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Supramolecular Liquid-Crystal Gels Formed by Polyfluorene-Based π-Conjugated Polymer for Switchable Anisotropic Scattering Device

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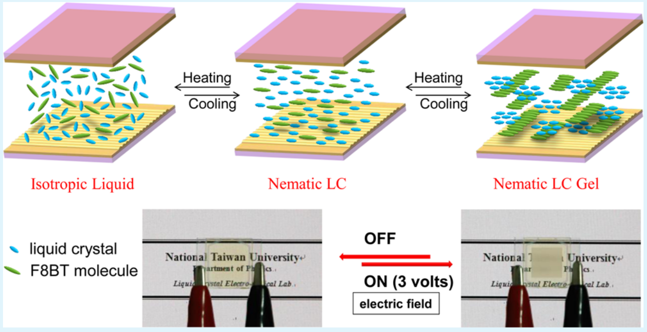
Supporting Information



ABSTRACT: To overcome the problem of high driving voltage and low contrast ratio in the switchable scattering device of conventional liquid-crystal (LC) physical gel, a new type of supramolecular LC physical gel has been developed and fabricated through the fibrous self-assembly of the polyfluorene-based π-conjugated polymer, poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT), in nematic LC mixture E7. It was found that the rubbed interface between the LC molecules and polyimide layer can induce the LC physical gels to demonstrate fantastic light scattering characteristic. The gels with oriented self-assembled supramolecular structures exhibiting significant anisotropic light scattering in the main-chain direction of the F8BT molecules under an extremely low driving voltage (ca. 2.7 V) are reported for the first time. In addition, the contrast ratio can be reached exceeding 1000. In contrast to conventional LC physical gels, the large reduction of driving voltages of the supramolecular gel provides great possibility for application in various electro-optical devices such as tunable polarizers, transflective displays, and polarized light modulators.

KEYWORDS: *anisotropic scattering, molecular self-assembly, liquid-crystal physical gels, electrically switchable devices, supramolecular structures, polyfluorene-based π-conjugated polymer*

1. INTRODUCTION

Organic gelator molecules have attracted significant attention for the ability to form physical network structure through self-assembly in solvents.[1−9] The non-covalent interactions like hydrogen-bonding, $\pi-\pi$ stacking, and van der Waals force induce the formation of fibrous aggregates of the organic gelators. In recent years, the thermal-reversible fibrous network assembling in LCs leads to the construction of physical gels,[10−16] which have been developed as soft functional materials. The functional gel materials have been widely used in various electro-optical devices, such as LC semiconductors with high mobility,[17,18] fast-response switching in twisted nematic cells,[19−21] stabilization of the orientation of ferroelectric LCs,[22] etc. In particular, switchable scattering devices based on the LC physical gels have attracted more and more interests for their potential to apply to a new mode of display.[23−28] However, in these gels, high driving voltages of about 40 V are still needed to switch the bright and dark states. And the contrast ratios are also not high enough for the use of displays. In this paper, we report for the first time that a supramolecular LC gel can be formed by the use of polyfluorene-based π-conjugated polymer as gelator and the gel demonstrates fantastic electro-optical properties. In contrast to conventional LC physical gels, the supramolecular gel possesses extremely low driving voltage less than 3 V which provides great applications in various electro-optical devices.

The π-conjugated gelator molecule used in this experiment is poly(9,9-dioctylfluorene-*alt*-benzothiadiazole) (F8BT). The electro-optical properties of the F8BT molecule as thin films have been studied in previous experiments in detail.[29−31] The F8BT molecule is one kind of the polyfluorene derivatives which have been developed as the active organic materials in the electro-optical device, such as polymer light-emitting diodes (PLEDs) and polymer field effect transistors (PFETs) with highly conducting properties caused by the π-conjugated chains.[32−36] Besides, many researchers found that the polyfluorene derivatives can gel a lot of organic solvents through the fibrous self-assembly of polymers induced by the $\pi-\pi$ stacking interactions between molecules.[37−39] Until now, however, only few studies have been investigated on the self-assembled behavior of polyfluorene derivatives in LCs. Here we first report that the LC mixture E7 can be gelled by the polyfluorene derivatives−F8BT polymer. In addition, the supramolecular anisotropic structures have been observed in an LC cell with anti-parallel alignment layer after the formation of the LC gels through fibrous self-assembly of the π-conjugated gelator F8BT. The presence of oriented polymer network in LCs makes the supramolecular π-conjugated gel exhibit extremely anisotropic scattering and high contrast ratio

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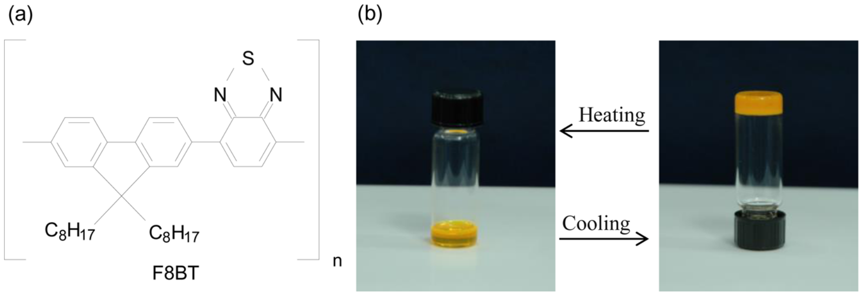

Figure 1. (a) Chemical structure of the polyfluorene-based π-conjugated polymer F8BT. (b) Photographs of the formation of LC gel with 1.0 wt % F8BT in E7. The pictures show the thermal reversibility which was examined by repeated heating−cooling processes.

under an ultra-low driving voltage (only 2.7 V) compared to the conventional gels formed by low-molecular-weight gelators. The unique properties of the polyfluorene-based supramolecular anisotropic LC gel provide the possibility to develop a novel electro-optical material for promising applications in switchable devices.

2. EXPERIMENTAL SECTION

2.1. Preparation of Supramolecular LC Gels. In this study, the nematic LC E7 (clearing point about 51 °C) and the polyfluorene-based π-conjugated polymer F8BT (average M_n 10,000−20,000) were used to construct the supramolecular LC physical gels. They were purchased from Fusol material and Sigma-Aldrich, respectively. The chemical structure of F8BT is shown in Figure 1a. The LC host E7 was used in our experiments due to the F8BT polymer had good solubility and stability in it. The nematic LC E7 is a mixture which consists of four kinds of basic LC molecules: [1,1′-biphenyl],4-carbonitrile,4′-pentyl, [1,1′-biphenyl],4-carbonitrile,4′-heptyl, [1,1′-biphenyl],4-carbonitrile,4′-octyloxy, and [1,1′,4′-1″-terphenyl],4-carbonitrile,4″pentyl with the percentages of 51, 25, 16, and 8, respectively.

To prepare the supramolecular LC physical gels, at first, a small amount of F8BT (0.1−1.6 wt %) was adding into E7 LCs in glass bottles. Then these materials were uniformly mixed by stirring and gently heating on a hot plate. In the beginning, the LC mixtures of F8BT and E7 displayed an opaque state in the room temperature. When the mixtures were heated to the temperature of about 60 °C, which is higher than the clearing point of E7, the mixtures became transparent for being an isotropic liquid. To make sure the F8BT polymers can be well dispersed in E7, the mixtures were further heated at 90 °C for 3 h. And then the mixtures were cooled down slowly at a rate of 5 °C min^{-1}. As the temperature cooled down to room temperature, the mixtures became opaque again and formed the supramolecular LC gels. The formation of the gel can be validated by the loss of the ability to flow under the influence of gravity as shown in Figure 1b. Figure 1b shows the photographs of the LC gel with the concentration of 1.0 wt % F8BT in E7. The occurrence of the thermal reversibility reflects the reason for the construction of the gel from the non-covalent network.

2.2. Examination of Phase Transition Behavior. To understand the phase transition behavior of the supramolecular LC gels, the E7 with different concentrations of F8BT polymers were examined. The sol−gel transition temperatures ($T_{\mathrm{sol-gel}}$) of F8BT and the isotropic−nematic transition temperatures ($T_{\mathrm{iso-ne}}$) of E7 were determined by differential scanning calorimetry (DSC) measurements and polarized optical microscope (POM) observations in the cooling process at a rate of 5 °C min^{-1}. The DSC measurements were performed on a Perkin Elmer Pyris 6 DSC instrument. By confirming that the exothermic peaks occur in the DSC data, the transition temperatures of $T_{\mathrm{iso-ne}}$ and $T_{\mathrm{sol-gel}}$ can be obtained. To observe the images of POM, the gels containing different concentrations of F8BT were injected into 9 μm thickness glass sandwich cells having anti-parallel rubbed polyimide films in isotropic liquid state. And the POM observations of cells were conducted using Olympus BX51 equipped with a hot stage. As the temperature decreases, the transition temperature of $T_{\mathrm{iso-ne}}$ and $T_{\mathrm{sol-gel}}$ can also be observed through the POM.

2.3. Observation of the Self-Assembled Structures of LC Gels on the Rubbed and Unrubbed Interfaces. The gels containing different concentrations of F8BT were prepared as described in Section 2.1. Then the gels were injected into the 9 μm thickness glass sandwich cells with anti-parallel rubbed polyimide films or unrubbed polyimide films. To confirm the mixing uniformity, the gels were heated to isotropic liquid state and then injected into the cells. Subsequently, the cells were cooled down slowly to room temperature at a rate of 5 °C min^{-1}, and the supramolecular LC gels were formed in the cells. To observe the structure of the gels in the cells, the dark-field mode of Olympus BX51 was conducted. For further realizing the main-chain direction of the F8BT polymer in the cells, the polarized PL spectra (excitation light λ_{ex} = 430 nm) were measured through the instrument of Edinburgh FS 920. By adjusting the polarization of polarizer between the cell and the detector to be parallel or perpendicular with the rubbing direction of the cell, the polarized PL spectra can be obtained.

2.4. Electro-Optical Measurements of Supramolecular Anisotropic Gels. For researching the electro-optical properties of the supramolecular LC gels, the gels were injected into the 9 μm thickness ITO (indium tin oxide) glass cell with anti-parallel rubbed polyimide films or unrubbed polyimide films by the method described in Section 2.3. To demonstrate the property of anisotropic scattering of the LC gel in the cell with rubbed surface, the LC cell was placed in front of a polarized LC display. By providing a low voltage (ca. 3 V), the electrode area of the LC cell presented an obvious scattering. And the detailed electro-optical properties of the supramolecular LC gels are further measured by our experiment system shown in Figure 2.

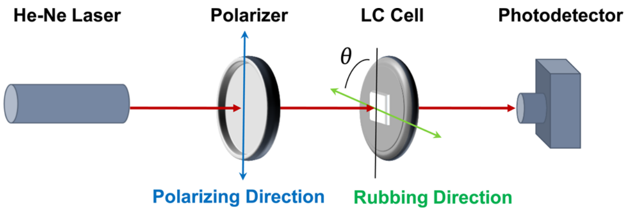

Figure 2. Illustration that shows the setup of the electro-optical measurement system. θ is defined as the rotation angle between the polarizing direction of polarizer and the rubbing direction of the LC cell.

The system is composed of a He−Ne laser, linear polarizer, LC cell, and the photodetector. An unpolarized He−Ne (632.8 nm) laser was used as an incident light source. To verify the property of directional scattering of the supramolecular LC gel, the polarizer mounted in a rotatable holder was placed between the He−Ne laser and the LC cell. An AC field (1 kHz, square wave) was applied to the cells by the function generator which was controlled by a computer with LabView programming. Then the transmittances under various applied voltages were recorded by the photodetector. The driving voltage was determined to be the voltage required for reaching 90% transmittance relative to the empty cell as background. And the data of rise time and the decay time were determined by measuring the response times needed for varying the transmittances 100−10% and 0−90% in the electric field (5 V) on and off, respectively. The transmittances in various rotation angles θ between the polarization of polarizer and the rubbing direction of the cell were recorded by rotating the polarizer. In addition, the broad transmittance spectra in the electric field on and off for two directions were measured by the SD1200-LS-HA system.

3. RESULTS AND DISCUSSION

3.1. LC Gel Preparation and Its Phase Transition Behavior. After the formation of supramolecular LC gels through the steps described previously, the phase behaviors of the gels were further researched. Figure 3 shows the phase diagram of the supramolecular LC gels with different concentrations of F8BT which was determined by the POM observations and DSC measurements (some representative DSC data are shown in Supporting Information Figure S1). In our experiments, the gels with the concentrations of F8BT below 1.6 wt % exhibit three states of isotropic liquid, nematic, and nematic LC gel in the phase diagram. And the mixtures undergo the isotropic−nematic transition of E7 first and then sol−gel transition of F8BT upon cooling. This finding implies that it is possible to align the F8BT molecules and form oriented molecular network structures through the template effect of the aligned LC materials.

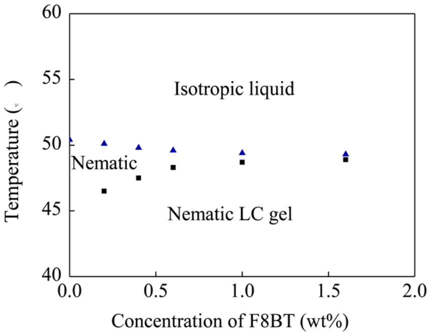

Figure 3. Phase diagram of the mixtures of E7 and F8BT. The mixtures with different concentrations of 0.2, 0.4, 0.6, 1.0, and 1.6 wt % F8BT were prepared. The $T_{\text{sol−gel}}$ of F8BT and $T_{\text{iso−ne}}$ of E7 are represented by ■ and▲, respectively.

3.2. Observation of Fibrous Structures of the Gels. To confirm this assumption, the gels with different concentrations of F8BT were filled into a 9 μm empty LC cells with anti-parallel rubbed alignment layers in isotropic liquid state. After the cooling processes described in the experiment part, we found that the anisotropic fibrous structures were formed in the LC cells through the observations with dark-field optical microscope. Figure 4a shows the dark-field optical picture of the cell with the gel containing 1.0 wt % of F8BT. The green self-assembled F8BT fibers perpendicular to the rubbing direction of the cell were observed in this figure. Figure 4b shows the optical picture of the cell (without rubbing treatment) with the gel containing 1.0 wt % of F8BT; the random polymer network can be observed. These results are supported by the phase diagram shown in Figure 3. It indicates that the anisotropic fibrous aggregates of the gelator F8BT can be formed through the use of rubbed surface, since the $T_{\text{iso−ne}}$ is higher than $T_{\text{sol−gel}}$. The template effect of the aligned nematic LCs is a key role to induce the formation of oriented fibrous aggregates of F8BT. Without the template effect (no rubbing treatment for the cells), there are only the random polymer networks formed in the cells.

There have been a number of studies that have investigated the properties of F8BT polymer, which reveal that the F8BT molecules with uniaxial alignment result in polarized photoluminescence (PL).[31,40] Therefore, to confirm the orientation of F8BT molecules in the cell with rubbed surface, the polarized PL spectra of the gels containing different concentrations of the gelator F8BT were measured. The polarized PL spectra were obtained by setting a polarizer, which was inserted between the cell and detector, with the polarization to be parallel or perpendicular in the rubbing direction of the cell. Figure 5a shows the PL emission spectra (λ_{ex} = 430 nm) of the LC gel containing 0.1 wt % F8BT, and the measured PL polarization ratio of parallel to perpendicular intensity at 540 nm is over 3. Figure 5b shows the PL polarization ratios with different F8BT concentrations between 0.1 and 1.6 wt %. For the LC cells with the gels containing F8BT below 1 wt %, high PL polarization ratios were observed. These findings reflect the degree of alignment of fibrous F8BT polymer network to a great extent. The higher PL polarization ratio was obtained in cell with a lower concentration of F8BT. Besides, the stronger PL signal was recorded when the polarization of polarizer was parallel to the rubbing direction of the cells. The result shows that the main-chain direction of F8BT molecules should align with the rubbing direction of cell. Supporting Information Figure S2 shows the polarized PL spectra for samples prepared in cells without rubbing treatment. It can be seen that the polarized PL spectra in two directions are almost the same. And no obvious tendency is found as the concentration of F8BT increases. It indicates that the F8BT

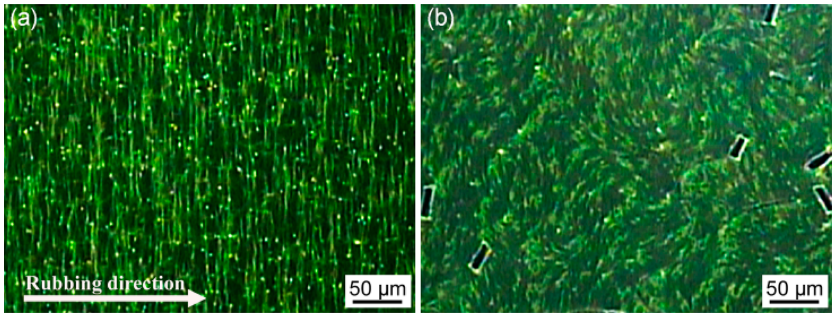

Figure 4. Dark-field optical pictures of F8BT/E7 gels containing 1.0 wt % of F8BT in E7 LCs in the cell (a) with anti-parallel rubbed alignment layer in which the anisotropic self-assembled fibers of F8BT was shown and (b) without rubbing treatment in which the polymer network of F8BT was found in the cell.

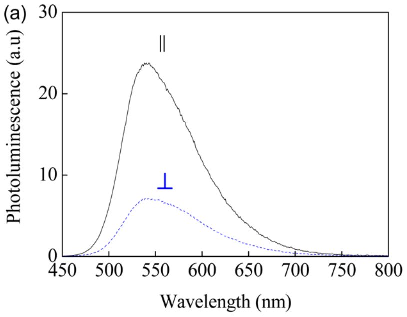

Figure 5. (a) Polarized PL spectra of a LC gel containing 0.1 wt % F8BT in E7. The solid and dashed curves denote the PL spectrum as the polarizing direction of polarizer was parallel and perpendicular to the rubbing direction of the cell, respectively. (b) The polarization ratios of LC gels with different concentrations of 0.1, 0.2, 0.4, 0.6, 1.0, and 1.6 wt % F8BT.

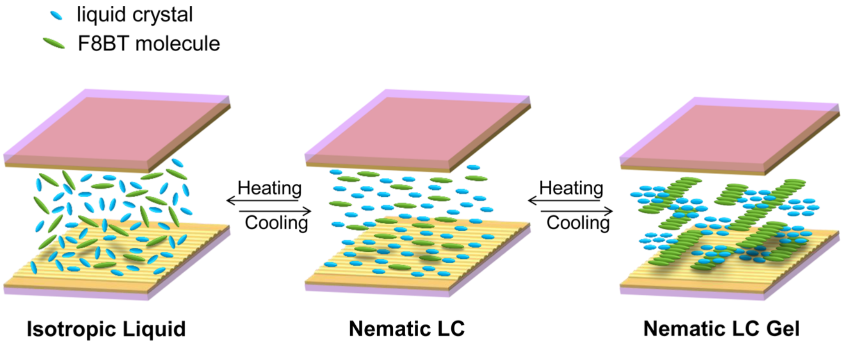

Figure 6. Schematics of the formation model of anisotropic π-conjugated F8BT fibers (shown as fibrous aggregates of green F8BT molecules) in three states of isotropic liquid, nematic LC, and nematic LC gel. In the cooling process, the F8BT/E7 mixture would undergo isotropic−nematic transition of E7 and then sol−gel transition of F8BT. With the $\pi-\pi$ stacking interaction between the aligned F8BT molecules, anisotropic fibrous polymer networks are formed through oriented self-assembly.

molecules would align randomly in the cells without rubbing treatment.

According to the measurements of polarized PL spectrum and the results of OM observations, we can build up the formation model of anisotropic π-conjugated F8BT fibers which is shown in Figure 6. In the beginning, the mixture of E7 and F8BT is in a state of isotropic liquid that the F8BT molecules are randomly dispersed in the LC host E7 after being injected into the cell and heated to the temperature higher than $T_{\text{iso−ne}}$. Then, as the cell is cooled down slowly to the temperature below $T_{\text{iso−ne}}$, the F8BT molecules can be aligned to the rubbing direction of the LC cell through the template effect of E7 LCs in the nematic LC state. Subsequently, as the temperature keeps cooling down to $T_{\text{sol−gel}}$, the $\pi-\pi$ stacking interactions between the main chains of F8BT molecules lead to the formation of nematic LC gel through the self-assembly of the anisotropic F8BT fibers with the growth direction perpendicular to the rubbing direction of the LC cell.[29] And we found the fibrous structure is thermal-reversible, which means the anisotropic fibers would disappear as the gel is heated to the temperature higher than the $T_{\text{sol−gel}}$ and become isotropic liquid again if the temperature is further heated to the temperature higher than the $T_{\text{iso−ne}}$.

The self-assembled behavior of the gelator F8BT is similar to the previous results reported by Kato et al.; low-molecular-weight π-conjugated gelator can form oriented fibrous aggregates which are perpendicular to the rubbing direction through $\pi-\pi$ stacking interaction.[41,42] To examine the existence of $\pi-\pi$ stacking interactions between F8BT polymers, we measure the ^{1}H NMR spectroscopy of F8BT polymers in $CDCl_3$ (10 mg/1 mL) with different temperatures of 248, 273, and 298 K (see Supporting Information Figure S3). It shows that, as the temperature decreases, the aromatic proton signals become not well-resolved. That indicates the stronger $\pi-\pi$ stacking interactions occur as the temperature decreases.[43] These results here provide the evidence for the existence of the $\pi-\pi$ stacking interactions between F8BT polymers. It is worth emphasizing that although the polyfluorene-based polymer F8BT is a high-molecular-weight molecule with a long π-conjugated chain, the F8BT polymers can also be aligned by the template effect of the oriented nematic LCs.

3.3. Electrically Switchable Anisotropic Light Scattering.

With the formation of oriented fibrous structure in the cell with rubbing treatment, we found such a supramolecular LC gel demonstrates an extremely anisotropic light scattering state by providing an electric field. Figure 7 illustrates the photographs of the cell with the LC gel containing 0.2 wt % F8BT and the mechanism of anisotropic scattering in the field-off and field-on states. These photographs were taken by using a polarized LC display screen as the light source, and its polarization was arranged to be parallel with the rubbing direction of the cell. And these pictures were obtained in the distance about 1 cm between cell and screen. The gel exhibits transparent state when the electric field is off. And when the electric field turns on, the gel would switch to the anisotropic scattering state. The state makes the light with the polarization axis parallel to the rubbing direction of the cell extremely scatter. Therefore, the gel presents an opaque state on the square electrode area of the cell. And when the electric field turns off, the LC gel is switched back to the transparent state again. It is remarkable to note that the driving voltage required to produce such electro-optical switching from a transparent state to an anisotropic scattering

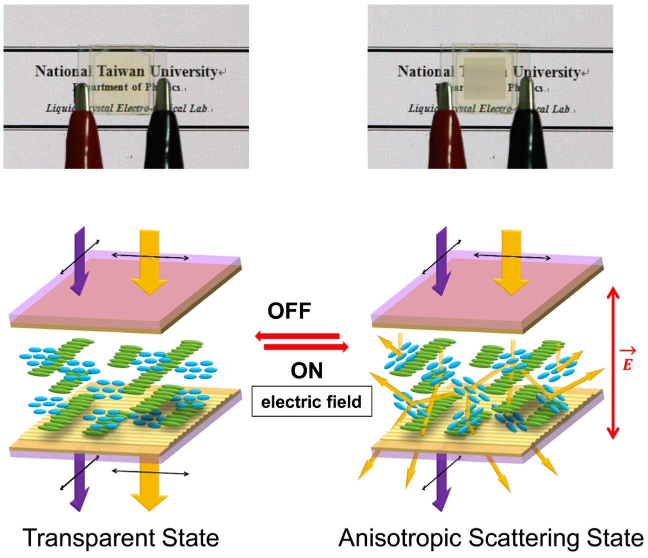

Figure 7. Schematics illustrating the anisotropic scattering mechanism and the corresponding photographs of the cell with the 0.2 wt % F8BT supramolecular LC gel in the electric field-off and field-on states, respectively. The two states can be electrically switched by a low applied voltage, less than 3 V.

state is extremely low, less than 3 V. We consider the reason leading to low operating voltages should be due to the presence of π-electrons. The π-electrons may play as a kind of radical here, since the aromatic rings in the conjugated polymer have a high π-electron delocalization degree.[44] After the formation of conjugated network through the π-stacking interactions between F8BT molecules, π-electrons would obtain a higher delocalization degree.[45] Therefore, we suggest that these π-electrons could rapidly redistribute around the conjugated network and form localized electric fields which can efficiently drive LC molecules in much lower operating voltages. Through the utility of polyfluorene-based π-conjugated polymer F8BT and rubbed surface, the supramolecular LC gel shows the unique property of low driving voltage and anisotropic scattering, which are not found in the conventional LC gel formed by the oriented self-assembly of low-molecular-weight gelator.[10,41,42,46]

Here we propose a model to explain the anisotropic scattering mechanism of the supramolecular LC gel. In the absence of electric field, the supramolecular LC gel exhibits the transparent state because the LCs present a monodomain with orientation aligned to the rubbing direction of the cell. And then, when the electric field turns on, the LCs are forced to align to the direction of electric field. Meanwhile, the LC molecules are still attracted by the π–π interactions from the oriented fibrous aggregates of the F8BT polymer. The

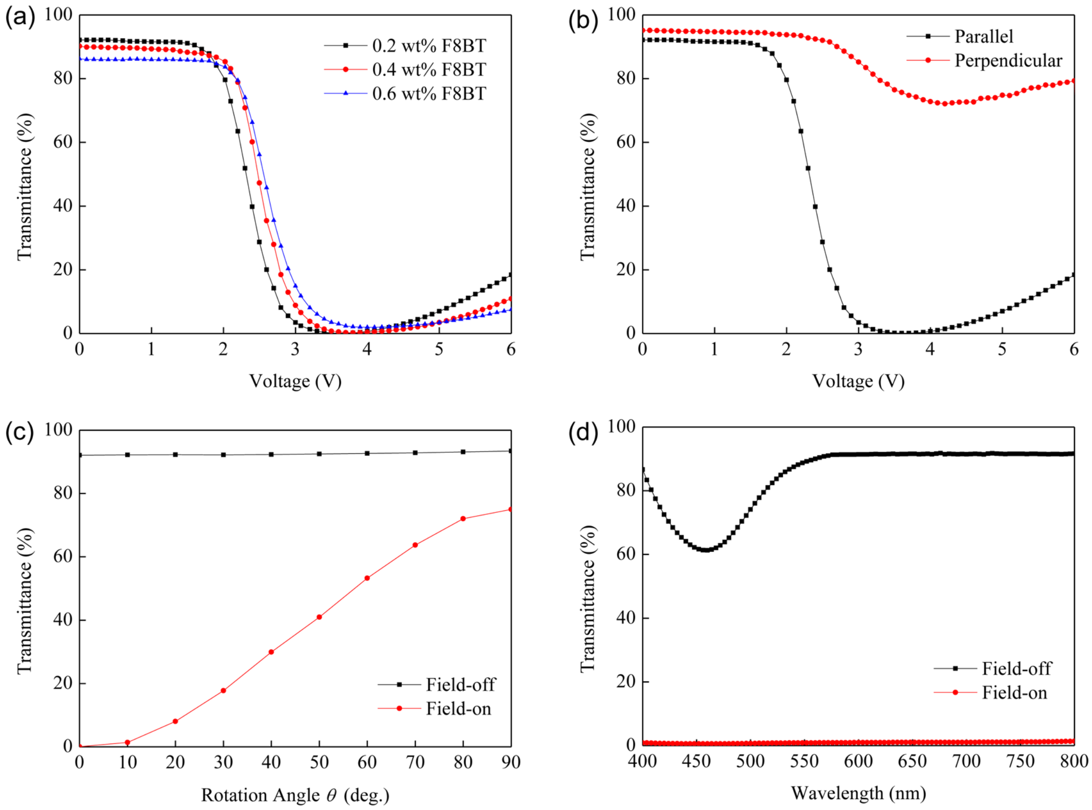

Figure 8. (a) Transmittance−voltage curves of the supramolecular LC gels with 0.2, 0.4, and 0.6 wt % of F8BT in a 9 μm thick LC cell with anti-parallel rubbing treatment. The transmittances were recorded in the rubbing direction of the cell parallel to the polarization direction of the polarizer. (b) Comparison of the transmittance−voltage curves of 0.2 wt % F8BT/E7 gel with the rubbing direction of the cell parallel and perpendicular to the polarization direction of the polarizer. (c) The transmittance of 0.2 wt % F8BT supramolecular LC gel at the field-off (0 V) and field-on (3.6 V) states in different rotation angles between the polarization direction of the polarizer and the rubbing direction of the cell. (d) The transmittance spectrum of 0.2 wt % F8BT LC gel in the wavelength range from 400 to 800 nm. The transmittances were recorded at the polarization direction of the polarizer parallel to the rubbing direction of the cell in the field-off (0 V) and field-on (3.6 V) states.

competition of two forces induces the transformation from uniform monodomain to multi-domains which align to the main-chain direction of F8BT polymer in the plane parallel to the rubbing direction. With the formation of oriented LC multi-domains, the supramolecular LC physical gel demonstrates the result of anisotropic light scattering. And the LC multi-domains would reverse to the monodomain again as electric field turns off.

3.4. Electro-Optical Properties of the Gels. The electro-optical properties of the LC gels were examined by the measurement system shown in Figure 2. The LC cells filled by the gels with different concentrations of the gelator F8BT through the fabrication process as described in Experimental Section were prepared. Figure 8a shows the voltage−transmittance ($V-T$) curves of the LC gels with different concentrations (0.2, 0.4, and 0.6 wt %) of the gelator F8BT. The parallel transmittance ($T_{\parallel}$) was recorded as the polarization direction of polarizer was set to be parallel with the rubbing direction of cell. As the electric field is off, the gel possesses the highest transmission state. When the electric field turns on, the transmittance starts to decrease due to the light scattering caused by the formation of multi-domains. As the driving voltage increases, the size of LC multi-domains becomes smaller and thus the transmittance further decreases. The transmittance reaches minimum as the size of LC multi-domains approaches the wavelength of visible light. But if the applied voltage continues to increase, the size of LC multi-domains would become larger and gradually transfer to monodomain, since the electric force is dominant as the driving further voltage increases over 4.5 V (as shown in Figure 8). Therefore, the transmittance starts to increase. In addition, the $V-T$ curves of the supramolecular LC gel are influenced by the concentration of the gelator F8BT.

For the lower concentration, the higher transmittance in the off state and lower driving voltage are obtained for little light absorption and faster response caused by the effect of higher ratio of LCs, respectively. The electro-optical properties of the supramolecular LC gels with different concentrations of the gelator F8BT are shown in Table 1. In our experiments, the LC gel containing 0.2 wt % F8BT polymer presents the best performance of anisotropic scattering. The transmittance is as high as 92% when the electric field is off. Then when the electric field turns on, the gel exhibits anisotropic light scattering state at the driving voltage of only about 2.7 V. And the contrast ratio can be achieved to exceed over 1000 at 3.6 V. But for the gel with concentration of 0.1 wt % of F8BT, no obvious scattering is observed. We speculate the reason why the LC gel with 0.2 wt % F8BT can exhibit better electro-optical properties could be due to the size of the LC multi-domain being most suitable for the scattering of the visible light. To further realize the anisotropic scattering properties of the supramolecular LC gel, the perpendicular transmittances ($T_{\perp}$) were measured by modulating the polarization direction of polarizer to be perpendicular with the rubbing direction of the cell. Figure 8b shows the $V-T$ curves of the LC gel with 0.2 wt % F8BT in parallel and perpendicular directions. Instead of the evident scattering occurred in the parallel direction, only slight scattering was observed as the light polarization perpendicular with the rubbing direction of cell. Besides, the initial transmittance in the parallel direction is slightly lower than that in the perpendicular direction because of the higher absorption along with the main chain of the F8BT molecule. The polarization efficiencies of these supramolecular LC gels with different F8BT concentrations are also shown in Table 1. The polarizing efficiency (PE) is calculated as follows:

$$\mathrm{PE} = (T_{\perp} - T_{\parallel})/(T_{\perp} + T_{\parallel}) \qquad (1)$$

Table 1. Electro-Optical Properties of the Supramolecular LC Gels with Different Concentrations of the F8BT Gelator

concentration of F8BT (wt %)	driving voltage (V)	maximum contrast ratio	maximum polarization efficiency
0.2	2.7	1170	860
0.4	2.9	355	264
0.6	3.2	44	32

The LC gel with 0.2 wt % F8BT demonstrates the best polarization efficiency at the voltage about 3.6 V. And the polarizing efficiency can be reached up to 860. The relationship between the transmittance and rotation angle was also investigated. The transmittance of the LC gels containing 0.2 wt % F8BT at the field-off (0 V) and field-on (3.6 V) states in a different rotation angle θ between the polarization direction of polarizer and the rubbing direction of cell are shown in Figure 8c. It can be seen in this figure that no obvious scattering occurs in the field-off state in all angles. As the voltage is applied to the cell, the gel displays the anisotropic scattering state due to the formation of oriented LC multi-domains. The maximum scattering is obtained when the polarization direction of the polarizer is parallel to the rubbing direction of the cell, while the minimum scattering occurs when the polarizer is set to be perpendicular to the rubbing direction of the cell. Therefore, the gel can be used as a switchable scattering polarizer whose field-on and field-off states can be controlled by an ultra-low voltage of only about 3 V. Figure 8d shows the transmittance spectrum of 0.2 wt % F8BT LC gel in the wavelength range from 400 to 800 nm. The transmittances were recorded as the polarization direction of polarizer was parallel to the rubbing direction of cell at field-off (0 V) and field-on (3.6 V) states. Although the transmittance of the gel has a little loss for the absorption at the 450 nm at the field-off state, the gel presents a low transmission state for a broadband range (500 nm−800 nm) as the electric field turns on. The rise and decay times of the supramolecular gel with the F8BT concentrations of 0.2, 0.4, and 0.6 wt % were obtained for (3, 90), (6, 58), and (10, 52) ms under 5 V bias voltage, respectively. The switching times of the supramolecular gel are influenced by the amount of the gelator F8BT, and the increase in the concentration of the F8BT polymers leads to longer rise time and shorter decay time because of stronger attraction from the oriented fibrous structure. Although the response time is not fast enough now, we consider that the problem could be solved by doping some nanoparticles or modulating a suitable cell gap in the near future.[47]

Figure 9 shows the transmittance−voltage curves of the supramolecular LC gels with 0.2, 0.5, and 1.0 wt % of F8BT in a 9 μm thick LC cell with unrubbed film. As the supramolecular LC gels formed in the cells with unrubbed polyimide film, we found that the gel exhibits an unstable light scattering phenomenon. The reason should be due to the formation of the random polymer network, as shown in Figure 4b, for the absence of the alignment interface. These fibrous fibers that induce the gel show the light scattering property in the field-off state for the formation of the LC multi-domains. However, with the lack of an alignment interface, the F8BT molecules were

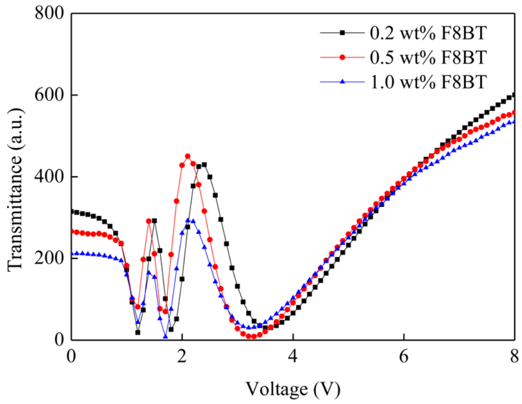

Figure 9. Transmittance−voltage curves of the supramolecular LC gels with 0.2, 0.5, and 1.0 wt % of F8BT in a 9 μm thick LC cell with unrubbed film. Without the aid of an alignment interface, the supramolecular LC gel exhibits unstable electro-optical properties.

randomly dispersed, such that the strongly $\pi-\pi$ stacking structure could not be formed after the sol−gel transition. It is believed that the $\pi-\pi$ interactions between the F8BT molecules and LC molecules become too weak to avoid the LC molecules rotating as the electric field turns on. Therefore, this supramolecular LC gel with random fibers is very unstable and has difficulty operating its electro-optical properties. To sum up, effectively combining the supramolecular π-conjugated gelator and LC molecules in a cell with rubbed alignment interface succeeds in generating a new kind of anisotropic scattering LC physical gel with ultra-low operating voltage and extremely high contrast ratio, which provides great possibility for application in various electro-optical devices such as tunable polarizers, transflective displays, and polarized light modulators.

4. CONCLUSION

In summary, we report a new type of supramolecular LC gels which are formed by the fibrous self-assembly of the polyfluorene-based polymer F8BT in nematic LC E7. This new material can form a functional physical network through the $\pi-\pi$ stacking interactions between the π-conjugated main chains of the F8BT molecules. As the molecular self-assembly occurs in the anti-parallel rubbed LC cell, the oriented fibrous aggregates induce the formation of the anisotropic fibers which are perpendicular to the director of the LC molecules. The rubbed interface between the LC molecules and polyimide layer greatly influence the characteristics of the LC physical gels. In the paper, we first report that the supramolecular LC physical gels with aligned π-conjugated fibrous structures exhibit significant anisotropic scattering. The incident light is highly scattering as the light polarization is parallel to the long-axis direction of LC molecules and the main-chain direction of the F8BT molecules. Opposite to the LC gels formed by low-molecular-weight gelators which need high voltage to drive LCs, the driving voltage required to switch the transparent and scattering states in the supramolecular LC gels is extremely low, only 2.7 V. In addition, the contrast ratio can be achieved as high as exceeding 1000. Although the response times of the supramolecular LC physical gels still need to improve, the excellent characteristics such as dramatically decreased driving voltage and high contrast ratio provide the possibility to be a promising candidate for use in transflective display technology and electrically switchable smart polarizer.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Results of representative DSC data (Figure S1), polarized PL spectra for samples prepared in cells without rubbing treatment (Figure S2), and the ^{1}H NMR spectroscopy of F8BT polymers in $CDCl_3$ with different temperatures (Figure S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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