-gel and B-gel in the DMSO/water mixtures.

2.5. Packing Modes in Gel State

To assess how water affected the fluorescence of the gel, X-ray diffraction (XRD) and FT-IR spectroscopy were employed. It is widely accepted that the fluorescence of aggregates depends on the molecular structures and relevant packing modes. If the molecular structures are unaltered, it is packing modes that affect the fluorescence of aggregates.[18] As expected, a significant discrimination of xerogels prepared from G-gel (15% water) and B-gel (choosing the gel with 30% water for the next discussion) was observed in the whole XRD patterns (Figure 5a). For the xerogel prepared from G-gel, weak and tanglesome diffraction signals were shown in its XRD pattern, implying a low crystallinity of G-gel. In addition, the first peak at 2.80° with a dspacing of 3.15 nm in the small-angle region was considered as the intermolecular distance in orthogonal direction. In view of the columnar assemblies which most BTA structural molecules tended to form and the fibers like microstructure of the gel (Figure 1a), the intermolecular distance might be supposed to the intercolumnar distance.^[19] And density functional theory results demonstrated that BTTPA molecule adopted a perfect equilateral triangle-like structure and the dimension was estimated to be 2.70 nm (Scheme S1). The d-spacing value of first peak (3.15 nm) was larger than the molecular dimension, indicating a kind of relative loose arrangement. While sharper peaks obtained from B-gel standed for better rigidity and crystallinity. The xerogel prepared from B-gel exhibited main peaks at 4.29°, 7.23°, 8.72° and 11.38°, affording a ratio of 1 : $\sqrt{3}$: 2 : $\sqrt{7}$ (d-spacing values were 2.06 nm, 1.22 nm, 1.04 nm and 0.78 nm), showing a hexagonal packing arrangement.^[20] In addition, the reflection peak at 22.02°, corresponding to a dspacing value of 0.401 nm, was ascribed to π - π stacking between cyanostilbene moieties.^[20c] The d-spacing value of first peak (2.06 nm) was shorter than the molecular dimension, indicating tighter hexagonal packing arrangement and overlap of molecules owing to the enhanced π - π interactions.

Considering that most BTA system was supposed to selfassemble through amide-based H-bonds, FT-IR spectroscopy, a sensitive tool to detect amide bonds, was employed to identify the variation of H-bonds (Figure 5b). In the spectrum of sample prepared from G-gel, the amide bonds could be reflected in two N-H stretching vibrations at 3412 cm⁻¹, 3322 cm⁻¹ and one sharp C=O stretching vibration at 1678 cm⁻¹, indicating onedimensional aggregates through different types of H-bonds.^[10f,21] But in the spectrum of sample prepared from B-gel, both kinds of vibration peaks produced great shifts. Two N-H stretching vibration peaks shifted to 3312 cm⁻¹, 3259 cm⁻¹ and the C=O stretching vibration peak shifted to 1644 cm⁻¹ respectively, revealing stronger H-bonding interactions and tighter onedimensional aggregates formation.^[22] While cyano group stretching vibrations of both samples was located at 2216 cm⁻¹, confirming that the effects of water had nothing to do with cyano group. Thereby, the H-bonding interactions were enhanced in Bgel in comparison to G-gel due to different water content, which might lead to quite different packing structures.



Figure 5. (a) X-ray diffraction patterns and (b) FT-IR spectra of xerogels prepared from G-gel and B-gel.

The structures influenced by water were further investigated using a computational model. From the ¹H NMR spectrum of **BTTPA** in DMSO-*d*₆ with D₂O (Figure S7), the proton peak of amide bonds can't be detected due to the H-D exchange, suggesting water contacted with the amide bonds and may influence the packing.^[23] Based on the optimized results (Scheme S2), at high water content, **BTTPA** dimer was stabilized by water molecules through N-H···O and O-H···O hydrogen bonds, an overlapped structure was obtained. However, at low water content, fewer water molecules can't form sufficient hydrogen bonds to sustain such overlapped structure, leading to a slipped structure.

Based on the above results and discussion, a schematic illustration can be proposed for the formation of G-gel and B-gel (Scheme 2). For G-gel (at low water content), neighboring molecules stacked aslant and formed a loose packing. In this

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case, the great slippage contributed to a red-shifted emission (green emission).^[18a] Whereas, for B-gel (at high water content), H-bonding interactions and π - π interactions were enhanced owing to the high degrees of aggregation of molecules, which were demonstrated by the FT-IR and UV-Vis absorption results, resulting in a tight hexagonal packing arrangement of molecules. Therefore, B-gel exhibited a quite different blue emission in comparison to the green emission of G-gel because of the different packing modes of B-gel and G-gel influenced by water.



Scheme 2. Proposed illustration of the self-assembly behaviors of BTTPA in G-gel and B-gel.

2.6. Photomechanical Effect Accompanied with Fluorescence Switching

Cyanostilbene unit could undergo trans-cis photoisomerization upon UV light irradiation at 365 nm. It is worth mentioning that the occurrence of photoisomerization needs sufficient space in which molecules located in.^[9a] The photoisomerization happened easily in solution owing to the free state of molecules. Herein, ¹H NMR spectroscopic measurements were carried out to examine the photoisomerization process of BTTPA in DMSO-d₆ (Figure 6). In the initial state, the cyanostilbene unit adopted a transform evidenced by ¹H NMR signals and the peaks were assigned in Figure S1. Proton peaks of amide bonds and aromatic rings shifted to higher field upon UV light irradiation from the results of the ¹H NMR spectroscopy, indicating the photoisomerization process happened authentically.^[9b,24] Proton peaks from the double bond containing cyano group were used as the indicator to tell us the proportion between trans-isomers and cis-isomers. With the irradiation time increasing, the proton peak (H_a) for trans (8.05 ppm) decreased but that (H_b) for cis (7.68 ppm) increased. When the photostationary state was achieved, about 72% cis-isomers were obtained through the integral analysis of the proton peaks. It is noted that no new peaks could be found from the mass spectrum upon UV light irradiation, implying that there wasn't any other photoproducts like the [2 + 2] photodimer but the cis-photoisomers generated (Figure S8).^[24b,25] Optical properties were also changed during the trans-cis photoisomerization (Figure S9). When a solution of BTTPA in DMSO was irradiated with UV light at 365 nm, the

absorption peak (λ = 347 nm) was blue-shifted to 332 nm while the intensity of the absorption peak decreased dramatically, indicating the photoisomerization happened rapidly in dilute solution. This phenomenon was due to the fact that the conjugation length of *cis*-isomers was shorter than that of *trans*isomers.^[9a] As to the fluorescence spectra, the original dim bluish violet emission became weaker when being irradiated.





To gain more insight into the contributions of supramolecular interactions in the photoresponse behaviors of self-assembly materials, the photoresponsivity of the gels were further investigated. Whether the photoisomerization happened or not in the condensed state was attributed to the space in which cyanostilbene moieties situated, which was mentioned above. Most compounds based on cyanostilbene in the aggregation state are stable upon UV light irradiation due to the close packing modes of molecules or strong interactions. $^{\left[5a,18a,26\right] }$ In this work, two kinds of gels exhibited distinct photoresponse behavior. Upon UV light irradiation, G-gel collapsed and transformed into viscous sol quickly (Figure 7a). There is no doubt that the driving force for the gel-to-sol transition was ascribed to the photoisomerization of the cyanostilbene moieties, which was additionally proved by ¹H NMR spectroscopic measurements of G-gel in DMSO-d₆/H₂O (v/v, 85/15) before and after UV light irradiation (Figure S10). Proton peaks shifted to higher field like the results in pure DMSO- d_6 solution, suggesting the occurrence of photoisomerization in the gel state.^[24] The conversion rate was about 57% calculated by the proton peaks variation of cyano group. And all proton peaks became

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sharpened and clear, implying the disappearance of aggregates after UV light irradiation, as well as the gel-to-sol transition.^[27] However, B-gel failed to exhibit any change upon UV light irradiation. Thus, we think that no photoisomerization happened in B-gel. As we know that the occurrence of photoisomerization was related to the space in which molecules located in. And the space was influenced by the arrangement of molecules. The loose packing structures of G-gel provided sufficient space for the photoisomerization to allow the switching event to happen. Nevertheless, B-gel exhibited tight hexagonal packing structures. Such packing structures restricted the freedom of molecules and inhibited configuration transformation of cyanostilbene. Thereby, B-gel showed outstanding photostability, while G-gel showed superior photosensitivity because of the different packing modes as well.



Figure 7. G-gel before and after UV irradiation: (a) Photographs; (b) Fluorescence spectra (λ_{ex} = 345 nm); (c) Normalized UV-Vis absorption spectra; (d) Fluorescence kinetic profiles (λ_{ex} = 365 nm).

Further investigations were designed to characterize the nature of the sol state obtained by G-gel after UV light irradiation. Comparing the XRD data and SEM images of G-gel before and after UV light irradiation, we found that there was no noticeable diffraction in wide-angle region of the XRD pattern (Figure S11) and also disordered planar aggregates were observed in the SEM image (Figure S12), indicating the amorphous feature in the sol state.^[28] Next, optical properties of the sol were investigated. In the fluorescence spectra, the sol displayed a dim dark blue emission (λ = 441 nm) with a low intensity in comparison to the green emission with a high intensity of the initial gel (Figure 7b). As far as UV-Vis absorption spectra were concerned, a significant blue shift from the absorption peak of the gel (λ = 345 nm) to that of the sol (λ = 280 nm) was Meanwhile, the time-resolved observed (Figure 7c). fluorescence revealed that the average fluorescence lifetime (T = 19.24 ns) of the initial gel state reduced to 3.38 ns upon UV light irradiation (Figure 7d). The fluorescence lifetimes are determined by two component exponential fitting as follows; τ_1 =

2.93 ns (22.08%), T_2 = 19.92 ns (77.92%) for the gel and T_3 = 0.63 ns (67.08%), T_4 = 4.22 ns (32.92%) for the sol. The *trans*isomers had great gelation abilities and exhibited green emission in the gel state. Based on the above results and discussion, it could be concluded that the *trans*-isomers possessed better gelation ability and emission intensity in contrast to the *cis*-isomers. As a result of UV light irradiation, plentiful *cis*-isomers emerged and disturbed the ordered architectures, leading to the collapse of the gel and weaker fluorescence.^[9]



Figure 8. Photographs of photoinduced confidentiality pattern made from G-gel (at the corner) and B-gel (in the center).

The disparate photoresponse behavior of G-gel and B-gel could be extended to graphic photoinduced confidentiality pattern (Figure 8). Four circles at the corner were equipped with G-gel and one circle in the center was equipped with B-gel. Five of circles with green and blue fluorescence were visible under UV light. Upon UV light irradiation, green fluorescence parts decayed but blue fluorescence part still sustained. Only the circle in the center was presented to us.

3. Conclusions

gelator BTTPA containing a benzene-1,3,5novel tricarboxamide (BTA) central unit functionalized by three cyanostilbenes has been synthesized. The special structure results in favourable gelation ability in the mixture of DMSO and water. Depending on the water volume content, two kinds of gels exhibit disparate AIEE properties with one emitting a green emission (G-gel, containing 15% water), while the other emits a blue emission (B-gel, containing 30%-50% water). Meanwhile, G-gel and B-gel show different photoresponse behaviors as well. G-gel exhibits a gel-to-sol transition accompanied with fluorescence switching upon UV light irradiation. But B-gel fails to exhibit any gain upon UV light irradiation, revealing great photostability. The observation is ascribed to the different packing structures influenced by water. Loose structures and great freedom of molecules are disclosed for G-gel, providing sufficient space for the configuration transformation (photoisomerization) of cyanostilbene. For B-gel, H-bonding interactions and π - π interactions are enhanced, resulting in tight hexagonal packing structures and restricting the space in which cyanostilbene moieties locate and inhibiting the configuration transformation. Consequently, graphic photoinduced а

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confidentiality pattern is performed. Furthermore, this work helps people to gain more insight into the contributions of supramolecular interactions in regulating luminescence of the self-assembly materials and opens a door to a new class of developing novel smart materials.

4. Experimental Section

Synthesis of 2-(4-nitrophenyl)-3-phenylacrylonitrile (1): Benzaldehyde (2.04 ml, 20 mmol) and pyrrolidine (3.31 ml, 40 mmol) were added to a solution containing 4-nitrophenylacetonitrile (3.24 g, 20 mmol) in ethanol (80 ml). The reaction mixture was stirred at room temperature for 6h and filtered to remove liquid. The solid was washed with ethanol for 3 times to give a faint yellow powder (4.66 g, yield 93%). ¹H NMR (500 MHz, DMSO-d6) δ /ppm = 8.40 – 8.35 (m, 2H), 8.34 (s, 1H), 8.08 – 8.05 (m, 2H), 8.02 – 8.00 (m, 2H), 7.62 – 7.56 (m, 3H).

Synthesis of 2-(4-aminophenyl)-3-phenylacrylonitrile (2): SnCl₂·2H₂O (18.11 g, 80 mmol) was added to a solution containing compound **1** (4.66 g, 18.6 mmol) in ethanol (120 ml), which was refluxed at 75 °C for 5h. The resulting solution was then neutralized with sodium bicarbonate saturated aqueous solution and extracted by ethyl acetate. The obtained organic phase was washed with saturated salt water for 3 times, dried over with anhydrous Na₂SO₄ and filtered. The resulting solution was concentrated by rotary evaporation to give a yellow solid (2.91 g, yield 71%). ¹H NMR (500 MHz, DMSO-d6) δ /ppm = 7.87 – 7.83 (m, 2H), 7.70 (s, 1H), 7.49 (dd, J = 8.3, 6.8 Hz, 2H), 7.44 (dd, J = 8.4, 6.6 Hz, 3H), 6.68 – 6.62 (m, 2H), 5.62 (s, 2H).

Synthesis of benzene-1,3,5-tricarboxylic acid tris-{[4-(1-cyano-2-phenyl-vinyl)-phenyl]-amide} (BTTPA): Triethylamine (1.77 ml, 13.3 mmol) and a solution of 1,3,5-Benzenetricarboxylic acid chloride (1.07 g, 4.1 mmol) in DCM (10 ml) were slowly added to a solution containing compound 2 (2.91 g, 13.3 mmol) in DCM (60 ml), which was stirred at room temperature for 20h. The resulting mixture was filtered to remove the liquid and the solid was washed with DCM and water for many times to obtain the final yellow powder (2.71 g, yield 82%). ¹H NMR (500 MHz, DMSO-d6) δ /ppm = 10.85 (s, 3H), 8.80 (s, 3H), 8.05 (s, 3H), 8.02 (d, J = 8.5 Hz, 6H), 7.95 (d, J = 7.6 Hz, 6H), 7.84 (d, J = 8.5 Hz, 6H), 7.58 – 7.50 (m, 9H); ¹³C NMR (126 MHz, DMSO-d6) δ /ppm = 165.07, 142.08, 140.39, 135.75, 134.35, 130.92, 130.55, 129.62, 129.47, 126.84, 121.08, 118.38, 110.46; MALDI-TOF-MS: calcd for C₅₄H₃₆N₆O₃: C 79.41, H 4.41, N 10.29; found: C 79.09, H 4.51, N 10.08.

Materials and Methods: All solvents and reagents were obtained from commercial supplies and used directly without further purification. The silicon wafers used here were first treated in concentrated sulphuric acid-hydrogen peroxide solution (v/v, 3/1), then cleaned with pure water. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 500 MHz spectrometer (TMS as the internal standard). UV-Vis absorption spectra were performed on a Shimadzu UV-2600 spectrophotometer. Fluorescence spectra were performed on a Shimadzu RF-6000 spectrofluorophotometer. Time-resolved fluorescence lifetime (with TCPSC technology) was collected on an Edinburgh FLS 980. PLQY was obtained using FLS 920 in gel state. The rheological properties were investigated on a TA instrument (AR2000 Rheometer) equipped with an aluminum plate of 25 mm diameter. The samples were sandwiched between the two plates with a gap of 0.5 mm throughout the experiments. FT-IR spectra were recorded on a Bruker Optics VERTEX 80v Fourier transform infrared spectrometer, equipped with dried CaF2 windows. Powder X-ray diffraction (XRD) patterns were performed on a Rigaku

D/MAX 2500/PC X-ray diffractometer with CuKa radiation ($\lambda = 0.15418$ nm). Scanning electron microscopy (SEM) images were collected on a JEOL JEM-6700F at 3 kV, with the samples coated with Au. Transmission electron microscope (TEM) was performed on a JEOL JEM-2100F transmission electron microscope. Samples were prepared by wiping a small amount of gel samples onto a carbon-coated copper grid followed by naturally evaporating the solvent. Mass spectra were recorded on a Brucker Autoflex speed TOF/TOF mass spectrometer. The solution of **BTTPA** was irradiated using two 365 nm-handheld UV lamps (12 W). The model was WFH-204B. **BTTPA** gel was irradiated using Tank 007 UV-AA01 flashlight (25000 μ W cm⁻²).

Gelation test: **BTTPA** was dissolved in DMSO in a glass vial beforehand. When water was added into the solution, white precipitates appeared. For G-gel (15% water), white precipitates dissolved completely when being heated at 90 °C. Yellow gel was formed when cooled to room temperature. For B-gel (30%-50% water), the glass vial needed to be stirred slightly to make sure the precipitates were fully dispersible in solution. Then, the mixture was heated at 90 °C for only 15 seconds. White suspension turned into white stable gel. For all of the measurements, the gel concentration was set to 10 mg ml⁻¹.

Theoretical and computational method: The molecular structure of **BTTPA** was optimized in gas phase using density functional theory calculations at the B3LYP/3-21G* level with the Gaussian 09 package.^[29] For the simulation of the stabilized stacking dimer of **BTTPA**, a semiempirical method (PM7) was employed, as implemented in the Mopac 2016 program.^[30]

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Keywords: fluorescence switching • photoresponsivity • aggregation-induced emission enhancement • supramolecular interactions • cyanostilbene

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FULL PAPER

The modulation of fluorescence properties can be achieved at the unimolecular level by controlling ordered molecular self-assemblies. This paper reports that a novel gelator, **BTTPA**, can form two kinds of gels with one emitting a green emission (G-gel), while the other emits a blue emission (B-gel) depending on the water content in DMSO/water mixtures. Only G-gel displays highly photosensitive, while B-gel fails to exhibit any gain upon UV irradiation.



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Fluorescence Regulating and Photoresponsivity in AIEE Supramolecular Gels Based on a Cyanostilbene Modified Benzene-1,3,5-tricarboxamide Derivative