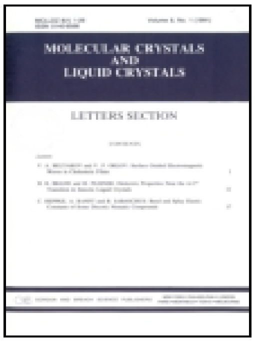

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The Function of Self-Assembled Polyfluorene-Based π-Conjugated Supramolecular Structures Formed in Twisted Nematic Liquid Crystals

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We demonstrate that the supramolecular structure can be formed through the fibrous self-assembly of the polyfluorene-based polymer F8BT in liquid crystal (LC) 5CB. With the utility of alignment layer, the F8BT molecules can be aligned and formed oriented polymer network. We found that the presence of oriented polymer network makes twisted nematic LC exhibit excellent electro-optical properties (EO) of driving voltage reduction and EO bump peak elimination. The polyfluorene-based supramolecular structure provides the function of stabilizing LC molecules. We consider this functional self-assembled network has potential to apply in various devices for the ability of improving performance in operating property.

Keywords Liquid Crystals; Physical Gels; π-Conjugated Gelator

1. Introduction

The supramolecular network structures formed by self-assembled gelator molecules in organic solvent have attracted significant attention in this decade [1–6]. The physical formation of fibrous aggregates of the organic gelators is induced by the non-covalent interactions such as hydrogen-bonding, π-π stacking and van der Waals force. In recent years, the fibrous supramolecular polymer network combining with the electrically switchable liquid crystal (LC) system have been developed as soft functional materials - LC physical gels [7–10]. The LC physical gels have been widely applied in various electro-optical devices, such as switchable scattering devices [11–14], LC semiconductors with high mobility [15,16], and stabilization of the orientation of ferroelectric LCs [17], etc. In particular, fast-response switching in twisted nematic (TN) cells based on the aid of fibrous polymer network have attracted more and more interests for their potential for improving the quality of LC displays (LCDs) [18–20]. However, there is no research discussing the properties of TN LC system with the supramolecular π-conjugated polymer network structure. In the prior work, we have already reported that the electrically switchable anisotropic scattering device with the properties of high contrast ratio and low operating voltage can be formed through assembling the supramolecular π-conjugated polymer network structure into the

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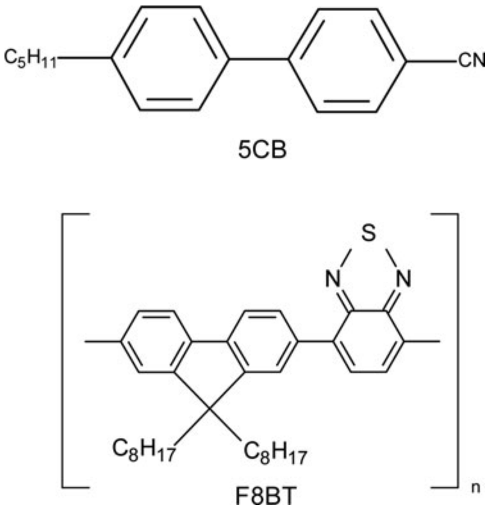

Figure 1. The molecular structures of LC host 5CB and π-Conjugated gelator F8BT.

nematic LC mixture E7 with anti-parallel alignment layers [14]. Therefore, we would like to know the function of the supramolecular π-conjugated polymer network structure which is formed in the TN LC systems.

In this paper, we found that the supramolecular π-conjugated polymer network can be formed in LC host 5CB through the self-assembly of the polyfluorene-based gelator F8BT. In addition, the oriented fibrous structures have been observed in a LC cell with mutually perpendicular alignment layer after the formation of the supramolecular LC gels. And this supramolecular functional polymer structure makes the TN LCs demonstrate fantastic electro-optical properties on reducing the electro-optical (EO) bump peak and the driving voltage which provide great applications in various electrically switchable devices.

2. Experimental Details

In our experiment, the LC gels were fabricated through the use of the nematic LC 5CB (clearing point about 35 °C) and the gelators molecule, poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT). And their molecular structures are shown in Figure 1a. They were purchased from Merck and Sigma-Aldrich, respectively. The gelator F8BT is a kind of polyfluorene-based π-conjugated molecule with average M_n 10,000–20,000.

To prepare the supramolecular LC physical gels, at first, a small amount of F8BT (0.1–1.6 wt%) was added into LC 5CB in glass bottles. Then these materials were uniformly mixed by stirring and gently heating in a hot plate. In the beginning, the LC mixtures of F8BT and 5CB displayed an opaque state in the room temperature. When the mixtures were heated to the temperature about 60°C, which is higher than the clearing point of 5CB, the mixtures became transparent for being isotropic liquid. To make sure the F8BT polymers can be well dispersed in 5CB, the mixtures were further heated at 90°C for 3h. And then the mixtures were cooled down slowly at a rate of 5 °C min^{-1}. As the temperature cooled down to required temperature, the mixtures became opaque again and formed the supramolecular LC gels.

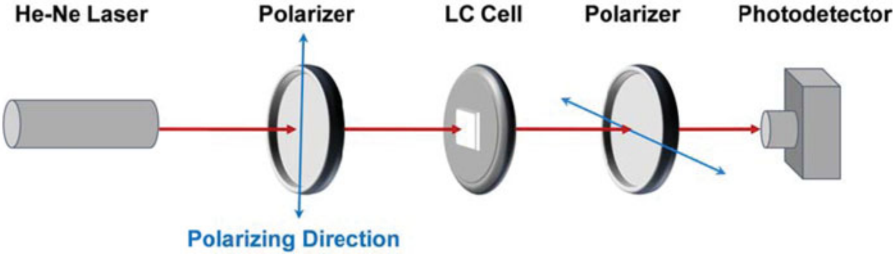

Figure 2. The illustration shows the setup of the electro-optical measurement system. The LC cell is placed between a pair of polarizers with mutually perpendicular polarizing directions for the operation of a normally white TN mode.

To understand the phase transition behavior of the supramolecular LC gels, the 5CB with different concentrations of F8BT polymers were examined. The sol-gel transition temperatures ($T_{\text{sol-gel}}$) of F8BT and the isotropic-nematic transition temperatures ($T_{\text{iso-ne}}$) of 5CB were determined by differential scanning calorimetry (DSC) measurements 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 the exothermic peaks occur in the DSC data, the transition temperatures of $T_{\text{iso-ne}}$ and $T_{\text{sol-gel}}$ can be obtained. The gels containing different concentrations of F8BT were prepared as described in previous procedures. Then the gels were injected into the 9 μm thickness glass sandwich cells with anti-parallel rubbed polyimide films or mutually perpendicular polyimide films. To make sure of 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. To verify the main-chain direction of the F8BT polymer in the cells with anti-parallel alignment layer, the polarized PL spectra (excitation light $\lambda_{\text{ex}} = 430$ nm) were further 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.

For researching the properties of the supramolecular polymer network in LC 5CB, the gels were injected into the 4.2 μm thickness indium tin oxide (ITO) coated glass sandwich cells with mutually perpendicular rubbed polyimide as alignment layers by the method described before. The detailed electro-optical properties of the supramolecular LC gels with different concentration of F8BT in TN cell are further measured by our experiment system shown in Figure 2. The system is composed of a He-Ne laser, a pair of polarizers, sample cell mounted in rotatable holder and the photodetector. An unpolarized He-Ne (632.8 nm) laser was used as an incident light source. At the beginning, the polarizers were tuned to be perpendicular to each other to make sure the transmittance minimum. Then the sample cell with LC gels was placed between the crossed polarizers and tuned to make the transmittance reach maximum. And the sample cell was driven by an AC field (1 kHz, square wave) supplied by the function generator SRS DS360 which was controlled by a computer with LabView programming. Then the transmittances under various applied voltage were recorded by the photodetector. The voltage required for reaching 90% and 10% transmittance relative to the initial light intensity was defined as driving voltage V_{90} and V_{10}, respectively. The contrast ratio is determined by the initial transmittance to

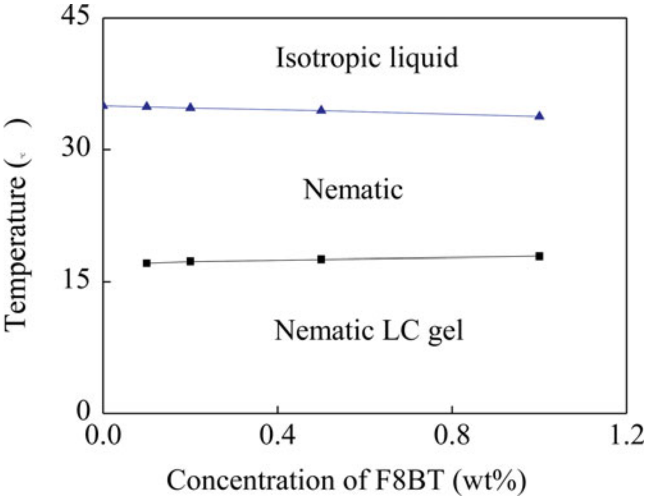

Figure 3. Phase diagram of the mixtures of 5CB and F8BT. The mixtures with different concentrations of 0, 0.1, 0.2, 0.5, and 1.0 wt% F8BT were prepared. The $T_{\text{sol-gel}}$ of F8BT and $T_{\text{iso-ne}}$ of 5CB are represented by ■ and ▲, respectively.

the transmittance under 3 V. And the data of rise time τ_{on} and the decay time τ_{off} were determined by measuring the response times needed for varying the transmittances 90–10% and 10–90% in the electric field on (5V) and off, respectively.

3. Results and Discussion

The phase behavior of the gels with different concentrations of F8BT was shown in Figure 3. The transition temperatures of the supramolecular LC gels were determined by the DSC measurements. In our experiments, the gels exhibit three states of isotropic liquid, nematic, and nematic LC gel in the phase diagram. And the mixtures undergo the isotropic-nematic transition of 5CB first and then sol-gel transition of F8BT upon cooling. It means that the F8BT molecules could be aligned through the template effect of the LC materials.

To confirm this assumption, the gels with different concentrations of F8BT were filled into a 9 μm empty LC cells with anti-parallel or perpendicular rubbed alignment layers in isotropic liquid state. After the cooling process described in the experimental section, we found that the anisotropic fibrous structures were formed in the LC cells through the observations with dark-field optical microscope. Figure 4(a) shows the dark-field optical picture of the cell with the gel containing 1.0 wt% of F8BT. The green self-assembled F8BT fibers parallel to the rubbing direction of the cell were observed in this figure. And Figure 4(b) shows the optical picture of the cell with mutually perpendicular alignment layer injected the gel containing 1.0 wt% of F8BT, the oriented polymer network can be observed.

Figure 5 shows the PL emission spectra ($\lambda_{\text{ex}} = 430$ nm) of the LC gel containing 0.1 wt% F8BT in the anti-parallel alignment cell. The measured PL polarization ratio of parallel to perpendicular intensity at 540 nm is around 3.4. This finding shows that the main-chain direction of F8BT molecules should align with the rubbing direction of cell, that is, the long-axis direction of LC molecules. This result is consistent with the phase behavior shown in Figure 3 since the $T_{\text{iso-ne}}$ is higher than $T_{\text{sol-gel}}$. Therefore, we

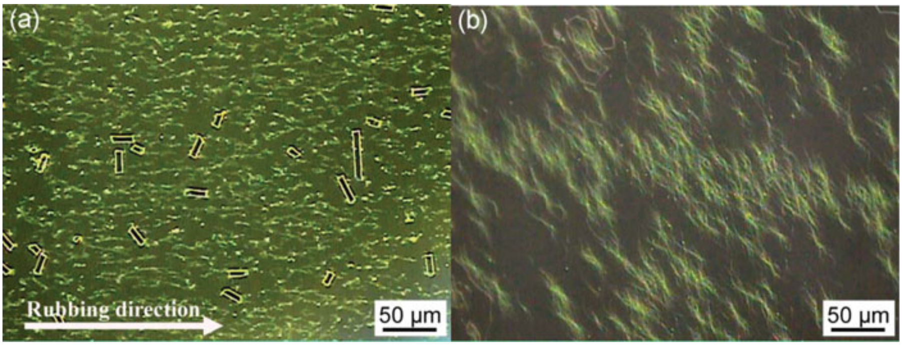

Figure 4. The dark-field optical pictures of F8BT/5CB gels containing 1.0 wt% of F8BT in 5CB LCs in the cell with (a) anti-parallel rubbed alignment layer and (b) mutually perpendicular rubbing treatment. The anisotropic self-assembled fibers of F8BT were found in the cells.

consider that the F8BT polymer should be aligned to the direction of LC molecules in the anti-parallel and TN cells, and then forms the anisotropic fibrous structures as shown in Figure 4. And then the electro-optical properties of the supramolecular LC gels in TN cells 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. With the formation of oriented supramolecular polymer structure, we found the LC 5CB demonstrates the effect of EO bump peak suppression and driving voltage reduction.

Figure 6 shows the voltage-transmittance (*V*-*T*) curves of the LC gels with different concentrations (0, 0.1, 0.2, and 0.4 wt%) of the gelator F8BT in TN cells. As the electric field is off, the gels present the bright transmission state. When the electric field turns on, the transmittance starts to decrease. However, there is a bump peak found clearly in transmittance in the case of pure LC 5CB. This bump peak would influence the performance

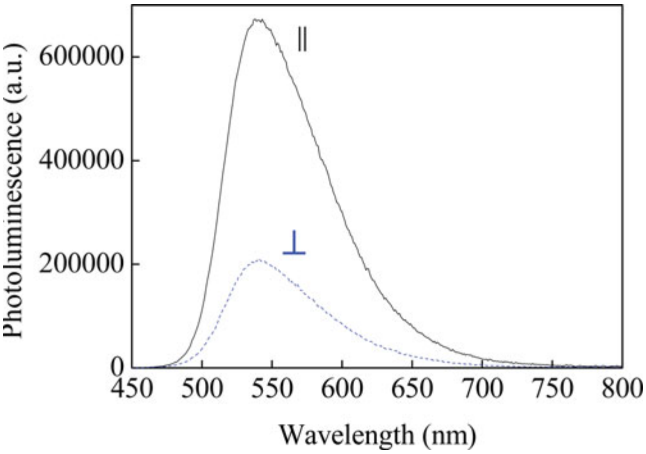

Figure 5. The polarized PL spectra of a LC gel containing 0.1 wt% F8BT in 5CB in the cell with anti-parallel alignment layers. The solid and dashed curves denote the PL spectrum as the polarizing direction of polarizer was parallel and perpendicular to the rubbing direction of the cell, respectively.

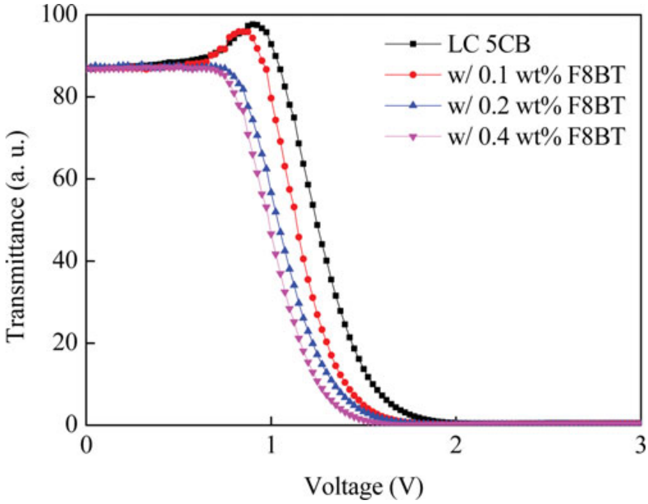

Figure 6. The transmittance-voltage curves of the 4.2 μm thick TN LC cells with the supramolecular LC gels containing 0, 0.1, 0.2, and 0.4 wt% of F8BT.

of the TN LC cells which is not the results we expected for the display applications. In our experiments, we found the bump peak could be eliminated due to the formation of self-assembled supramolecular structures of F8BT polymer in LC 5CB. As the concentrations of F8BT gelator reach 0.2 wt%, the bump peak is almost removed. It means that the fibrous structure can be used to stabilize the LC molecules by avoiding them to over-rotate during the operating process. And the bump peak would be further reduced with the increasing concentration of the F8BT gelator. Besides, with the remove of bump peak, we found the TN LCs exhibit the better EO performance with lower driving voltages and higher contrast ratios.

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 0.4 wt% F8BT polymer presents the best performance with the lowest driving voltage about 0.83 and 1.28 in V_{90} and V_{10}, respectively. And the contrast ratio can also be improved. In addition, the response times (switching times) of the supramolecular LC gel are only slightly influenced by the amount of the gelator F8BT. We can see that as the 0.1 wt% of F8BT gelator was added into LC 5CB, the response time would slightly rise. And as the higher concentrations of F8BT were used, the response times started to decrease. For the concentration of 0.4 wt% of F8BT in LC 5CB, the response time is compatible with the pure 5CB. Through the utility of polyfluorene-based π-conjugated polymer F8BT and

Table 1. The electro-optical properties of supramolecular LC gels containing 0, 0.1, 0.2, and 0.4 wt% of F8BT

Material Type	V_{90} (V)	V_{10} (V)	τ_{on} (ms)	τ_{off} (ms)	CR
5CB	1.10	1.58	1.77	10.50	243
w/ 0.1 wt% F8BT	1.00	1.43	2.20	12.68	332
w/ 0.2 wt% F8BT	0.88	1.35	1.87	12.28	460
w/ 0.4 wt% F8BT	0.83	1.28	1.79	10.47	435

rubbed surface, the oriented supramolecular structures induce the unique characteristic of EO bump suppression and voltage reduction.

4. Conclusions

In summary, we have reported that the supramolecular structure can be formed through the fibrous self-assembly of the polyfluorene-based polymer F8BT in nematic LC 5CB. And the F8BT molecules can be aligned and formed oriented polymer network by utility of alignment layer. The presence of oriented polymer network makes TN LC 5CB exhibit excellent EO properties such as driving voltage reduction and EO bump peak elimination. Further, the unique properties of the polyfluorene-based supramolecular structure provide the function of stabilizing LC molecules. Therefore, this functional self-assembled network has potential to apply in various devices for the ability of improving performance in operating property.

Acknowledgments

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References

[1] Abdallah, D. J. & Weiss, R. G. (2000). *Adv. Mater.*, *12*, 1237.

[2] Brotin, T., Utermöhlen, R., Fages, F., Bouaslaurent, H., and Desvergne, J.-P. (1991). *J. Chem. Soc., Chem. Commun.*, *6*, 416.

[3] Geiger, C., Stanescu, M., Chen, L. H., and Whitten, D. G. (1999). *Langmuir*, ;*15*, 2241.

[4] George, M. & Weiss, R. G. (2006). *Acc. Chem. Res.*, *39*, 489.

[5] Hanabusa, K., Hiratsuka, K., Kimura, M., and Shirai, H. (1999). *Chem. Mater.*, *11*, 649.

[6] van Esch, J. H. & Feringa, B. L. (2000). *Angew. Chem., Int. Ed.*, *39*, 2263.

[7] Guan, L. & Zhao, Y. (2000). *Chem. Mater.*, *12*, 3667.

[8] Kato, T. (2002). *Science*, *295*, 2414.

[9] Kato, T., Hirai, Y., Nakaso, S., and Moriyama, M. (2007). *Chem. Soc. Rev.*, *36*, 1857.

[10] Sangeetha, N. M. & Maitra, U. (2005). *Chem. Soc. Rev.*, *34*, 821.

[11] Janssen, R. H. C., Stumpflen, V., Broer, D. J., Bastiaansen, C. W. M., Tervoort, T. A., and Smith, P. (2000). *J. Appl. Phys.*, *88*, 161.

[12] Mizoshita, N., Suzuki, Y., Kishimoto, K., Hanabusa, K., and Kato, T. (2002). *J. Mater. Chem.*, *12*, 2197.

[13] Suzuki, Y., Mizoshita, N., Hanabusa, K., and Kato, T. (2003). *J. Mater. Chem.*, *13*, 2870.

[14] Chen, J. W., Huang, C. C., and Chao, C. Y. (2014). *ACS Appl. Mater. Interfaces*, *6*, 6757.

[15] Hirai, Y., Monobe, H., Mizoshita, N., Moriyama, M., Hanabusa, K., Shimizu, Y., and Kato, T. (2008). *Adv. Funct. Mater.*, *18*, 1668.

[16] Mizoshita, N., Monobe, H., Inoue, M., Ukon, M., Watanabe, T., Shimizu, Y., Hanabusa, K., and Kato, T. (2002). *Chem. Commun.*, *5*, 428.

[17] Tolksdorf, C. & Zentel, R. (2001). *Adv. Mater.*, *13*, 1307.

[18] Mizoshita, N., Hanabusa, K., and Kato, T. (1999). *Adv. Mater.*, *11*, 392.

[19] Mizoshita, N., Hanabusa, K., and Kato, T. (2003). *Adv. Funct. Mater.*, *13*, 313.

[20] Nair, G. G., Prasad, S. K., Jayalakshmi, V., Shanker, G., and Yelamaggad, C. V. (2009). *J. Phys. Chem. B*, *113*, 6647.