Emission ellipsometry used to probe aggregation of the luminescent 2,1,3-benzothiadiazole dyes and ordering in an E7 liquid crystal matrix

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Introduction

Since the discovery that dyes dissolved in liquid crystals are preferentially aligned along the director vector, according to the so-called guest–host effect, intermolecular interactions have been studied particularly aiming at applications in liquid crystal displays (LCDs). The guest–host displays are advantageous in comparison to white–black displays owing to the brighter images, no need of a polarizer, the level of contrast geous in comparison to white–black displays owing to the intermolecular interactions. For example, such interactions have been reported to yield increased birefringence and an enhanced optical Kerr effect upon incorporating a dye into the LC matrix. Steric repulsion of aliphatic lateral groups favored dye alignment and caused aggregation of substituent groups in the dopants in a LC matrix. Kosa and Palffy-Muhoray studied the alignment of nematic domains using photoinduced alignment of azo dyes in a polyimide layer. Self-assembled films made using azodyes were also shown to be efficient to align liquid crystals for electro-optical devices.

Spano and coworkers demonstrated that the intermolecular interactions in \( \pi \)-conjugated systems lead to J or H-type aggregates, with distinct dependencies on the electron–phonon coupling. When H-aggregates are formed, both absorption and emission spectra are blue shifted with lower emission efficiency. Opposite effects occur for J-aggregates. The identification of J aggregates is difficult owing to the structural disorder at room temperature, as is the case of light-emitting polymers. Such difficulty may be circumvented if nematic liquid crystals below the phase transition temperature are doped with \( \pi \)-conjugated luminescent dyes, because disorder would be decreased leading to a higher definition of the line shape of the spectra.

We have recently proposed an alternative approach where the luminescent dye 4,7-bis((2-(4-decylpiperazin-1-yl)phenyl)ethynyl)-[2,1,3]-benzothiadiazole was used in the guest–host...
system with the liquid crystal E7,\textsuperscript{15} whose advantage lies in the fact that the optical transitions for the dye absorption (\(\pi \rightarrow \pi^*\)) and emission (\(\pi \rightarrow \pi^*\)) are in the visible–near infrared region (\(\sim 400–800\) nm). We observed ordering in the matrix and energy transfer processes for the dye up to its solubility limit in the LC (0.25\% mol), and could determine the temperature for the nematic–isotropic phase transition upon analyzing the polarization of the emitted light by the dye. In this study, we employ the approach to compare interactions with 4,7-bis(4-decylpiperazin-1-yl)phenyl]ethynyl]-[2,1,3]-benzo-thiadiazole (1A) and 4,7-bis[2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl]-[2,1,3]-benzo-thiadiazole (5A) dissolved in the E7 LC. From the analysis of the line shape in a procedure suggested by Spano and coworkers,\textsuperscript{12,13} we show that the dyes form J-aggregates. We should also mention the novelties in comparison with the previous work.\textsuperscript{15} In addition to discussing the guest–host interaction in detail, particularly with regard to the possible formation of dye aggregates, the new approach is advantageous owing to the use of dyes that absorb in the visible range. The comparison of the two dyes leads to a new, crucial result to raise awareness of the community that employs probes to infer the properties of a matrix.

**Experimental**

The structures of the luminescent dyes 4,7-bis[2-(4-(decyloxy)-phenyl)ethynyl]-[2,1,3]-benzo-thiadiazole (1A) and 4,7-bis[2-[4-(4-decylpiperazin-1-yl)phenyl]ethynyl]-[2,1,3]-benzo-thiadiazole (5A), synthesized as described in ref. 16, are shown in Fig. 1. These dyes were selected because they absorb and emit light in the visible range, and are sufficiently different in size which will be shown to be relevant for alignment in the liquid crystal matrix. They were dissolved in the liquid crystal E7 (Merck\textsuperscript{16}) at the molar concentrations of 0.0125\%, 0.025\%, 0.075\% and 0.25\%. The cell in which the liquid crystal was dropped was prepared as follows. Spin-coated films were obtained from a 2\% (in mass) solution of polyvinyl alcohol (PVA-Merck)\textsuperscript{10} on glass substrates rotating at 3000 rpm for 30 s. The films deposited on the glass substrates were then rubbed unidirectionally with a soft piece of velvet in order to induce a homogeneous alignment for the liquid crystal along the rubbing direction,\textsuperscript{17} referred to here as the parallel direction. The cell was assembled by superimposing two PVA-coated glass substrates with the two films in the internal part and with their rubbing directions in an antiparallel fashion so as to obtain a homogeneous planar alignment without disclination lines. A spacer of ca. 20 \(\mu\)m made from "mylar" was used to keep this cell gap for inserting the liquid crystal by capillarity. For the sake of comparison, \(10^{-5}\) mol L\(^{-1}\) chloroform solutions were also prepared with 1A and 5A dyes.

UV-Vis absorption spectra were recorded on an USB2000 Ocean Optics spectrometer with a deuterium–tungsten lamp. For polarized absorbance, a linear polarizer (400–700 nm) was inserted after the light source. Photoluminescence (PL) spectra were recorded with excitation at 457 nm by a CW (Continuous Wave) argon laser from Spectra Physics Inc, model Stabilite 2017, with the beam diameter of \(\sim 1.4\) mm and the samples being excited with the incidence beam perpendicular to the surface, with \(\sim 7\) mW laser radiation power. The emitted light was collected in an USB2000 Ocean Optics spectrometer, where a high-pass filter was inserted to eliminate the excitation light. Emission ellipsometry measurements were performed with the experimental setup described in ref. 18, with an achromatic quarter wave plate and a linear polarizer in the region from 400 to 700 nm. The polarizer axis was fixed in the vertical direction, parallel to the grooves on the PVA rubbed films. The quarter wave plate placed on a goniometer could be rotated from 0\(^\circ\) to 360\(^\circ\) in steps of 10\(^\circ\).

**Results and discussion**

Fig. 2 shows the absorption spectra of the dyes 1A and 5A dissolved in the liquid crystal E7 at various concentrations, to be compared with the spectra of the dyes in solution shown in the insets. The spectral ranges for absorption are similar for both samples. The red shifts of 6 and 16 nm in the maximum of the spectra of 1A and 5A, respectively, compared to the solution, indicate that the \(\pi \rightarrow \pi^*\) transitions are affected when the dyes were dissolved in the liquid crystal matrix. Also worth noting in Fig. 2, the absorbance red shift does not depend on the dye concentration up to the dyes solubility limit (0.25\% mol), and the same applies to the line shape and the peak position. The only exception is the spectrum for the lowest concentration of 5A (0.0125\%), where the bands are better defined, similarly to the solvation effects in conjugated molecules.\textsuperscript{19} The redshift could be ascribed to the orientation of the dyes, which contain alkyl groups\textsuperscript{5} in the matrix with an ensuing increase in the planarity of their conformation and decrease of the band gap.

![Fig. 1 Chemical structures of 1A and 5A.](image)

**Fig. 2 Normalized absorption for (a) 1A and (b) 5A dissolved in the liquid crystal E7 at distinct molar concentrations, viz. 0.0125, 0.025, 0.075, and 0.25\%.** The inset shows the spectrum of the dye in solution (solid line), to be compared with that of the dye in the liquid crystal at 0.25\% (dashed line).
Since the full width at half maximum (FWHM) is larger than typical vibrational modes (100 meV), we were not able to use the spectra to infer dye aggregation in the matrix. The absorption spectra recorded after the laser excitation experiments were the same as before the irradiation, and therefore no dye photodegradation occurred.

The photoluminescence spectra of 5A and 1A in the E7 matrix and in chloroform solution are shown in Fig. 3. Emission for 5A occurs at much longer wavelengths, probably because of its larger degree of conjugation and of the strong electron-donor character of the group (–NR<sub>2</sub>), than for 1A. Though the line shape is preserved, the spectra in E7 are wider than in solution, especially at long wavelengths, in the vibrational progression range. For 1A there is almost no dependence on the concentration in E7, whereas a small red shift of the maximum is observed for 5A, consistent with the absorption data in Fig. 2a. Deconvolution of the spectra was performed with three Gaussian functions taken to represent the electronic transition (zero-phonon) and the first and second replicas (electron-vibrational coupling modes), where we used an effective vibrational mode for the C–C ring stretching of 125 meV. The spectra in Fig. 3b and c for 1A and 5A, respectively, show that the shifts in the experimentally-observed PL spectra are not reflected in the Gaussian curves: instead, there is an inversion in the relative contribution of the first and second emission bands. The fitting parameters used are given in Table 1. We also dispersed the dyes in a polymeric (PMMA) solution with a concentration similar to the one used in the liquid crystal matrix and measured the polarized PL of cast films under non-polarized UV irradiation. We observed similar shapes for the curves as in the liquid crystal matrix, but without any polarization effect. This confirms the isotropic organization of the dyes in a polymer matrix (not shown).

Because spectral shifts may not be useful to infer aggregation, when various processes compete, we used the work by Spano to calculate the electron–phonon coupling, or the Huang–Rhys (S) parameter. S may be calculated from the ratio I<sub>02</sub>/I<sub>00</sub>, where I<sub>00</sub> is the emission intensity for a purely electronic transition and I<sub>02</sub> is the emission intensity for the first phonon replica. The values obtained in Table 1 are S<sub>01</sub> ~ 0.7 and 0.3 for 1A and 5A in solution, while in the liquid crystal matrix S<sub>E7</sub> ~ 1.9 and 1.6 for 1A and 5A, respectively. Therefore, the Huang–Rhys parameter increases considerably when the dyes are in the matrix. This is corroborated by the emission efficiency dependence on the dye concentration in Fig. 3d. The relative quantum efficiency was calculated using

\[
\eta_{\text{rel}} = \frac{I_{\text{PL}}}{P_{\text{abs}}(\lambda_{\text{exc}})}
\]

where I<sub>PL</sub> is the integrated PL intensity, P<sub>abs</sub>(\lambda_{exc}) is the absorbed power by the sample at the excitation wavelength, P<sub>abs</sub>(\lambda_{exc}) = I<sub>0</sub>[1 - 10^{-A(\lambda_{exc})}], I<sub>0</sub> is the intensity of the incident light and A(\lambda_{exc}) is the sample absorption at the excitation wavelength \lambda_{exc}. There is very little decrease in efficiency for 1A when the concentration increases, but the decrease is significant for 5A. This difference occurs because the emission efficiency of the dye depends on the dye–dye and dye–matrix interactions, and the interaction with the matrix is more likely to increase with concentration for the larger 5A dye. The considerable increase in the Huang–Rhys factor is indicative of J aggregate formation.

The matrix–dye interactions may be evaluated indirectly by probing the molecular ordering of the dyes through the UV-vis spectra (\pi \to \pi^* transitions). The polarized absorption spectra of 1A and 5A dissolved in E7 at 0.25% molar concentration are shown in Fig. 4. Absorption is higher for light polarized parallel (A||) to the director vector defined by the rubbing direction on the PVA film, leading to parameters of molecular ordering \beta, obtained using eqn (1) as given in Table 2.

\[
\beta = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}
\]
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where the absorbances $A_0$ and $A_\perp$ were taken at their maximum values. Note that the order parameter is calculated for the dye, not for the liquid crystal molecules. The order parameter may also be obtained using the equation $\beta = \frac{A_0 - A_\perp}{A_0 + A_\perp}$ (ref. 22) and in subsidiary calculations we noted that the interpretation is not altered. Consistent with a previous paper, $\beta$ depends on the dye concentration. Molecular ordering is higher for the larger dye 5A because it is less prone to losing the alignment than the smaller dye 1A.

The difference in the ordering factor between the two dyes decreases with increasing concentration since 5A was initially more aligned than 1A, until eventually being very small when the limit of solubility was reached at the highest concentrations.

The polarization of the emitted light was determined from the Stokes parameters using eqn (2).

$$I(\theta) = [A + B \sin(2\theta) + C \cos(4\theta) + D \sin(2\theta)]$$

(2)

where $I$ is the emitted light, $(\theta)$ is the quarter waveplate angle (with a vertical reference frame), $A = S_0 + S_1$, $B = S_3$, $C = S_1$, and $D = S_2$, $S_0$, $S_1$, $S_2$ and $S_3$ are the Stokes parameters defined in ref. 18. The degree of polarization is calculated from eqn (3),

$$P = \frac{\sqrt{S_1^2 + S_2^2 + S_3^2}}{S_0}$$

(3)

Fig. 5 shows typical emission ellipsometry curves for the dyes 1A and 5A in E7 at 0.025%, room temperature ($\sim 25$ °C) and with excitation light polarized parallel to the vector direction. The solid lines were obtained from eqn (1) and the Stokes parameters are given in Table 3, together with the degree of polarization $P$. For all samples, $|S_1| > |S_2| > |S_3|$, with higher intensity in the E7 alignment direction, i.e. in the parallel direction with $S_1/S_0 < 0$, regardless of the dyes concentration.

The anisotropy factor for emission, given by $r = \frac{I_{||} - I_{\perp}}{I_{||} + 2G I_{\perp}}$, where $I_{\text{exc,em}}$ is the PL intensity of the excitation and emission polarization parallel (\|$\|$) and perpendicular (\$\$) to the liquid crystal alignment and $G = \frac{I_{||}}{I_{\perp}}$ is a geometric factor introduced to compensate the difference in transmission in the spectrometer diffraction grating for vertically and horizontally polarized light, is shown in Table 3.

The degree of polarization as well as the anisotropy in emission in Table 3 do not follow the order parameter for the following reason: all the dye molecules absorb light, but only the aligned molecules emit light owing to the energy transfer processes. This can be inferred by observing a negative $S_1$ when the liquid crystal is aligned in the vertical direction, while a positive value is obtained for the liquid crystal in the horizontal direction, regardless of the type of excitation. The emission in the liquid crystal direction is consistent with the larger energy transfer and/or diffusion of excited carriers from the perpendicular to the parallel direction. Such transfer occurs because the dye molecules aligned in the liquid crystal direction have a lower bandgap than those that are not aligned, as indicated by the polarized photoluminescence results where a 20 nm redshift was observed for the emission of the aligned dye molecules in comparison with the emission of the non-aligned dyes. Significantly, the degree of polarization is much higher for 5A, consistent with the results of polarized absorption in Fig. 4. Therefore, one has to be cautious while using dopants to infer ordering in liquid crystals (or other organized systems), since the values found may vary strongly depending on the chemical structure of the dopant. Furthermore, the high values for $S_3$ point to birefringence effects on the E7 matrix in the visible region, with a partially rotated component at the 45° axis being 33% for 5A and 21% for 1A. A similar effect was predicted with theoretical calculations by Simpson and coworkers,6 where dyes were able to increase the matrix birefringence. Subsidiary experiments were performed by varying the laser power from 5 up to 35 mW, and a linear dependency was observed for the PL intensity with the laser power. Moreover, the absorption and emission ellipsometry spectra were not affected, thus confirming that no dye photolysis occurred.
In order to understand why the emission data are useful to determine the orientation of E7 molecules, we recall that polarized emission takes place because only the low bandgap molecules emit owing to energy transfer mechanisms. Let us assume that each E7 molecule occupies a cylinder with an average diameter of 5 Å and a length of 20 Å, leading to a volume of 0.39 nm³. With the dye concentrations used, each dye molecule is surrounded by 400 up to 8000 E7 molecules, and therefore the largest volume of surrounding E7 molecules is 3210 nm³. Hence, the average distance between dyes varies from 5 to 14 nm – even assuming negligible aggregation – which allows for energy transfer to the low bandgap molecules.24

Conclusions
In this paper we showed that photoluminescence emission from dyes may be used to infer ordering in a liquid crystal matrix, as well as to interrogate the aggregation state of the dyes. This latter achievement is significant owing to the difficulties in obtaining cast or spin-coated films from small molecules, such as the dyes investigated here, with which aggregation could be probed. For the 1A and 5A dyes, J-type aggregates were inferred by analyzing the line shape of the emission spectra, with deconvolution using Gaussian curves to represent the electronic transitions corresponding to the zero-phonon and the two first replicas. Important in this context was the polarized emission of the dyes induced by energy transfer mechanisms due to dye-dye interactions. With regard to the ordering of the LC matrix, emission ellipsometry allowed us to determine the alignment of the E7 molecules based on the emission of the dyes. Here caution should be taken because the smaller 1A dye was not able to align entirely in the director vector direction. This can have important implications since not only the electronic structures of the dyes are affected by the matrix, but also the ordering inferred for the dyes may differ from that of the molecules in the matrix.

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Notes and references