

Dynamic orientation of oligothiophenes in nematic liquid crystalline matrices

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Abstract

Polarized photoluminescence is observed from conjugated oligomers dissolved in nematic liquid crystalline matrices. In this host-guest system, conjugated oligomers (guest) exhibit an emission spectrum well separated from the emission of the liquid crystalline matrix (host). Therefore, the polarization of the photoluminescence spectrum in these systems is a well-defined measure of the orientation of the guest molecules (oligothiophenes) within the host matrix. The results clearly demonstrate the spontaneous orientation of the oligothiophenes along the director of the nematic matrix. Furthermore, upon applying an electric field perpendicular to the direction of the spontaneous orientation, the oligomers are dynamically reoriented (switched) with the host. This results in switching of the polarized photoluminescence.

Keywords: Oligothiophene; Dynamic orientation; Crystals; Nematic matrices

1. Introduction

The physical properties of conjugated polymer films are heavily influenced by the intrinsic disorder phenomena within the solid state structure. The fundamental reason for the large degree of disorder in macromolecular solids can be expressed in thermodynamic terms by the relation of the free energy for crystallization per mole of crystallizing unit, ΔF_c , as the sum of two opposing entities: the enthalpy of crystallization, ΔH_c , and the entropy, ΔS_c [1]:

$$\Delta F_c = \Delta H_c - T \Delta S_c \quad (1)$$

Compared to the enthalpy of crystallization in covalent, ionic or metallic solids, the enthalpy of crystallization in molecular solids is very weak, for it is based only on weak van der Waals intermolecular forces [1]. Opposing this fact, highly perfect crystalline polymeric solids have high entropies to pay for; e.g. the opportunity of disorder in a long chain with almost freely rotating segments is much higher than a small molecular covalent or ionic crystal. As a consequence of two unfavorable factors, low enthalpy of crystallization and high entropy cost of crystallization, the net free energy of crystallization per crystallization unit is very low in polymeric molecular solids [1]. This fact of built-in disorder, resulting in the Anderson localization and associated metal-

insulator (M-I) transitions is studied deeply in these heavily doped polymeric π -electron semiconductors (conducting polymers) [2-5]. With material quality getting better through high degree of uniformity of chemical coupling [6-8] as well as through controlled recrystallization from solutions in the doped conducting state [9] and further refining of the synthesis conditions, conducting polymers can now be prepared well on the metallic side of the disorder induced M-I transition [2,3,5]. Thus, creating macroscopic order within the conjugated polymeric structures has always been a continuing, important, scientific challenge.

The idea of using liquid crystalline host matrices for macroscopic orientation of guest molecules is quite well known (see, for example, [10] and Refs. therein). Araya et al. [11] showed that synthesis of polyacetylene in liquid crystalline matrices results in highly oriented materials. Furthermore, synthetic efforts of modifying the side chains of a conjugated polymer with liquid crystalline side groups have been reported in detail (see, for example, [12-20] and Refs. therein). Recently, polarized photoluminescence has been reported from liquid crystalline polymers with phenylenevinylene segments on the main chain [21]. Taliani et al. [22] reported on a liquid crystalline phase of the α -sexithienyl (T_6) above $T=312^\circ\text{C}$. Molecules such as thiophenes and bithiophenes embedded in liquid crystalline matrices have been investigated with nuclear magnetic resonance techniques to obtain accurate structural information [23,24].

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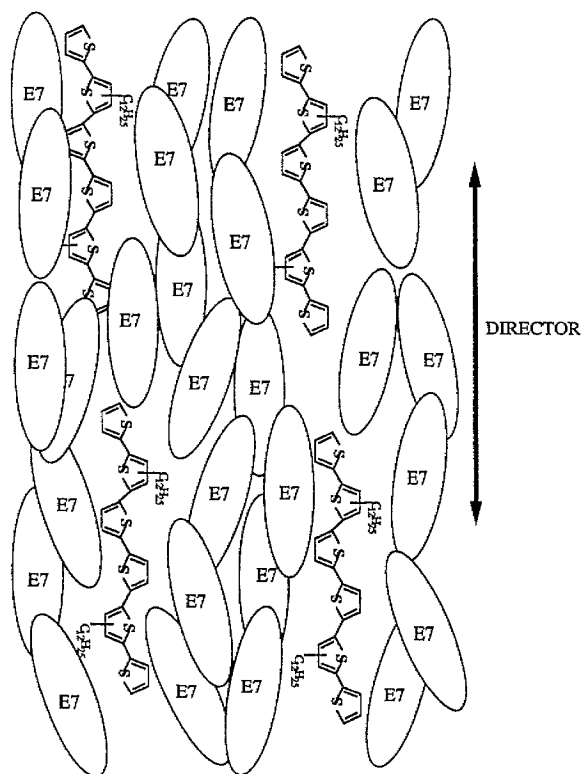


Fig. 1. Schematic illustration of the ordering of oligothiophenes (T_6) within a homogeneously aligned nematic liquid crystalline matrix.

In this contribution we report the macroscopic orientation of conjugated oligomers (six-membered oligothiophenes; e.g. T_6) dissolved within a nematic liquid crystalline matrix (Fig. 1). The orientation of the oligothiophenes can be dynamically switched with the host nematic matrix upon application of an electric field, as observed through switching of the polarized photoluminescence of T_6 .

2. Experimental

The six-membered oligothiophene used in the present study carries dodecyl substituents on different thiophene rings and is designated as T_6 d(2,5). The synthesis has been described previously [25,26]. The room temperature nematic liquid crystal E7 (clearing point 60.5 °C, $\Delta\epsilon = 13.8$ at 1 kHz, $\Delta n = 0.224$ at 589 nm) was obtained from EM Industries, Hawthorne, NY, and used as received.

The solution was prepared by dissolving 3.5 mg T_6 in 1 ml E7 by slightly heating above the clearing point and magnetically stirring. The solutions are clear in the isotropic phase.

The 10 μm (1 cm^2) liquid crystal display cells were purchased from Displaytech Inc., Boulder, CO. The inner walls of the cells were coated with polyimide and treated to give surface orientation. The filling of the cells was simply obtained using the capillary forces of the two filling holes. After uniform filling, the cells were sealed using epoxy resin on the filling holes and electrically contacted with silver paste.

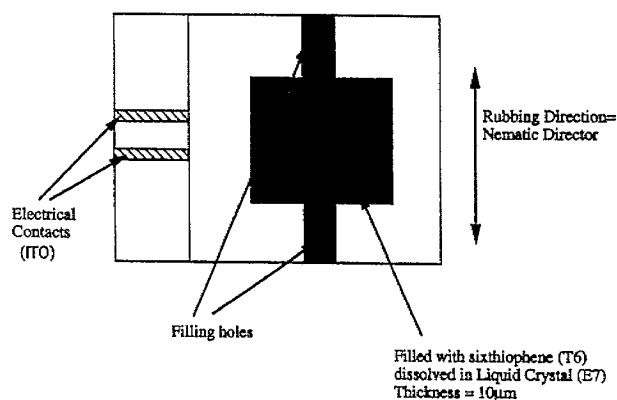


Fig. 2. Top view of the commercial liquid crystalline cells used in this study. The cells contained indium-tin oxide (ITO)-coated glass substrates with a 10 μm spacer. The inner surfaces were rubbed using polyimide coatings to achieve homogeneous alignment. The rubbing direction, thus the nematic director, is parallel to the surface alongside the filling holes.

The schematic description and the geometry of the cells are displayed in Fig. 2.

Absorption studies were carried out using a Perkin Elmer Lambda 9 spectrophotometer. For photoluminescence excitation profile studies a SPEX Fluorolog emission spectrophotometer was used. For all other emission studies an argon ion laser (457.9 nm) incident on the sample was used, whereas the emission was collected and analyzed through a single monochromator equipped with a Si detector. All experiments were carried out at room temperature.

3. Results and discussion

The liquid crystal cells filled with the solutions of T_6 in E7 show uniform brightness under the cross-polarized microscope suggesting a homogeneous alignment of the liquid crystals. To estimate the achieved degree of homogeneous alignment of T_6 in the nematic matrix we performed linear dichroism experiments using polarized linearly optical absorption and emission. Fig. 3 shows the optical absorption recorded with a polarizer parallel and perpendicular to the rubbing direction, respectively. The guest molecules are aligned with the director parallel to the surface of the cell alongside the rubbing direction, as demonstrated in this figure. A degree of absorption polarization at the maximum of the $\pi-\pi^*$ optical absorption band of T_6 , $N_A = OD_{\text{par}} / OD_{\text{perp}} > 3.5$, could be easily achieved. This result demonstrates that the guest molecules (oligothiophenes) can be spontaneously aligned with the homogeneous alignment of the host (liquid crystal) matrix. Since the $\pi-\pi^*$ absorption of the oligothiophenes is polarized alongside the molecule backbone, the guest molecules are aligned parallel to the director of the nematic host.

Investigations of the photoluminescence of the system strongly confirm the results of the dichroic experiments. Fig. 4 shows the polarization dependence of the emission spectra. The emission spectrum of T_6 obtained by exciting

and probing parallel to the rubbing direction (parallel to the director of the nematic matrix) is an order of magnitude stronger than the case where excitation and emission are perpendicular to the director. Since the active emission originates from the guest molecules, T_6 , this result confirms the orientation of the guest within the nematic host.

Fig. 5 shows the excitation profile of the photoluminescence at 550 nm (maximum of the π - π^* emission band of T_6) together with the total luminescence of the host-guest system excited at 350 nm. The excitation maximum at 450 nm reflects the optical absorption of the guest (T_6). However, the high energy maximum in the excitation profile at around 350 nm originates from the absorption of the host nematic E7 as confirmed in reference studies. This result suggests a rapid excitation transfer from the nematic host to the guest. The details of this excitation transfer are not yet known. However, due to the luminescence of the nematic host at around 400 nm (as confirmed in the reference studies without

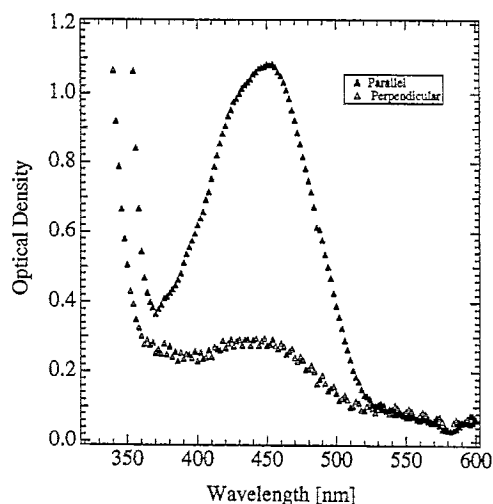


Fig. 3. Optical absorption dichroism of T_6 in E7 (10 μm cell) obtained through a polarizer parallel and perpendicular to the rubbing direction (nematic director).

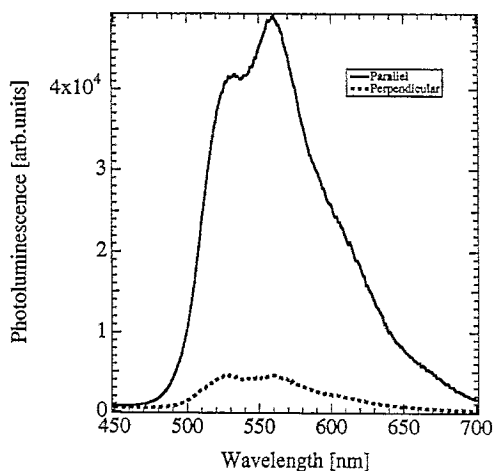


Fig. 4. Photoluminescence dichroism of T_6 in E7 (10 μm cell) obtained through a polarized excitation and emission, both parallel and perpendicular to the rubbing direction (nematic director), respectively.

T_6), it is likely that an emission-reabsorption process is responsible for this excitation transfer.

After demonstrating the spontaneous, homogeneous alignment of the T_6 guest molecules within the nematic host matrix, we studied the dynamic reorientation. In an electric field a torque is generated which tries to orient the spontaneously ordered domains in such a way that the axis of maximum dielectric polarizability of the liquid crystal is parallel to the field direction [10]. In the case of a positive dielectric anisotropy the directors of the spontaneously ordered domains are rotated in a direction parallel to the electric field [10]. Homogeneously ordered bulk samples can be easily prepared in d.c. field strengths of the order of 10^4 V/cm.

As shown in Fig. 6, the T_6 molecules embedded into the E7 nematic host matrix can be dynamically reoriented by applying an electric field to the liquid crystal cells filled with the solutions. The π - π^* emission of T_6 is quenched by an order of magnitude upon applying an electric field of 18 V per 10 μm thickness. Since the excitation and emission polar-

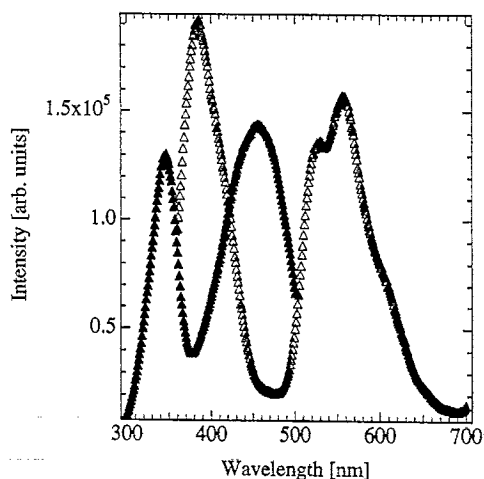


Fig. 5. Excitation profile for the emission T_6 in E7 at 550 nm (filled triangles) and emission spectrum for an excitation at 350 nm (unfilled triangles) of T_6 and E7 (10 μm cell).

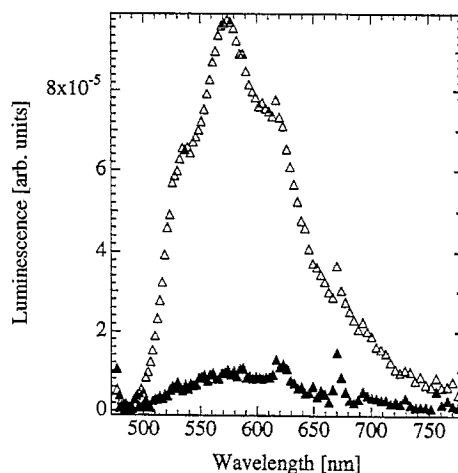


Fig. 6. Emission of T_6 in E7, excited and probed parallel to the rubbing direction with no E field (unfilled triangles) and with an applied E field of 18 V per 10 μm (filled triangles).

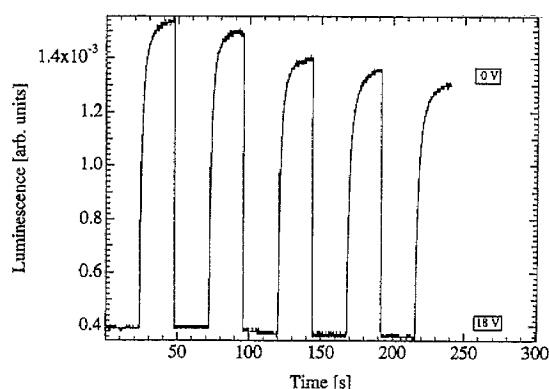


Fig. 7. Switching of the photoluminescence of T_6 in E7 by switching an electric field (18 V/10 μm) on and off.

izations in this figure are chosen parallel to the rubbing direction, which results in maximum photoluminescence without E field, the quenching of the photoluminescence by the field is attributed to the reorientation of the T_6 molecules parallel to the electric field, i.e. perpendicular to the excitation and emission polarizations. This process is reversible which is demonstrated in Fig. 7 by monitoring the emission upon switching the field on and off. Response time of the switching by turning the E field on is quite fast ($t_{\text{on}} \ll 1$ s). On the other hand, the relaxation back to the homogeneous alignment by turning the field off is quite slow (t_{off} is in the order of several seconds).

4. Conclusions and outlook

The possibility that an extended conjugated oligomer can be macroscopically aligned by simply embedding in a liquid crystalline matrix and utilizing the properties of the host has been demonstrated. This opens up areas for detailed studies of the properties of conjugated oligomers and polymers using, for example:

- (i) optical dichroism to obtain polarization information on the excited states;
- (ii) high resolution nuclear magnetic resonance spectroscopy to get anisotropic interactions;
- (iii) electron spin resonance to determine detailed parameters of the radical ions (polarons) and triplet states by doping and photoexcitation, respectively.

Furthermore, the combination of the liquid crystalline display technologies with the emerging new area of conjugated polymer light-emitting diodes is interesting.

Finally, the study of the photoinduced electron transfer from conjugated polymers onto C_{60} [27–31] within liquid crystalline matrices is promising for photonics applications [32–34].

Dedication

This paper is dedicated to Alan J. Heeger on the occasion of his 60th birthday.

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I should like to thank Alan J. Heeger for giving me the possibility of conducting scientific research within the distinguished Institute for Polymers and Organic Solids at UCSB. His encouragement and support, as well as his broad knowledge and scientific intuition, have been most valuable. I am sure he will inspire many more oncoming scientists in our field as he has done for me.

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