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Molecular alignment effects on spectroscopic properties 2,1,3-benzothiadiazole gusted in liquid–crystalline compounds

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ABSTRACT

This Letter reports about the molecular alignment effects on absorbance and emission properties of a new compound based on 2,1,3-benzothiadiazole gusted in liquid crystals. The molecular ordering is available for different chromophore concentrations. Despite of the increasing in molecular disorder above the concentration of 0.20%, samples always present a high degree of linear polarization in fluorescence. A considerable amount of polarized emission is observed during the isotropic phase ($T > 58$ °C), which is attributed to emission of light by aligned molecules before losing the coherence among them. Finally, we demonstrate the feasibility of ellipsometry technique to investigate phase transitions in fluorescent systems.

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1. Introduction

Liquid crystals are a class of molecular materials widely used in many fields of technological applications, e.g., from their most common use in flat-panel displays [1] to their employment as soft materials in supramolecular assembly [2]. The design of novel thermotropic liquid crystals as advanced functional materials involves suitable selection of a core fragment, linking group and edge moieties with terminal functionality. For many years, a large number of liquid–crystalline compounds containing heterocyclic units have been synthesized [3–5]. Heterocycles are of great importance as core units in thermotropic liquid crystals due to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [6]. Interest in highly π -conjugated liquid crystal molecules containing heterocycles [7] has increased enormously over the past few decades due to the possibility of using them in organic light emitting diodes (OLEDs) [8,9], where electron-deficient heteroaromatic rings can potentially offer good charge-transport properties, allied to their inherent self-organization ability and strong fluorescence. Luminescent liquid crystals are also of great interest [10], since their self-organizing properties can be exploited to achieve linearly polarized electroluminescence for emissive displays [11]. 4,7-Disubstituted 2,1,3-benzothiadiazole derivatives are efficient fluorophores which are able to afford well-ordered crystal structures. Main chain conjugated polymers

containing such unit has shown excellent charge-transport and electroluminescence properties [12]. For the last application, a particular interest is focused on finding molecules that present polarized light emission as a result of the molecular alignment. Recent studies have shown that polarized light emission can be obtained from anisotropic thin films of organic molecules [13] and also from aligned molecules in a liquid crystal medium [14]. This system shows strong polarized absorption and emission with useful applications. Therefore, guest–host (solute–solvent) interactions in liquid crystal solvents have been the subject of much interest in recent years. Homogeneously oriented nematic liquid crystals are highly suited as anisotropic solvents for polarized spectroscopy.

In this work, we investigate the molecular alignment effect on the absorbance and emission properties of a new fluorescent molecule based on 2,1,3-benzothiadiazole gusted in aligned liquid crystals samples. The dye molecules present isometric forms similar to the nematic liquid crystal matrix, exhibiting liquid crystal behavior at high temperatures ($T > 185$ °C) and strongly fluorescence, in the red region, in both solution and solid state structures. The compound (guest) was dissolved in a commercial liquid crystal (host), where it tends to adopt the liquid crystal director configuration. By using treated cells built with rubbed polymer substrates it was possible to align the liquid crystal medium aiming to obtain the anisotropic organization of the emitting molecules. To completely characterize the polarization state of the emitted light, we performed ellipsometry experiments in the scope of the Stokes' theory for electromagnetic field in association with polarized photoluminescence and absorbance measurements. Moreover,

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polarized emission, with polarization degree of around 38%, was observed in the liquid crystal isotropic phase (above 58 °C). This behavior was attributed to the emission of light by aligned molecules before losing the coherence between them, by molecular misalignment processes [15]. In addition, we have also verified the feasibility of ellipsometry technique, through the analysis of the polarization factor, to investigate transitions from ordered to no-ordered structures in fluorescent systems.

2. Experimental section

The benzothiadiazole compound used was 4,7-Bis[2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl]-[2,1,3]-benzothiadiazole whose synthesis route is described in Ref. [16], and the structure is shown in the inset of Fig. 1. To prepare the samples, the compound was dissolved at different molar concentrations (0.0125%, 0.025%, 0.075%, 0.15%, 0.20%, and 0.25%) in a commercial liquid crystal E7, purchased from Merck. Solutions were introduced by cells capillaries to induce molecular alignment. Cells were prepared using unidirectional rubbed polyvinyl alcohol (PVA) substrates, leaving a gap of 20 μm with mylar spacers. PVA films were produced by spinning a solution of 2 wt.% in water at 3000 rpm for 30 s, resulting in a very homogeneous thin film. The films were then unidirectionally rubbed with soft velvet, a well known procedure for inducing homogeneous planar alignment of liquid crystals in the rubbing direction [17].

The liquid crystal orientation was checked with and without the doping compound, through the use of a polarizing microscope. In both cases a homogenous alignment was observed along the rubbing direction of the PVA substrates. Although, the liquid crystal orientational order parameter was not measured for the samples without the benzothiadiazole compound, we got the care of systematically treat the cells in the same conditions in order to assure that the observed differences are related only to changes in the dye concentration.

The absorbance spectra in the UV–vis region was obtained with a homemade assembly, using an Ocean Optics' deuterium-tungsten lamp model DTmini as light source. The transmitted light was acquired by a USB2000 Ocean Optics CCD spectrometer. For polarized absorbance measurements, a polarizer was inserted between the light source and the sample. In the photoluminescence (PL) experiments, the samples were excited to near front-face configuration, with a spectra Physics Inc.' Argon ion laser, model Stablite 2017, at 457 nm (2.71 eV). The emitted light was guided by a set of lenses into the USB2000 Ocean Optics spectrometer. A

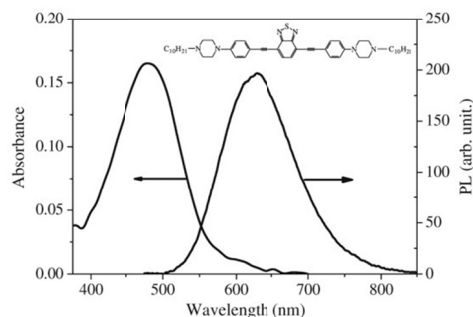


Fig. 1. Non-polarized absorbance, and photoluminescence spectra for sample with concentration of 0.025% of benzothiadiazole. The inset shows the molecular structure of the benzothiadiazole compound 4,7-Bis[2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl]-[2,1,3]-benzothiadiazole.

low pass filter, with cutoff at 475 nm, was placed in front of the spectrometer to eliminate the excitation wavelength. Polarized photoluminescence measurements were performed, inserting a polarizer in front of the spectrometer and pumping the films with horizontal and perpendicular polarizations in relation to the liquid crystal orientation (rubbing direction).

Although well described in previous manuscripts [18], we summarized here few details about the experimental setup used in the ellipsometry measurements. A quarter-wave plate was inserted just after the collecting lens set used in the previous setup employed to measure the luminescence signal, while a fixed polarizer was placed in front of the spectrometer entrance, and used as an analyzer. The films were placed in a perpendicular plane to the optical path of the emitted light. In a way that the luminescence, guided by the lens set, passed through the quarter-wave plate (633 nm) and the polarizer, before reaching the spectrometer. Furthermore, the compensator was mounted on a goniometer which enabled us to rotate the axis of the wave plate, from 0° to 360° around the axis parallel to the optical path of the emitted light, in steps of 10°. To perform ellipsometry measurements with temperature variation, we employed the same system described above, by placing the samples in a homemade heating system with a temperature control precision of 1 °C.

3. Results and discussion

Fig. 1 presents the typical absorbance and photoluminescence spectra of the benzothiadiazole compound in molar concentration of 0.025%. The absorption and emission line shape does not change significantly with the chromophore concentration. Such fact means that the intermolecular interaction between the benzothiadiazole molecules and their interaction with the liquid crystal E7 molecules do not affect the electronic structure of the dye molecules for a molar concentration below 0.25%. It is worth to mention that the concentration of 0.25% is the upper limit for the compound solubility in this guest/host system. In general, the absorbance band ranges from 400 to 600 nm being assigned to chromophores $\pi \rightarrow \pi^*$ transitions. The PL spectrum is located in the red region of the spectrum and presents a Stokes shift ca. 155 nm. When compared with the Stokes shift presented by the compound in solution, we have a 14 nm red shifted spectra (from Ref. [16] we have that the Stokes shift of the chromophore in chloroform solution is ca. 141 nm). This effect is related to the stronger interaction between the liquid crystal and the dye, and it is understood as a perturbation of the ground and excited state energy levels by the polarity of the solvent [19].

Aiming the verifying of the dye ordering, we carried out the polarized absorbance measurements depicted in Fig. 2a. It shows the spectra acquired for sample with 0.025% compound concentration. A_{\parallel} (A_{\perp}) is the absorbance intensity obtained when the samples are excited with parallel polarized light (perpendicular) to the liquid crystal alignment direction. It is clear that the line shape of the absorbance spectrum obtained with polarized light at perpendicular direction (A_{\perp}) presents more defined vibrational modes (note the appearance of a shoulder in the spectrum in Fig. 2a). Based on this observation we can speculate that the chromophore molecules aligned in parallel direction are more susceptible to interactions with the solvent (liquid crystal), which contribute to the increase of dye alignment. The quantitative information about the molecular orientation is obtained by calculating the dichroic ratio $\delta = A_{\parallel}/A_{\perp}$ and the order parameter $\beta = (A_{\parallel} - A_{\perp})/(A_{\parallel} + A_{\perp})$. In the spectral range of $\pi \rightarrow \pi^*$ transitions, considering the curve in Fig. 2a, both parameters β and δ are approximately constant and equal to ~ 0.51 and ~ 3 , respectively, for sample with molar concentration of 0.025%. The non-dependence of the order

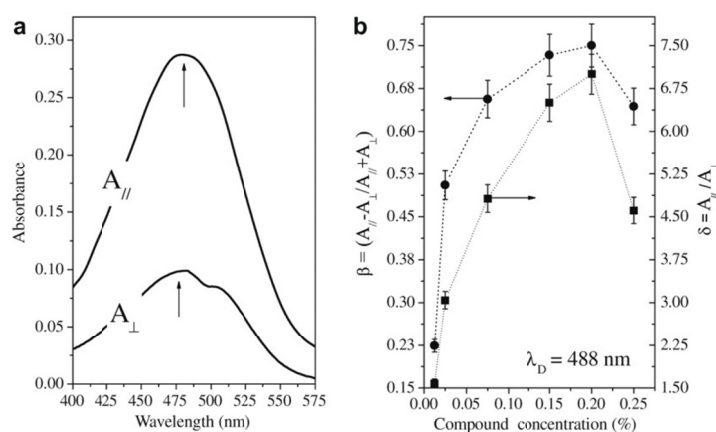


Fig. 2. (a) Polarized absorbance spectra for sample with 0.025% of molar concentration of benzothiadiazole. The excitation was performed with linear polarized light, parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the liquid crystal alignment direction. (b) Dichroic ratio δ and order parameter β calculated at $\lambda_D = 488$ nm for samples with different benzothiadiazole molar concentration.

parameter on the probed spectrum wavelength means, as expected for the time scale involved, that the vibrational modes of the dye do not affect the molecular alignment. It is also expected that the anisotropy is caused by the strong alignment of the dye in the liquid crystal medium. In order to study the effects of the compound concentration on the molecular orientation, Fig. 2b displays the evolution of parameters δ and β for samples with different concentrations. Curves in Fig. 2b were mapped at $\lambda_D = 488$ nm, which is next of the maximum in the absorbance spectrum. They show a non-linear increase of the parameters up to the dye concentration of 0.20%; next to the dye solubility limit (0.25%). So, we conclude that the dye concentration is a parameter that contributes to the enhancement of the molecular alignment, probably due to the competition among the intermolecular forces. This result alerts to the fact that: the dye concentration needs to be considered in experiments that use dye doping to determine the order parameter of nematic liquid crystals. Besides, we also observe an increase in the disorder of the system, for concentrations above 0.20%. This behavior can be attributed to the fact that the dye solubility limit, where it is expected an orientation losing of the chromophores, is reached for concentrations above 0.20% resulting in a reduction of the order parameter. It worths to mention that the increasing in the disorder of the system with the augment of the dye concentration can not be related to an entanglement of the chromophores once that in the concentration range used we have very diluted solutions (around 1 molecule of dye for 400 of liquid crystal).

To quantify the influence of the dye molecular ordering on the amount of polarized light emitted, we introduce the anisotropy factor $r = \frac{I_{\parallel} - G I_{\perp}}{I_{\parallel} + 2G I_{\perp}}$ [20]. $I_{Ex,Em}$ is the PL intensity for excitation (Ex) and emission (Em) polarization parallel (\parallel) or perpendicular (\perp) to the sample alignment and $G = \frac{I_{\perp, \parallel}}{I_{\parallel, \perp}}$ is a geometrical factor introduced to overcome problems associated with differences in the transmission of the diffraction grating for light vertically and horizontally polarized. Fig. 3 shows the PL spectra considering the polarization of Ex and Em and the dependence of the parameter r on the spectral wavelength. As shown previously by the polarized absorbance (Fig. 2a), the emission spectra detected in perpendicular direction displays better resolved vibrational modes, independently of the excitation beam polarization. Also here, the result corroborates with the observation that the chromophore and the

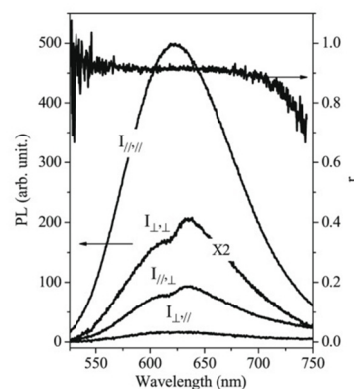


Fig. 3. Polarized fluorescence spectra for sample with molar concentration equal to 0.025% of benzothiadiazole. The sample was excited with linear polarized light, parallel (P_{\parallel}) and perpendicular (P_{\perp}) to the alignment direction. The light was collected with the analyzer parallel (E_{\parallel}) and perpendicular (E_{\perp}) to the alignment direction.

host liquid crystal interaction diminishes in the perpendicular direction. The parameter r shows no significant dependence on probed spectral wavelength; above 700 nm the PL signal decreases substantially and the calculation of the parameter is not precise. For all samples, the value of r parameter is constant in this spectrum range (~ 0.91), indicating a high anisotropic system. Table 1 lists the average values (r) between 550 and 700 nm for the samples with different chromophore concentrations where non-dependence is observed. The last result indicates the preponderance of the linear polarized emitted light independently of the dye concentration. Such observation is surprising, due to the great dependence of the order parameter (see Fig. 2b) on the chromophore concentration, and can be understood by assuming that the emission process is finalized in the parallel direction without the excited carrier migrating from parallel to perpendicular direction, independently on the dye concentration used.

Table 1
Average order parameter r as function of the chromophores molar concentration.

Sample concentration (r)	0.0125%	0.025%	0.075%	0.15%	0.20%	0.25%
	0.91 (± 0.02)	0.91 (± 0.02)	0.91 (± 0.02)	0.92 (± 0.02)	0.93 (± 0.02)	0.93 (± 0.02)

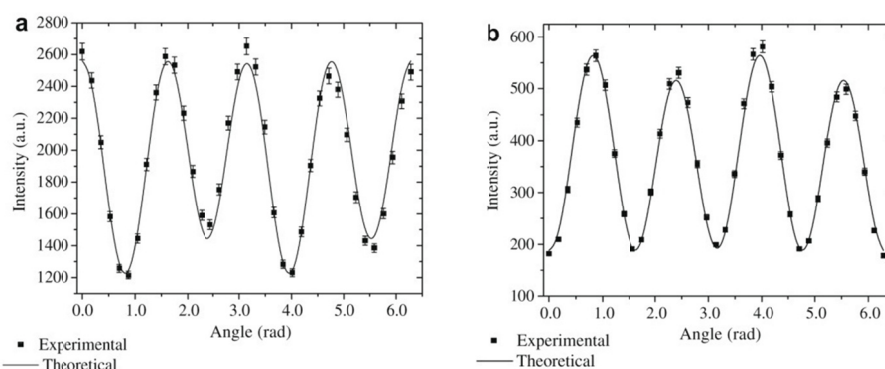


Fig. 4. Sample ellipsometry measurements with concentration equal to 0.025%, at room temperature. The excitation was performed employing laser beam with polarization parallel (a) and perpendicular (b) to liquid crystal alignment direction. The sample was excited at 457 nm and the emission was probed at 633 nm. Solid full squares represent experimental data and the solid line is the theoretical fitting obtained with Eq. (1).

Ellipsometry experiments were carried out to determine the state of polarization of the emitted light, for which the use of the Stokes' theory for the electromagnetic field was made [21]. We employed the excitation at 457 nm and the emission was detected at 633 nm. The polarization of the excitation light was set to be parallel and perpendicular to the liquid crystal alignment direction in order to infer different possible arrangements of benzothiadiazole molecules. Stokes' parameters for the optical field were obtained by fitting the ellipsometry data with Eq. (1) [21]

$$I(\theta) = \frac{1}{2}[A + B \sin(2\theta) + C \cos(4\theta) + D \sin(4\theta)], \quad (1)$$

where I is proportional to the light intensity, θ is the angle between the fast axis of the quarter-wave plate and the axis of the analyzer (vertical direction), $A = S_0 + \frac{S_2}{2}$, $B = S_3$, $C = \frac{S_1}{2}$, and $D = \frac{S_2}{2}$. S_0, S_1, S_2 and S_3 are the Stokes' parameters that describe the polarization state of the emitted light. S_0 parameter is associated with the total intensity of the optical field, S_1 describes the quantity of linear polarization at parallel or perpendicular directions, S_2 gives the quantity of linear polarization rotated by $+45^\circ$ or -45° , and S_3 provides information about the existence of right or left circularly polarized light. In fact, as the light intensity is acquired in arbitrary units, S_1, S_2 and S_3 parameters should be normalized by S_0 in order to be compared. In addition to the Stokes' parameters, the polarization degree (P) reveals the amount of polarized light of the fluorescence being defined as [20]

$$P = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0}, \quad (2)$$

where S_i are the respective Stokes parameters. In Fig. 4, we show a typical result obtained by the ellipsometry experiment for sample concentration 0.025% at room temperature ($\sim 25^\circ\text{C}$) and excited with polarization parallel (Fig. 4a) and perpendicular (Fig. 4b) in relation of the liquid crystal orientation. Table 2 summarizes the Stokes' parameters obtained from the theoretical adjustment (Eq. (1)) of the experimental data presented in Fig. 4 and the polarization degree P calculated from Eq. (2); both obtained for different

excitation beam polarization: non-polarized and polarized, parallel and perpendicular, to liquid crystal alignment direction. Similar results were obtained for all compounds concentration. Table 2 shows that even when excited with non-polarized light the emission presents a high value for P parameter, which attests the great anisotropy of the system. Besides, we were also able to detect, using ellipsometry, that the sample also emits linear polarized light in the parallel direction, corroborating with the results obtained by the anisotropy experiment (see Fig. 3). The advantage in carrying out the ellipsometry experiment, alongside its non-dependence with magic angle and any type of correction factors due to experimental setup, is that with this technique we are able to completely characterize the polarization state of the emitted light, not being constrained to the linear portion. As a result, for all samples, we determine that the linear birefringence and circular emission are non-significant (small values presented by S_2 and S_3 parameters, respectively). Although small, we are capable to infer that the circular polarized light component, obtained from the normalized S_3 parameter, is left-hand oriented (right-hand oriented) if the sample is pumped with parallel (perpendicular) polarization. For an excitation beam with non-polarized and parallel polarization, the light emitted is preferentially in the parallel direction, $S_1 < 0$. On the other hand, for perpendicular polarization, the emission is in the perpendicular direction, $S_1 > 0$ and the parameter P decreases ca. 0.66. We attribute the polarized light emitted in the perpendicular direction to dyes aligned in this direction which is corroborated by the polarized absorbance and the anisotropy of the emission (see Figs. 2 and 3), where a small absorption and emission in the perpendicular direction are detected. This result is consistent to the fact that the energy transfer and/or charge diffusion of the excited carriers from parallel to perpendicular direction is smaller than in the reverse direction.

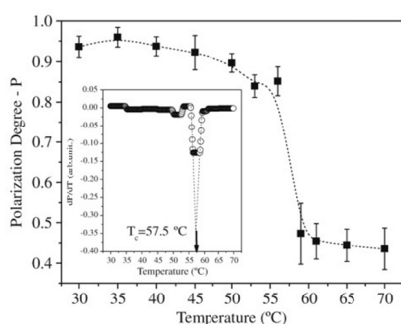
Finally, we performed ellipsometry measurements above phase transition temperature (58°C), varying and controlling the temperature with a homemade heating system. Table 3 lists the Stokes parameters obtained at 70°C for different excitation beam polarization. We see that, for non-polarized excitation, the parameter P is not significant (~ 0.04), showing the isotropic phase with the

Table 2Stokes parameters and polarization degree (P), for samples with concentration of 0.025%, excited with different polarization states, at room temperature.

Excitation	Temperature (°C)	P (± 0.02)	S_1/S_0 (± 0.02)	S_2/S_0 (± 0.02)	S_3/S_0 (± 0.02)
Non-polarized	25	0.95	-0.95	-0.02	0.02
Parallel	25	0.94	-0.94	-0.11	0.08
Perpendicular	25	0.66	0.66	-0.10	-0.04

Table 3Stokes parameters and polarization degree (P), for samples with concentration of 0.025%, excited with different polarization states, at 70 °C (isotropic phase).

Excitation	Temperature (°C)	P (± 0.02)	S_1/S_0 (± 0.02)	S_2/S_0 (± 0.02)	S_3/S_0 (± 0.02)
Non-polarized	70	0.04	-0.02	-0.02	0.02
Parallel	70	0.38	-0.38	-0.04	0.03
Perpendicular	70	0.37	0.37	-0.02	0.00

**Fig. 5.** Polarization degree obtained for sample with concentration equal to 0.025% at different temperatures. The sample was pumped at 457 nm with parallel polarization and the fluorescence was probed at 633 nm. The inset shows the first derivative of the parameter P in the applied temperature range.

homogeneous distribution of the dyes on the sample. However, when the sample was excited in the parallel or perpendicular direction, we observed that the chromophore presents fluorescence with around 38% of polarization. This observation is in agreement with the previous one which shows chromophores, even dissolved in isotropic solvents, emitting partially polarized light in the same direction of the excitation light polarization. This behavior can be explained by the coherent emission of fluorescence which is faster than the chromophore misalignment processes (e.g., molecular diffusion or rotation). In fact, this effect was previously reported for polymer in liquid solution [15]. Fig. 5 shows the evolution of the parameter P for different sample temperatures. Next to the phase transition temperature, the parameter P decreases abruptly, as expected, to a first order transition. In the inset we show the first derivative of the parameter P with temperature, estimating the transition temperature (T_c) ca. 57.5 ± 0.5 °C. Such result shows the feasibility of the ellipsometry technique in order to detect phase transitions in ordered systems.

4. Conclusions

Summarizing, we have studied the polarization state of emitted light by benzothiadiazole molecules guested in liquid crystals. We observed that the chromophores emit a great amount of polarized light due to their alignment induced by a liquid crystal anisotropic structure. The alignment increases with dye concentration up to a saturation point next to solubility limit of the dye in the liquid

crystal. For higher chromophore concentrations an increasing in the disorder is observed, affecting the alignment. Despite of the dye disorder increasing no alteration is observed in the amount of polarized light emitted. Besides, we were able to detect a small portion of circularly polarized light emitted by the system whose direction depends on the pumping polarization direction. Moreover, we also observed that the chromophores are able to emit partially polarized light even in the isotropic phase due to coherent emission of fluorescence before chromophore misalignment, as reported previously [15]. Finally, we show that the ellipsometry technique is a practical tool to be employed in structural phase transition studies of fluorescent systems.

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References

- [1] D. Demus, J.W. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds.), *Handbook of Liquid Crystals*, Wiley-VCH, Weinheim, 1998.
- [2] K. Okumoto, Y. Shirota, *Chem. Mater.* 15 (2003) 699.
- [3] J. Bartulin, R. Martinez, H. Gallardo, H. Muller, T.R. Taylor, *Mol. Cryst. Liq. Cryst.* 225 (1993) 175.
- [4] E. Meyer, C. Zucco, H. Gallardo, *J. Mater. Chem.* 8 (1998) 1351.
- [5] S. Qu, M. Li, *Tetrahedron* 63 (2007) 12429.
- [6] A.J. Paraskos, T.M. Swager, *Chem. Mater.* 14 (2002) 4543.
- [7] H. Inomata et al., *Chem. Mater.* 16 (2004) 1285.
- [8] R. Cristiano, H. Gallardo, A.J. Bortoluzzi, I.H. Bechtold, C.E.M. Campos, R.L. Longo, *Chem. Commun.* 41 (2008) 5134.
- [9] R. Cristiano, E. Westphal, I.H. Bechtold, A.J. Bortoluzzi, H. Gallardo, *Tetrahedron* 63 (2007) 2851.
- [10] R. Gimenez, M. Piñol, J.L. Serrano, *Chem. Mater.* 16 (2004) 1377.
- [11] H. Tokuhisa, M. Eia, T. Tsutsui, *Appl. Phys. Lett.* 72 (1998) 2639.
- [12] K.R. Justin, J.T. Lin, M. Velusamy, Y.-T. Tao, C.-H. Chuen, *Adv. Funct. Mater.* 14 (2004) 83.
- [13] N.F. Marcelo, A.A. Vieira, R. Cristiano, H. Gallardo, I.H. Bechtold *Synth. Met.* 159 (2009) 675.
- [14] Y.G. Galyametdinov, A.A. Knyazev, V.I. Dzhabarov, T. Cardinaels, K. Driesen, C. Gortler-Walrand, K. Binnemans, *Adv. Mater.* 20 (2008) 252.
- [15] P. Alliprandini-Filho, R.A. da Silva, N.M. Barbosa Neto, A. Marletta, *Chem. Phys. Lett.* 469 (2009) 94.
- [16] A.A. Vieira, R. Cristiano, A.J. Bortoluzzi, H. Gallardo, *J. Mol. Struct.* 875 (2008) 364.
- [17] I.H. Bechtold, M.P. de Santo, J.J. Bonvent, E.A. Oliveira, R. Barberi, Th. Rasing, *Liq. Cryst.* 30 (2003) 591.
- [18] P. Alliprandini-Filho, G.B. da Silva, N.M. Barbosa Neto, R.A. Silva, A. Marletta, *J. Nanosci. Nanotechnol.* 9 (2009) 5981.
- [19] A. Ghanadzadeh, H. Ghanadzadeh, G. Ghasmi, *J. Mol. Liq.* 88 (2000) 299.
- [20] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Kluwer Academic/Plenum Publishers, New York, 1999.
- [21] E. Collet, *Polarized Light: Fundamentals and Applications*, Marcel Dekker Inc., New York, Basel, Hong Kong, 1993.