

# Polarized photoluminescence of oligothiophenes in nematic liquid crystalline matrices

**Citation for published version (APA):**

Sariciftci, N. S., Lemmer, U., Vacar, D., Heeger, A. J., & Janssen, R. A. J. (1996). Polarized photoluminescence of oligothiophenes in nematic liquid crystalline matrices. *Advanced Materials*, 8(8), 651-653.  
<https://doi.org/10.1002/adma.19960080810>

**DOI:**

[10.1002/adma.19960080810](https://doi.org/10.1002/adma.19960080810)

**Document status and date:**

Published: 01/01/1996

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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## Polarized Photoluminescence of Oligothiophenes in Nematic Liquid Crystalline Matrices\*\*

By N. Serdar Sariciftci,\* Uli Lemmer, Dan Vacar, Alan J. Heeger,\* and Rene A. J. Janssen

The idea of using liquid crystalline host matrices for macroscopic orientation of guest molecules is quite well known.<sup>[1]</sup> Araya et al. showed that synthesis of polyacetylene in liquid crystal matrices results in highly oriented

materials.<sup>[2]</sup> Furthermore, conjugated polymers synthesized with liquid crystalline side groups have been reported in detail.<sup>[3–11]</sup>

Recently, polarized photoluminescence has been reported from liquid crystalline polymers with phenylenevinylene segments on the main chain.<sup>[12]</sup> Taliani et al. reported a liquid crystalline phase of  $\alpha$ -sexithienyl ( $T_6$ ) above  $T = 312^\circ\text{C}$ .<sup>[13]</sup> Molecules such as thiophenes and bithiophenes embedded in liquid crystalline matrices have been investigated with nuclear magnetic resonance techniques to obtain accurate structural information.<sup>[14,15]</sup>

In this contribution, we report the macroscopic orientation of the conjugated oligothiophene,  $\alpha$ -sexithienyl ( $T_6$ ) dissolved in a nematic liquid crystalline matrix (Fig. 1). The

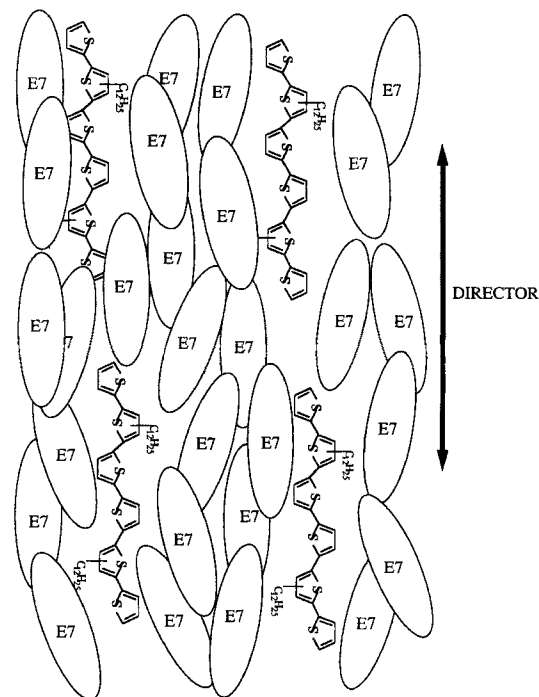


Fig. 1. Schematic illustration of the ordering of oligothiophenes ( $T_6$ ) within a homogeneously aligned nematic liquid crystalline matrix.

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  $T_6$ . This simple procedure to achieve macroscopic orientation in conjugated oligomers and polymers can be utilized to study the anisotropic absorption and emission of this class of materials.

The six-thiophene oligomer used in the present study carries dodecyl substituents on different thiophene rings (see Fig. 1) and is formally designated as  $T_6$  d(2,5). The synthesis has been described previously.<sup>[16,17]</sup>

Liquid crystal cells filled with the solutions of  $T_6$  in E7 show uniform brightness in a cross-polarized microscope, suggesting a homogeneous alignment of the liquid crystals. To estimate the achieved degree of homogeneous alignment

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[\*\*] We acknowledge Philips Research Laboratories for generously providing the oligothiophenes synthesized by W. ten Hoeve, H. Wynberg, E. E. Havinga, and E. W. Meijer. Valuable experimental help of Jim Bourassa, Mark Urish, and Günther Ahlers is gratefully acknowledged. The research at UCSB was supported by the National Science Foundation under DMR9300366.

of  $T_6$  in the nematic matrix we performed linear dichroism experiments using linearly polarized optical absorption and emission. Figure 2 shows the optical absorption recorded with a polarizer parallel and perpendicular to the rubbing direction, respectively. The guest  $T_6$  molecules are aligned

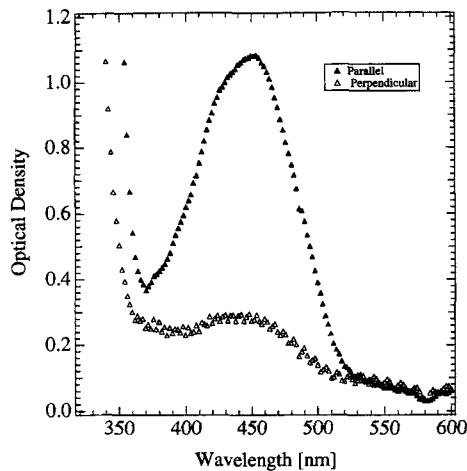


Fig. 2. Optical absorption dichroism of  $T_6$  in E7 (10  $\mu\text{m}$  cell) obtained through a polarizer parallel and perpendicular to the rubbing direction (nematic director).

with the director parallel to the surface of the cell, and parallel to the rubbing direction. A degree of absorption polarization at the maximum of the  $\pi$ - $\pi^*$  optical absorption band of  $T_6$ ,  $N_A \sim OD_{\text{par}}/OD_{\text{perp}} > 3.5$  could easily be 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 parallel to the molecular backbone, the guest molecules are aligned parallel to the director of the nematic host.

Investigations of the photoluminescence of the system confirm the results of the dichroic absorption experiments. Fig. 3 shows the polarization dependence of the emission

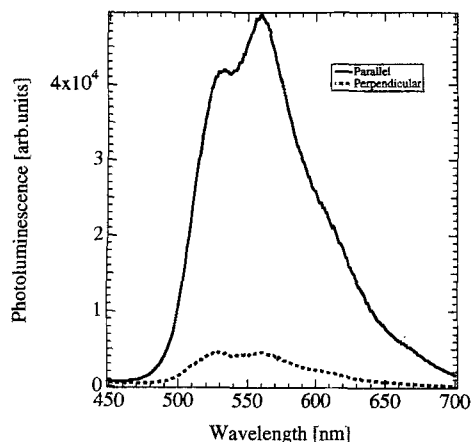


Fig. 3. Photoluminescence dichroism of  $T_6$  in E7 (10  $\mu\text{m}$  cell) obtained through polarized excitation and emission, both parallel and perpendicular to the rubbing direction (nematic director), respectively.

spectrum. 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 compared with 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.

Figure 4a shows the excitation profile of the photoluminescence at 550 nm (maximum of the  $\pi$ - $\pi^*$  emission band of  $T_6$ ). Figure 4b shows the total luminescence spectrum of the

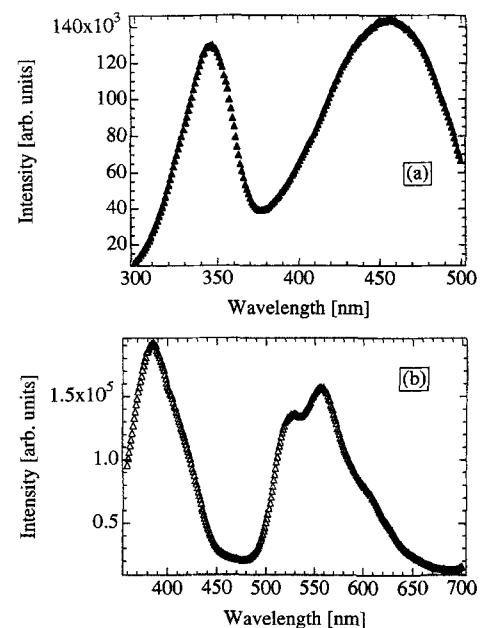


Fig. 4. a) Excitation profile for the emission of  $T_6$  in E7 at 550 nm (solid triangles) and b) emission spectrum for pumping at 350 nm (open triangles) of  $T_6$  and E7 (10  $\mu\text{m}$  cell).

host-guest system while pumping at 350 nm. The excitation maximum at 450 nm arises from 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.

Since the emission from  $T_6$  can be pumped through absorption by the nematic host, there is a relatively rapid excitation transfer from the nematic host to the guest. The details of this excitation transfer are not yet known. However, because the luminescence of the nematic host is directly observed at around 400 nm (and confirmed in the reference studies without the  $T_6$ ), it is likely that an emission-reabsorption process is responsible for the excitation transfer.

After demonstrating the spontaneous, homogeneous alignment of the  $T_6$  guest molecules within the nematic host matrix, we studied the dynamic re-orientation. 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.<sup>[1]</sup> 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.<sup>[1]</sup> Homogeneously ordered bulk samples can easily be prepared using dc field strengths of the order of  $10^4 \text{ V cm}^{-1}$ .

As shown in Fig. 5, the  $T_6$  molecules embedded in the E7 nematic host matrix can be dynamically reoriented by applying an electric field to the liquid crystal cells filled with the solutions. The  $\pi$ - $\pi^*$  emission of  $T_6$  is quenched by an

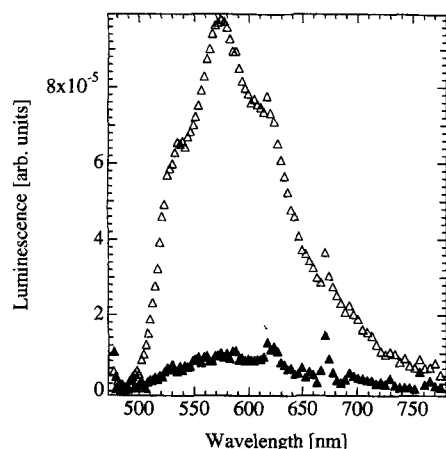


Fig. 5. The emission of  $T_6$  in E7, excited and probed parallel to the rubbing direction with no electric field (empty triangles) and with an applied electric field of 18 V per  $10 \mu\text{m}$  (solid triangles).

order of magnitude upon applying an electric field of 18 V per  $10 \mu\text{m}$  thickness. Since the excitation and emission polarizations in this Fig. 5 are chosen parallel to the rubbing direction, resulting in maximum photoluminescence without the electric 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, as demonstrated in Fig. 6, by monitoring the emission upon switching the field on and off. The response time of the switching after turning on the electric field is relatively fast ( $t_{\text{on}} < 1$  sec). On the other hand,

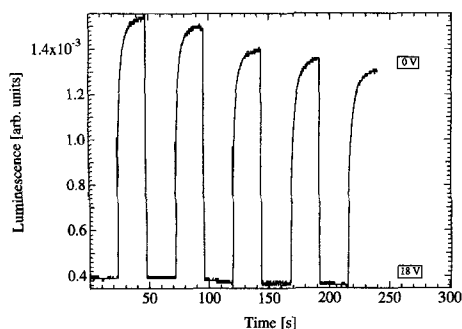


Fig. 6. The switching of the photoluminescence of  $T_6$  in E7 by switching on and off of an electric field (18 V per  $10 \mu\text{m}$ ).

the relaxation back to the homogeneous alignment when the field is turned off is somewhat slower ( $t_{\text{off}} \approx$  several seconds).

The possibility of an extended conjugated oligomer being macroscopically aligned by simply embedding in a liquid crystalline matrix and utilizing the properties of the host has been demonstrated. This opens up new areas of detailed studies of the properties of conjugated oligomers and polymers using, for example, optical dichroism to get polarization information on the excited states, high resolution nuclear magnetic resonance spectroscopy to get information on anisotropic interactions, and electron spin resonance to get detailed parameters of the radical ions (polarons) and triplet states by doping and photoexcitation.

Furthermore, the potential combination of liquid crystalline display technologies with the conjugated polymer light emitting devices is interesting. Finally, photoinduced electron transfer from conjugated polymers onto  $C_{60}$ <sup>[18–22]</sup> in liquid crystalline matrices will be of potential use in photonics applications.<sup>[23–25]</sup>

### Experimental

The room temperature nematic liquid crystal E7 (clearing point  $60.5^\circ\text{C}$ ,  $\Delta\epsilon \sim 13.8$  at 1 kHz,  $\Delta n = 0.224$  at 589 nm) was obtained from EM Industries, Hawthorne New York, and used as-received. Solutions were prepared by dissolving up to 3.5 mg  $T_6$  in 1 mL E7 by heating just above the clearing point and magnetic stirring. The solutions are clear in the isotropic phase.

Liquid crystal display cells ( $10 \mu\text{m}$  thickness,  $1 \text{ cm}^2$  area) were purchased from Displaytech Inc., Boulder Colorado. The inner walls of the cells were coated with polyimide and treated to give surface orientation. After uniform filling through the two filling holes (using the capillary forces), the cells were sealed using epoxy resin. Electrical contacts to the indium–tin–oxide electrodes were made with silver paste.

Absorption studies were carried out using a Perkin Elmer Lambda 9 spectrophotometer. Photoluminescence excitation profiles were obtained with a SPEX Fluorolog emission spectrophotometer. For all other emission studies, an Argon ion laser (457.9 nm) was used to pump the sample while the emission was collected and spectrally resolved using a single grating monochromator equipped with a Si detector. All experiments were carried out at room temperature.

Received: March 27, 1996.

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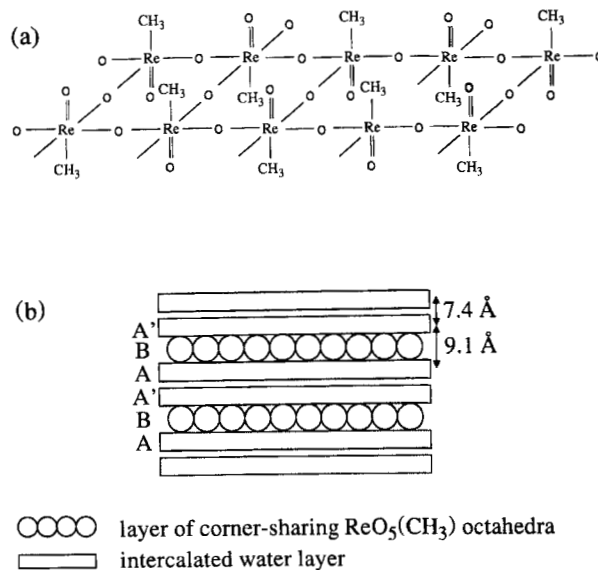
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## Scanning Probe Microscopy of Polymeric Methyltrioxorhenium\*\*

By Mike R. Mattner, Wolfgang A. Herrmann,\* Rüdiger Berger, Christoph Gerber, and Jim K. Gimzewski

The synthesis and properties of organometallic compounds in solid state chemistry are still at the exploratory stage. Progress in this field is highly desirable technologically because organometallic precursors cover virtually all the metallic elements and are accessible to electronic and steric tailoring. Recently, we reported the synthesis of the first known polymeric organometallic oxide, which has the empirical formula  $\{H_{0.5}[(CH_3)_{0.92}ReO_3]\}_\infty$  **1**, from the monomeric precursor compound methyltrioxorhenium(VII) (MTO).<sup>[1–4]</sup> The structure of this polymer, called poly-MTO for simplicity, is best described in terms of double layers of corner-sharing  $CH_3ReO_5$  octahedra (AA') (Scheme 1a) with intercalated water molecules (B) in a AA'BAA'... layer sequence (Scheme 1b).

The interest in poly-MTO results not only from its structural novelty but also from its unusual properties. For example, a unique pressure-induced depolymerization is observed if the polymer is compressed to  $\approx 150$  bar.<sup>[1]</sup> Expanded to atmospheric pressure, crystallites of the monomeric MTO grow within days. This behavior indicates



Scheme 1. Structure of polymeric methyltrioxorhenium.

a subtle equilibrium between the solid state forms of the monomer and polymer.

Early in the discovery of **1**, the remarkable possibility of depolymerization with chelating ligands in water was discovered.<sup>[5]</sup> Using the polymerization–depolymerization process in an acetate-buffered MTO solution, thin layers of **1** can be produced on glass surfaces. This is an important thin-film preparation method with possible future applications. We suggest that the system MTO–poly-MTO forms a new concept for bistable systems, triggered by temperature changes and consisting of solid and dissolved species. Poly-MTO is a member of a family of intercalation compounds in which the water layer in **1** is a guest in the lamellar host lattice. Since similar layered materials exhibit superconductivity,<sup>[6]</sup> the exchange of water with other intercalates may provide a synthetic route to new superconductors.

The structural details of **1**, shown in Scheme 1, were derived by several methods, and in particular by powder diffraction techniques.<sup>[1]</sup> Despite concerted attempts, single crystals of **1** have not been grown to date. It was found, however, that small regions of poly-MTO are crystalline, whereas most areas are amorphous.<sup>[1]</sup> Further progress in characterizing these polymeric crystallites was achieved using scanning probe microscopy (SPM), as described below. SPM techniques are routinely used to characterize surface topography and allow non-destructive characterization under ambient conditions. The latter condition is important because other methods employing UHV conditions can partially remove the intercalated water and hence alter the structure. Owing to the presence of intercalated water layers, the spacings of different poly-MTO layers are not known exactly and have not been visualized in real space. SPM techniques permit direct analysis of the spacing between layers of poly-MTO under ambient conditions.

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[\*\*] This work was supported by the Swiss National Science Foundation, the Kommission zur Förderung der wissenschaftlichen Forschung, and the Fonds der Chemischen Industrie (Ph.D. scholarship for M. R. M.). The support of H. Güntherodt (University of Basel) is gratefully acknowledged.