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The photophysical properties of Nile red and Nile blue in ordered anisotropic media

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Abstract

The absorption and fluorescence spectra of a highly fluorescent laser dye, Nile red, were investigated in nematic solvents and isotropic liquids as a function of the solvent polarity and type. The interaction of the dye with the anisotropic surrounding and with that of the isotropic solvents was investigated and compared using optical spectroscopy. The spectral behavior of the cationic oxazine dye, Nile blue, was also investigated in anisotropic and isotropic environments for comparison. The spectral shifts were correlated by the solvent polarity and nature. The electro-optical effect of the guest–host systems was also investigated in an electro-optical system using polarized spectroscopic method and the dichroic ratios *R* and degree of anisotropies *S* of these dyes in the liquid crystalline hosts were investigated.

Keywords: Nile red; Nile blue; Solvatochromic behavior; Guest–host interactions; Anisotropic host

1. Introduction

Oxazine dyes containing polar chromophores are an important group of laser dyes frequently used as an active medium in tuning lasers [1,2]. They have strong absorption and fluorescence bands in the visible region. However, their spectral behavior and laser properties are strongly influenced by the solvent properties. A large amount of investigation has been carried out in recent years on solvation and spectroscopic properties of this group of dyes [3–5].

Nile red, NR, a fluorescence laser dye, is a neutral, hydrophobic and solvatochromic dye with interesting photophysical and lasing properties [1]. This dye in the presence of a hydrophobic environment is strongly fluorescent. Due to the environmental sensitivity and photochemical stability, it has been extensively used as a molecular probe to determine the micro-polarity in polymers, LB films and binary mixtures [6–10]. NR has recently been shown to be an excellent fluorescence probe for biological systems, because of its remarkable sensitivity to the polarity of the medium [11–13].

The solvatochromic behavior of the dye is such that polar media cause a red shift but decreased fluorescence intensity [2]. The absorbance and fluorescence spectra of NR were examined in a series of polar and non-polar solvents with various dielectric constants and refractive index properties. The observed data serve to exhibit the existence of strong molecular-level interactions between the solvent and the solute in the dye solutions. NR has been described as displaying positive solvatochromism leading to a large red shift in absorption and emission maxima in going from non-polar solvents to polar solvents [14–16]. The strong solvatochromic behavior observed for NR arises from the fact that it undergoes large dipole moment changes during transition between two electronic states. This corresponds to charge transfer between diethylamino group which acts as an electron donor and the aromatic acceptor system (quinoid), producing a twisted intra-molecular charge transfer state that is stabilized in more

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polar solvents [6]. This electronic arrangement probably accounts for its highly fluorescent properties [17].

Nile blue, NB, (a cationic oxazine dye) has also been established to be a solvatochromic dye because of its remarkable environmental sensitivity [2]. The structure of both the dyes consists of an electron donor (diethylamino group) and an electron acceptor. However, NR and NB have different electron acceptors, a carbonyl and an iminium group, respectively.

Nematic liquid crystals are highly anisotropic materials owing to their large molecular anisotropy and intermolecular ordering. Nematic compounds are known to form partially ordered structure and are brilliantly suited as anisotropic solvents for polarized spectroscopy [18–22]. Moreover, the use of nematic phases as model systems for the investigation of anisotropic intermolecular interaction is important scientific application of nematic liquid crystals [18].

In this present work, a low-polar nematic liquid crystal, 2-chloro-4-heptylphenyl-4-pentylbicyclo[2,2,2]octane-1-carboxylate (7CP5BOC) with negative dielectric anisotropy together with three polar nematic liquid crystals with positive dielectric constants (5CB, 6CB and a nematic mixture of 1294-1b) were used as anisotropic solvents for the photophysical investigations.

We have recently reported the influence of anisotropic environment on the spectral properties of some ionic oxazine dyes [23]. It was concluded that the absorption characteristics of the ionic dyes could be affected by anisotropic solvation. In the present work the authors have studied the guest–host interactions and the spectral behavior of positive solvatochromic dyes, NR and NB, in anisotropic and isotropic media. The spectroscopic properties of the dye in isotropic solvents were studied for comparison.

The choice of NR and NB as guest molecules in liquid crystalline host was motivated by the following considerations. In spite of massive reports on the spectroscopic properties and solvation of these dyes in isotropic solvents, based on the authors' literature review, anisotropic solvation has attracted relatively little attentions.

Knowledge of the spectroscopic properties and solvation of the dyes in anisotropic uniaxial solvent is important in order to understand the effect of the anisotropic surrounding on their photophysical behavior and is of interest for potential application in dye laser. NR as a hydrophobic probe dye has the advantage of relatively good solubility in polar and low-polar liquid crystals.

2. Experimental

2.1. Materials

Fig. 1a shows the chemical structures of the phenoxazine dyes used in this study. The investigated dyes with high purity (laser grade) were used with no further purification. Nile red (NR) was obtained from Aldrich (97% purity). NR (phenoxazone-9) appears as red crystal and is chemically known as 9-diethylamino-5H-benzo[*a*]phenoxazine-5-one ($C_{20}H_{18}N_2O_2$). Laser grade Nile blue (NB) perchlorate was purchased from Exciton (95%). NB appears as dark green crystal and is chemically known as 5-amino-9-diethylamino-benz[*a*]phenoxazonium perchlorate ($C_{20}H_{20}N_3O\cdot ClO_4$). All isotropic solvents with high purity (spectroscopic grade) were purchased from Merck, and were used as received.

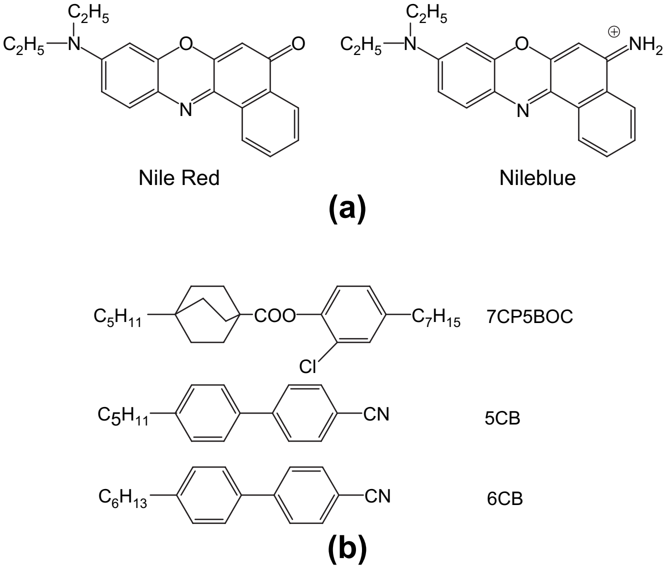

Fig. 1. Chemical structures of the compounds studied: (a) dyes and (b) nematic liquid crystalline hosts.

Three pure nematic liquid crystal molecules were used in our experiments as anisotropic hosts. They are the pentyl cyanobiphenyl (5CB) [24], hexyl cyanobiphenyl (6CB) [24], and the 2-chloro-4-heptylphenyl-4-pentylbicyclo[2,2,2]octane-1-carboxylate (7CP5BOC) [25]. 7CP5BOC has been laterally substituted by a single chlorine atom located in the neighborhood of the ester linking group. The presence of a chlorine atom in the lateral position leads to a good stability for polar and also for non-polar compounds. Therefore, 7CP5BOC is suited as anisotropic solvent for polarizing spectroscopy. The chemical structures of the liquid crystalline materials are shown in Fig. 1b. In this work, a nematic mixture of 1294-1b with high and positive dielectric anisotropy ($\Delta\varepsilon > 15$) was also used as anisotropic solvent. The liquid crystalline materials were synthesized in the Institute of Chemistry of the Military Technical Academy, Warsaw, Poland. The dyes were studied in the polar nematic hosts up to a concentration of about 0.1% w/w. it should be noted that the solubility of NB was extremely poor in 7CP5BOC. Samples used in these experiments were made fresh and changed daily.

2.2. Liquid crystal cell preparation

The guest–host cells were made by sandwiching the nematic solutions between two optical glass plates ($2 \times 1.2\ \text{cm}^2$). The planar homogeneous orientation of the guest and host molecules was achieved by surface treatment of a cast film of polyvinyl alcohol (Sigma) followed by the rubbing process. The spacing between the electrodes' surfaces was 50 μm and was set by use of a Mylar. The plates were sealed together by a sealing material (epoxy resin glue). The introduction of the dissolved dye in nematic liquid crystal solvent was achieved by capillary action [24].

For the measurement of the electro-optical effect and polarized absorption as a function of electric field strength, indium/tin oxide (ITO) coated parallel glass plates ($2 \times 1.2\ cm^2$) were used as transparent electrodes. Copper wires were connected to the plates using a two-part silver-loaded epoxy (RS components 567–604) and electrically conductive paint (RS components 555–156). The liquid crystal cells were checked under crossed polarizers, and used in subsequent electric linear dichroism studies. The temperature of the liquid crystal cells was controlled at 22 °C.

2.3. Measurement of absorption and fluorescence spectra

The absorption spectra of the dyes were recorded on a Cary UV–vis double-beam spectrophotometer (Model 100) at room temperature. The thermostatted sample holder was a quartz rectangular cell with 5 mm path length. The photophysical properties were determined in dilute dye solutions from 2×10^{-6} to 2×10^{-5} M. Precise values of λ_{max} and $\lambda_{shoulder}$ were obtained from the first derivative of the absorption spectra.

Fluorescence spectra were recorded on a Shimadzu RF5000 spectrofluorimeter at room temperature. The fluorescence spectra of NR and NB in isotropic organic solvents were determined in dilute dye solutions about 2×10^{-5} M.

2.4. LD measurements

The polarized absorption spectra of the dyes in the liquid crystalline hosts were scanned on a Cary UV–vis double-beam spectrophotometer (Model 100) equipped with sheet polarizers. The samples with homogeneous orientation of the guest and host molecules were mounted in a thermostatted holder. Dichroic ratios R of the dissolved dyes were obtained on the basis of polarized absorption measurements [18]. The polarizer was rotated by 90° to record the absorbances in parallel and perpendicular directions to the rubbing direction of the cell, $A_{\parallel}$ and $A_{\perp}$, respectively.

2.5. ELD measurements

The contrast ratios CR of the dissolved dyes were obtained using polarized spectroscopy in a guest–host system based on homogeneous–homeotropic alignment. The polarized absorption spectra of the dissolved dyes were taken with the electric field off and then with the electric field on.

3. Results and discussion

3.1. Absorption spectra and solvatochromic behavior

NR and NB are solvatochromic dyes, which absorb light at about 591 nm and 634 nm in dilute aqueous solutions, respectively, and are soluble over a very wide range of solvents. However, the water-solubility of NR is extremely poor.

The solvation characteristics and solvatochromic behavior of NR and NB in four anisotropic nematic hosts (5CB, 6CB, 1294-1b and 7CP5BOC) as well as some isotropic organic solvents were investigated. The solvatochromic behavior of a dye is the shift of absorption wavelength due to the presence of solvent with different polarities, which is due to the interaction between the solute and solvent molecules [26]. The spectral behavior of NR, a neutral dye, was then compared with that of NB, a cationic dye.

Fig. 3 shows the visible absorption spectra of NR in various isotropic solvents (2×10^{-5} M solutions of the dye) with different polarities. The absorption spectra of the dye in nematic solvents are also shown in Fig. 3 (0.1% w/w). The absorption band of the dye in visible region corresponds to a transition moment largely parallel to the long axis of the molecules ($\pi - \pi^*$ transition). The absorption spectrum of NR is strongly solvent dependent and shows a large red shift with increasing solvent polarity (from cyclohexane to ethanol). The shape of the dye spectrum and the variations in λ_{max} should be controlled by the solvent–dye interactions.

The structure of NR and NB (Fig. 2) consists of an electron donor (diethylamino group) and an electron withdrawing aromatic system. In the case of NR, the diethylamino group is able to donate electron density into the carbonyl group across the aromatic ring, while the iminium group is an acceptor group in NB dye. The twisted intra-molecular charge transfer process gives a highly polar state; therefore, the excited state with a large dipole is stabilized in more polar solvents. The large shifts in the absorption spectra of NR are due to the large changes in excited state dipole moment of the dye molecule (i.e. $\mu_g = 7D \rightarrow \mu_e = 15 - 17D$) [6, 27].

As it is evident from Fig. 3, apart from spectral shift, the shape of the absorption spectrum of the dye in the non-polar solvents with low dielectric constants is different from that of the polar solvents. The electronic spectra of NR in non-polar solvents (i.e. CCl_4 and cyclohexane) exhibit band splitting in the visible region of the electromagnetic spectrum. This phenomenon might be attributed to the vibronic progression, i.e. a high-energy double peak with vibronic structure is usually observed in absorbance spectra of the dye in a low-polar environment [28].

As it can be seen from Table 1, the absorption spectra of the dyes in nematic solutions are red shifted as compared to the dye spectra in the low-polar solvents. The red shifts observed for the dyes in the polar liquid crystalline hosts indicate relatively strong guest–host interactions between the dye molecules and the nematic hosts. However, apart from polarity, the spectrum might also be affected by other effective phenomena such as anisotropic environment. Noted that polar liquid or polar liquid crystals is considered effectively to stabilize the dyes in excited state, which have more polar structures than dye in ground state, i.e. the excited state with a large dipole is stabilized in more polar solvents.

The selected physical properties of the nematic solvents used in this work are given in Table 2. The choice of these nematic solvents was motivated by the following considerations. 5CB and 6CB have strong polar head group ($-C \equiv N$), capable

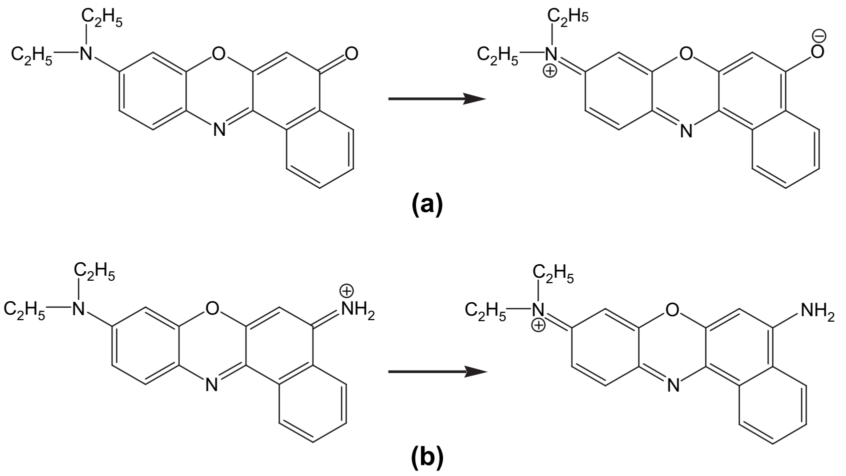

Fig. 2. Electron delocalization in (a) NR and (b) NB.

of dipole–dipole interactions with other polar groups existing in the dyes. 7CP5BOC with negative dielectric anisotropy [29] exhibit only a nematic phase with high chemical stability due to the bicyclooctane ring. The lack of a polar head group such as $-C{\equiv}N$ in 7CP5BOC leads to a high reduction in dielectric constant and permanent dipole moment. The polar nematic mixture of 1294-1b has a high dielectric anisotropy ($\Delta\varepsilon > 15$).

It is interesting to compare the spectral data of NR with that of NB. NB typically possesses a doublet band, i.e. a maximum (λ_{max}) and a shoulder ($\lambda_{shoulder}$). The appearance of a shoulder at shorter wavelength in the monomer spectrum of Nile blue arises from a perturbation in the molecular symmetry caused by solvent molecules. However, like other ionic dyes, the dye cations form dimers and even higher order aggregates in concentrated liquid solutions. The absorption spectrum of NB in nematic solution is relatively strong red shifted (ca. 30 nm) as compared to the dye spectrum in a non-polar isotropic solvent. The doublet band is centered at about 644 nm in a polar anisotropic solvent (5CB). A red shift of about 10 nm in the polar 5CB host with respect to protic solvent such as water was observed, indicating the stronger guest–host interaction in the polar anisotropic environment.

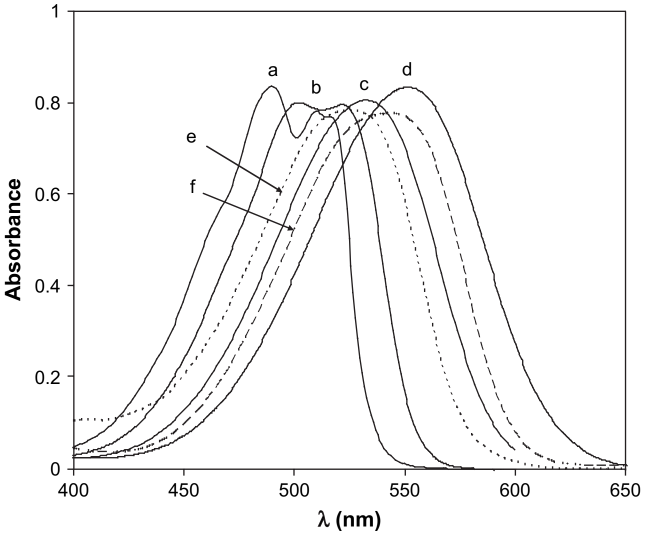

Fig. 3. Visible absorption spectra of NR (2×10^{-5} M) in different solvents: (a) cyclohexane, (b) carbon tetrachloride, (c) acetone, (d) ethanol, (e) 7CP5BOC, and (f) 5CB (0.1% w/w).

As can be seen from Table 1, the red shift for NB in nematic solution is higher than those observed for the isotropic polar solutions, indicating the existence of strong molecular-level interactions between the polar anisotropic solvent and NB, and is therefore, considered to effectively stabilize the dyes in the excited state, which have more polar structures than dyes in the ground state. Thus, the origin of the red shift observed for the dye in nematic solvent can be due to the stabilization of the dye in the excited state leading to the longer wavelength shift of the absorption maximum wavelength. In contrast, the absorption of the NR is blue shifted as compared to the dye spectrum in protic solvents such as ethanol, indicating different interactions between the dye and the polar anisotropic solvent. Probably, this can be explained by

Table 1
Solvatochromic behavior and maximum absorption wavelengths of the dyes in isotropic and anisotropic solvents and their solvatochromic behavior

Solvent	Nile red		Nile blue	
	λ_{max} absorption (nm)	λ_{max} emission (nm)	λ_{max} absorption (nm)	λ_{max} emission (nm)
Isotropic host				
Carbon tetrachloride	524	556	–	–
Toluene	524	569	494	574
Acetone	536	608	–	–
Ethanol	554	629	629	667
Water	591	657	634	674
Anisotropic host				
5CB	545	599	646	666
6CB	544	598	646	664
1294-1b	541	596	645	662
7CP5BOC	529	587	497	556

Table 2
Selected physical properties of nematic liquid crystals at 25 °C, T_c is the nematic to isotropic temperature, n_e and n_o the extraordinary and ordinary refractive indices, respectively, $\bar{\varepsilon}$ the mean dielectric constant, μ the dipole moment and $\Delta\varepsilon$ dielectric anisotropy, taken from references [24,28,31]

Nematic compounds	T_c/°C	n_e	n_o	$\Delta\varepsilon$	$\bar{\varepsilon}$	μ/D
Pentyl cyanobiphenyl (5CB)	35.0	1.70	1.53	11.5	10.8	4.75
Hexyl cyanobiphenyl (6CB)	28.8	1.67	1.54	10.5	9.8	4.78
Mixture 1294-1b	155.5	1.81	1.50	>15	–	–
2-chloro-4-heptylphenyl-4-pentylbicyclo [2,2,2]octane-1-carboxylate (7CP5BOC)	43.5	1.55	1.49	−0.7	3.5	3.50

the nature of the interactions of the nematic host and the dye molecules.

Fig. 4 shows the spectral change or solvent-induced shift in the absorption spectra of NR and NB dissolved in the two nematic hosts. It should be noted that the solubility of NB in 7CP5BOC is extremely poor. In the case of NR (Fig. 4a), a relatively large red shift of about 19 nm in the polar 5CB host with respect to the low-polar liquid crystal, 7CP5BOC, is obvious, indicating the stronger interaction in excited state rather than in ground state. This shift could be due to the dipole–dipole interaction between NR and 5CB; i.e. it is due to the interaction between the polar groups attached to the dye skeleton and the polar nematic host. For NR the polar interactions (dipole–dipole forces) play an important role in the dye spectral properties. However, van der Waals–London interactions (steric and dispersive) appear to dominate the dye alignment in 7CP5BOC. Fig 4b shows the extraordinary solvent-induced shift (149 nm) in the absorption spectrum of NB dissolved in the two nematic hosts. This very strong shift cannot be explained by the regular solvatochromic effect. The extraordinary solvent-induced shift in the absorption spectrum of NB is surprising. Probably, it might be due to the large aggregate formation of the dye in low-polar nematic host. The dye aggregate rather readily not only in solution but also on glass surfaces, and therefore, the spectrum is affected by dye aggregation.

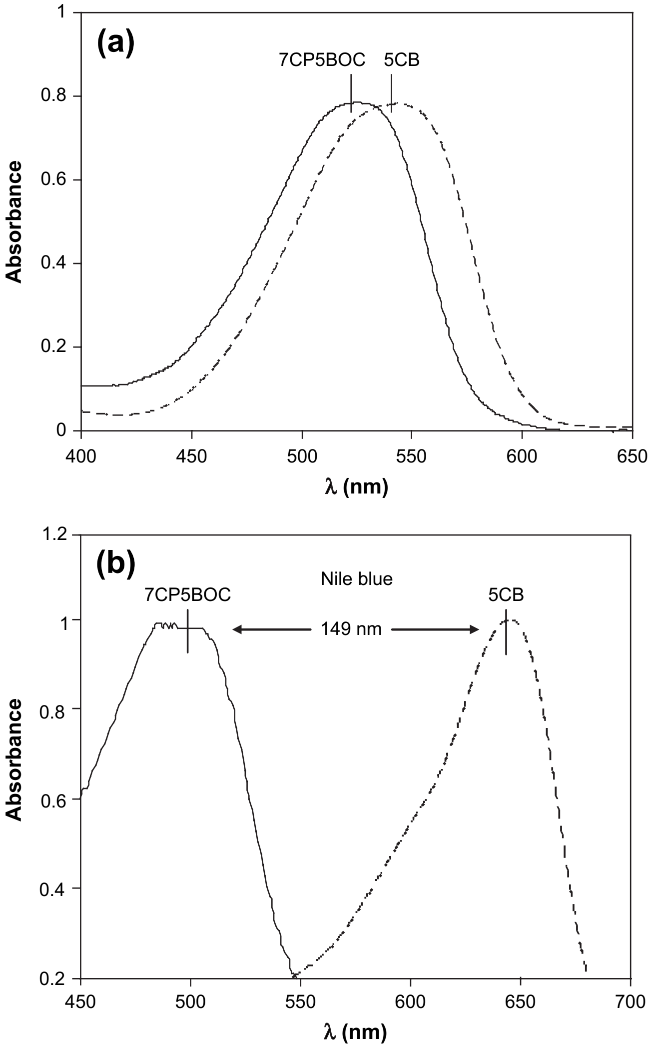

Fig. 4. Visible absorption spectra of (a) NR and (b) NB in low polar, 7CP5BOC, and polar, 5CB, liquid crystals.

The apparent difference between NB and NR is that the latter is neutral and former is cationic. Therefore, it seems that the nature of interactions of the polar nematic host and the two dye molecules is different. In the liquid crystalline host, NB and liquid crystal molecules are parallel with each other (the dye aligns in the direction of the LC long molecular axis), and mainly a strong dipole–dipole and ion–dipole interactions can be realized. Probably, ion–dipole interaction plays an important role in spectral behavior of NB in the nematic environment. Moreover, van der Waals–London interactions (steric and dispersive) should also be considered. 5CB (or 6CB) has also a high polarizable rod-like molecular structure with a big π-electron system mainly due to the presence of biphenyl core. Therefore, there is an extra π–π interaction between the aromatic systems of the dyes and the anisotropic medium, which can give extra solvent effect on the photophysical and alignment properties of the dyes.

However, the red shift observed for the cationic dye, NB, in the nematic matrix cannot be explained on basis of solvatochromic behavior. In contrast, the visible absorption spectra of the neutral dye, NR, were found to exhibit a strong solvent dependence which show a more regular variation, except for dichloromethane, with the dielectric constant of the solvent.

The mean dielectric constant and refractive index in the nematic phase can be calculated using the following equation [24]:

$$\bar{\varepsilon} = \frac{1}{3}\left(\varepsilon_{\parallel} + 2\varepsilon_{\perp}\right) \qquad (1)$$

where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric constants parallel and perpendicular to the molecular axis, respectively. The values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for 7CP5BOC have been reported to be 3.0 and 3.7, respectively [25]. Therefore, a value of 3.5 can be obtained for the mean dielectric constant of 7CP5BOC. So the dye

Table 3
Stokes shifts of NR and NB dissolved in nematic hosts under ambient condition

Dye	Stokes shift (cm^{-1})			
	5CB	6CB	1294-1b	7CP5BOC
NR	1671	1563	1702	1864
NB	478	433	410	2155

molecule in 7CP5BOC experiences a low-polar environment. So, in this investigation we might be able to determine the role of dipole–dipole and or van der Waals–London interactions between the dye and LC molecules.

The shape of optical spectrum of NR in both polar and low-polar anisotropic solvents is similar to that of polar protic and aprotic isotropic solvents such as ethanol and acetone. However, the position of absorption band in polar nematic host is between acetone and ethanol. These results suggest that NR molecules experience a more polar environment through $\varepsilon_{\parallel}$ rather than mean dielectric constant. While, the polarity encountered by NR within non- or low-polar liquid crystal was similar to the polarity between carbon tetrachloride and acetone.

3.2. Fluorescence spectra of Nile red and Nile blue

The type of solvent can strongly influence the photophysical properties of the dyes [27,28]. As $\mu_e > \mu_g$ the emission maxima appear at longer wavelengths (lower energies) in media with higher solvent polarity.

Table 3 summarizes solvent dependency of Stokes shift for Nile red and Nile blue in the anisotropic hosts. The Stokes shift is the difference between positions of the band maxima of the absorption and fluorescence spectra of the same electronic transition. In polar nematic hosts such as 5CB, however, the Stokes shifts observed for NB were smaller. These results indicate that NB absorbs light and emits fluorescence with little rearrangement. It should be noted that this parameter is high in low-polar nematic host (i.e. 7CP5BOC). In general, the Stokes shift for NB is larger in non-polar isotropic solvents. Solvent effects on magnitude of the Stokes shift have been well described in many papers. Jose and Burgess [2] reported that the Stokes shift for NB in non-polar solvent can be exceptionally high, but in polar solvents it is small. For example, the Stokes shift for NB in toluene is about 2862.4 cm^{-1}, but this parameter in water is about 911.2 cm^{-1}.

Fig. 5a–d and Fig. 6a–d present NR and NB absorption and fluorescence spectra in the various liquid crystalline hosts, respectively. As it can be seen, the shape and maximum wavelength of the fluorescence spectrum of the dyes is affected by the solvent's dielectric constant. As it is expected, Nile red and Nile blue show only single fluorescence band in high polar host [28]. As it can be seen from Fig. 5c, the absorption spectrum of NR in the nematic mixture (1294-1b) is broadened and an absorbance around 450 nm is noticeable, which might be due to the dye aggregation. The band broadening of the dye in 1294-1b might have multiple origins. It might also be due to the different molecular interactions between the dye molecules with the components used in the nematic mixture. It should be noted that, the physical properties of a nematic mixture depend on those of the components used and their relative concentrations.

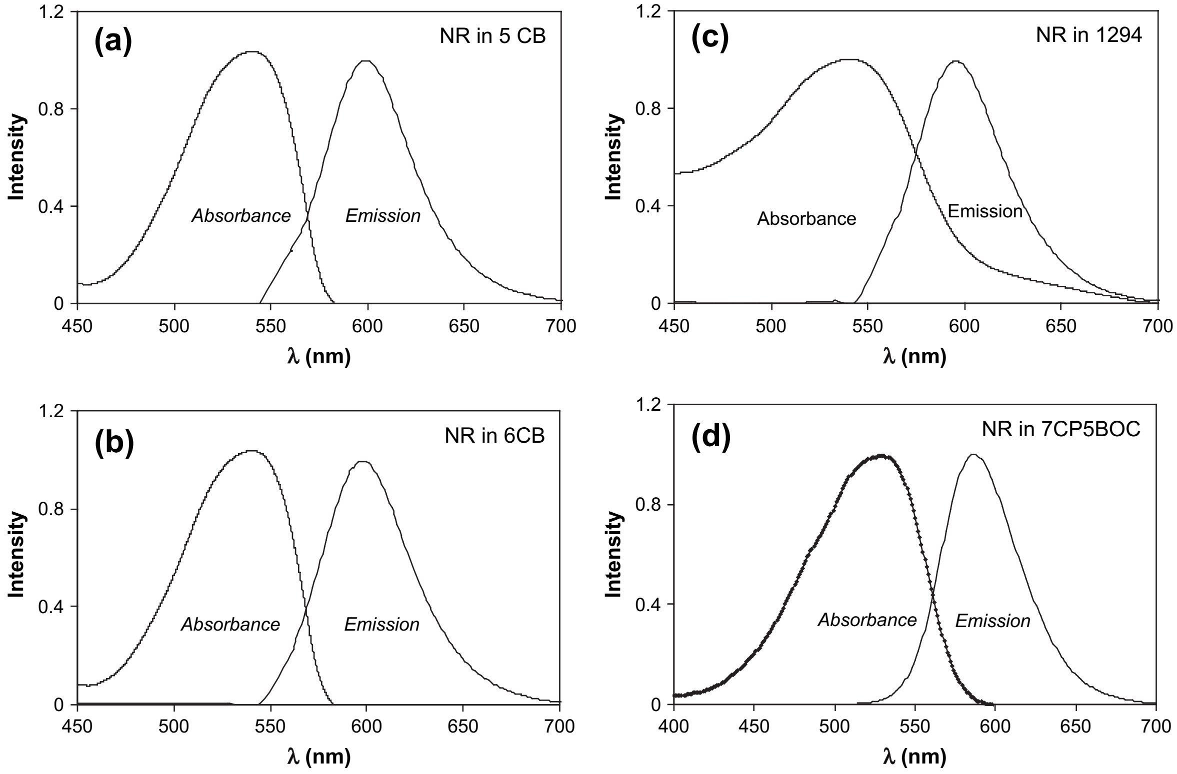

Fig. 5. Absorption and fluorescence spectra of NR in the nematic hosts.

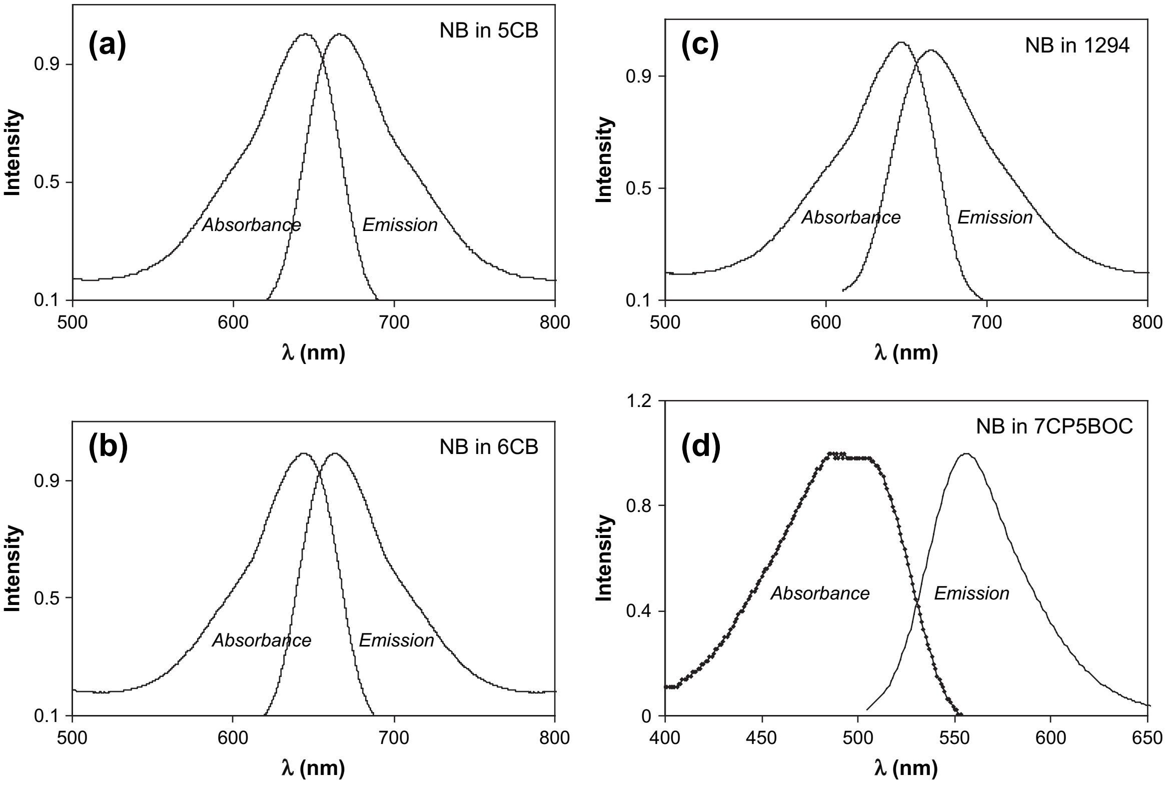

Fig. 6. Absorption and fluorescence spectra of NB in the nematic hosts.

Like polar isotropic solvent, NR and NB show single fluorescence band (non-symmetric) in the anisotropic environments. The $\lambda_{\text{emission}}$ values obtained for NR and NB in the polar nematic hosts are considerably lower than that obtained for ethanol. In general, the observed Stokes shifts for the dyes in the polar nematic hosts such as 5CB are small with respect to the polar protic and aprotic solvents. The value of the shift depends on several factors such as viscosity, molecular packing, solvent polarity, polarizability and host rigidity. Therefore, the anisotropic host provides a relatively rigid, more packed and polarizable environment for the dye molecules, indicating the influence of an anisotropic surrounding on the spectral properties of the dye.

The absorption and emission wavelengths of the dyes in liquid crystals are larger than expected from the value of the mean dielectric constant (the mean dielectric constant of 5CB is 10.8). Thus, it can be concluded that the anisotropic intermolecular interaction between the dye and polar liquid crystalline molecules with $\varepsilon_{\|} \cong 19$ (dielectric constant parallel to the molecular axis) has a major contribution. In fact, the dye molecules experience a more polar environment through $\varepsilon_{\|}$ rather than mean dielectric constant.

3.3. Polarized absorption of the dyes (LD)

The optical polarization measurements made using oriented nematic solvents give important information on the orientation of the solute molecules, the direction of the transition moments and the polarization of electronic absorption bands [18]. The linear dichroism of a sample is defined as the difference in absorbance between two linearly polarized beams of light possessing electric vectors perpendicular to each other. The linear dichroism basically depends on two factors, i.e. the alignment of the dye in the nematic host and the angle between the optical transition dipole moment and the long molecular axis of the dye.

The dichroic ratio R of a dye dissolved in a nematic host is defined as the ratio between absorption of light polarized parallel $(A_{\|})$ and perpendicular $(A_{\perp})$ to the nematic director (rubbing direction). The dichroic ratio, R, can be determined by measuring the polarized absorbances at $\lambda_{\max}$ by using Eq. (2):

$$R = A_{\|}/A_{\perp} \qquad (2)$$

The polarized absorption spectra of dissolved dyes in the nematic hosts were recorded using parallel-aligned guest–host cells with the thickness of $d = 50\ \mu\text{m}$ at room temperature. Fig. 7a–c shows the polarized spectra of NR in 5CB, 1294-b and 7CP5BOC, respectively. The polarized absorption spectrum of nematic solution of NB in 5CB is also shown in Fig. 8. The experimental data have been complied in Table 4.

The aromatic skeleton of both the dyes used in this study is approximately planar, so that the transition moment vector (direction of dipole moment change) of the dye molecules may be considered to be largely parallel to the long molecular axis. Since, the transition moment vector between two electronic states (π–π* transition) of the dye molecules lies within the molecular plane, a relation between the absorption anisotropy and the degree of anisotropy of the guest molecules, S, dissolved in oriented nematic host can be derived directly [30].

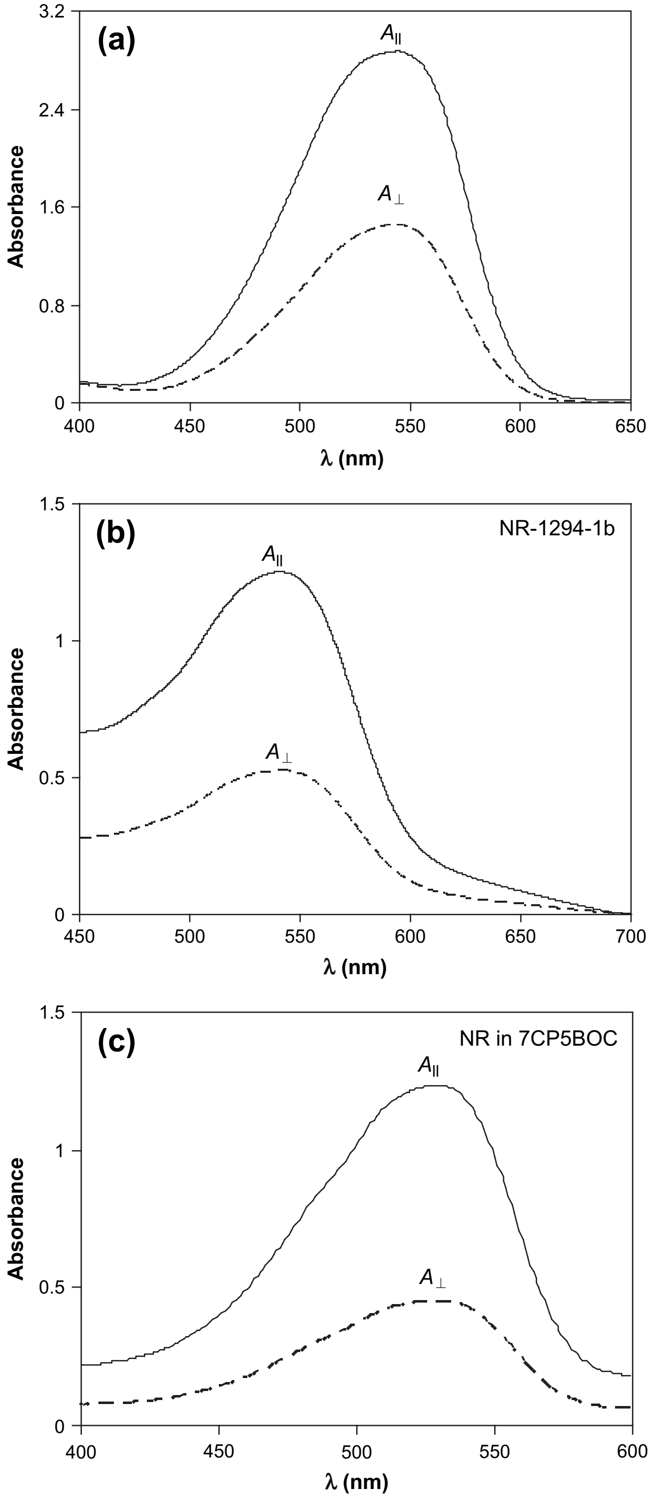

Fig. 7. Polarized absorption spectra of NR in the nematic solvents: (a) 5CB, (b) 1294-1b, and (c) 7CP5BOC. In the top spectrum the electric field vector of light is parallel ($A_{\parallel}$), and in the bottom spectrum perpendicular ($A_{\perp}$) to the nematic director.

$$S = \frac{R-1}{R+2} \tag{3}$$

It should be noted that the angle between the absorption oscillator and the long molecular axis (β) is unknown for the dyes under study. To a first approximation, we assume that $\beta = 0$, and estimate the degree of anisotropy of the dyes dissolved in the nematic host by using Eq. (3).

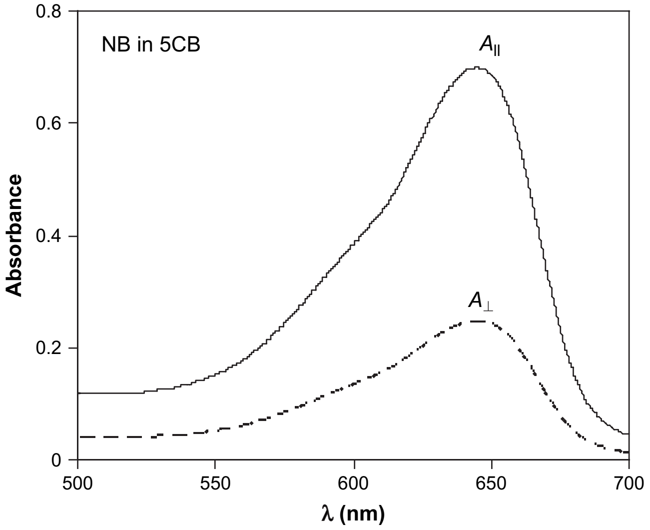

Fig. 8. Polarized absorption spectra of NB in the nematic solvent, 5CB.

It is interesting to compare the LD data, obtained in polar nematic host, of NR with that of NB. From Table 4, it can be seen that NR has lower dichroic ratio R and degree of anisotropy S compared to the cationic dye. Probably, this can be explained by that the ion–dipole forces play an important role in the orientational order of the ionic dye–polar LC, while dipole–dipole interactions control the alignment properties of the neutral polar dye and polar host.

On the other hand, the dichroic ratio and degree of anisotropy of NR in 7CP5BOC is higher than that of polar nematic hosts such as 5CB. Perhaps, it can be explained by the nematic alignment properties and the nature of the interactions of the host and the dye molecules. In this case, van der Waals interactions (steric and dispersive) seem to dominate the neutral dye alignment in the low-polar host [31]. The π–π interaction between the aromatic systems of the dye and the nematic host, which can play an important role in alignment properties of guest–host system, should be considered.

3.4. The electric linear dichroism (ELD)

The electric linear dichroism (ELD) is one of the electro-optic methods that measure the change in the absorption of the incident

Table 4
Dichroic ratio, R, contrast ratio, CR, and degree of anisotropy, S, measured for the dyes in nematic solvents

Dye	Nematic host	R	CR	S_{dye}
Nile blue	5CB	2.8	2.70	0.37
	6CB	2.8	2.57	0.37
	Mixture 1294-1b	2.9	2.78	0.39
	7CP5BOC	–	–	–
Nile red	5CB	2.0	1.98	0.25
	6CB	2.0	1.96	0.25
	Mixture 1294-1b	2.4	2.29	0.32
	7CP5BOC	2.7	–	0.36

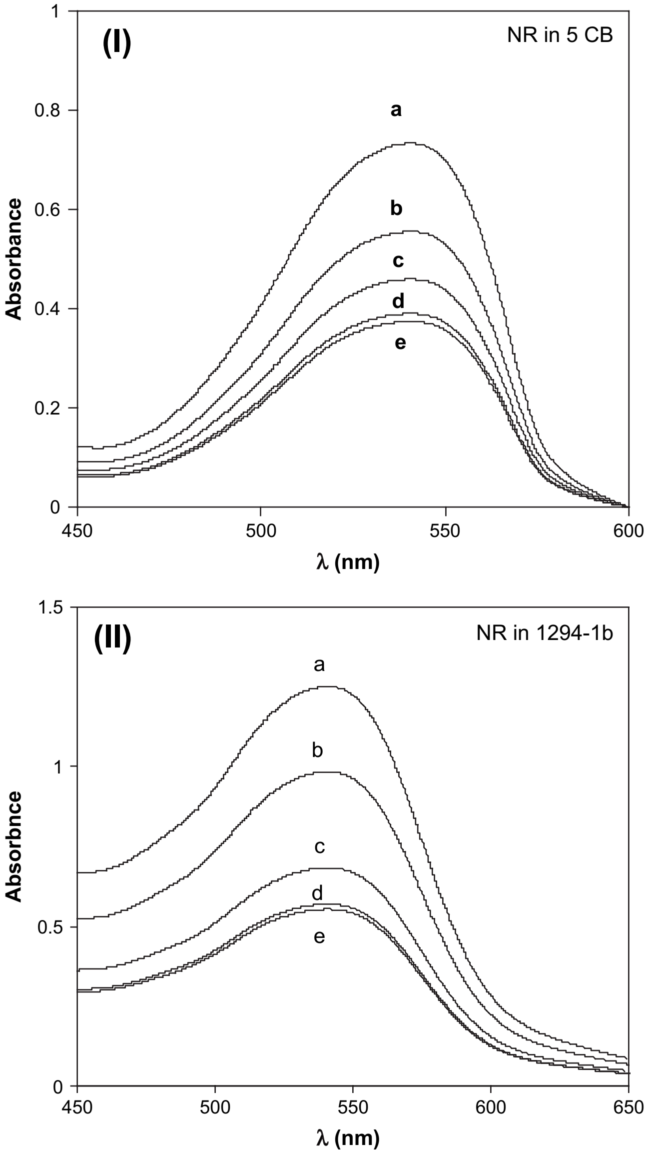

Fig. 9. Polarized absorption spectra of NR in the oriented nematic solvents, (I) 5CB and (II) 1294-1b at different voltages, AC field, 5 kHz, (a) 0 V, (b) 2 V, (c) 3 V, (d) 4 V, and (e) 5 V.

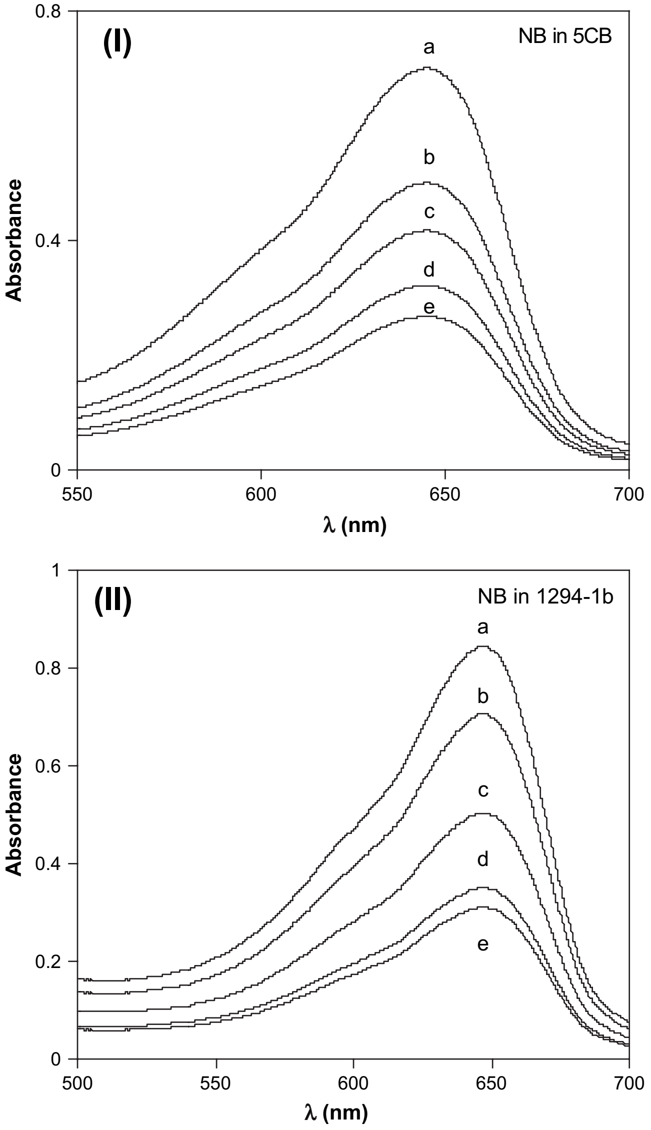

Fig. 10. Polarized absorption spectra of NB in the oriented nematic solvents, (I) 5CB and (II) 1294-1b at different voltages, AC field, 5 kHz, (a) 0 V, (b) 2 V, (c) 3 V, (d) 4 V, and (e) 5 V.

light beams linearly polarized in parallel and perpendicular to the applied field direction. The reorientation of the dissolved dye molecules in oriented nematic host under applied electric field is very important from technical and scientific point of view.

The electro-optical effect of the dissolved dyes in the anisotropic hosts was also measured using a parallel-aligned guest–host cell, and their contrast ratios ($A_{\mathrm{off}}/A_{\mathrm{on}}$) were obtained. Here, A_{off} is the absorbance at the absorption maximum wavelength in the off state and A_{on} is that in the on state. The contrast ratios, CR, of the dyes were obtained and listed in Table 4. It should be noted that, as A_{on} is an electric field direction dependence quantity and its value also depends on anchoring energy of the surface, the dichroic ratio, R, and the contrast ratio, CR, values are slightly different. However, the contrast ratio values obtained were slightly smaller than the dichroic ratios in the dyes.

Figs. 9 and 10 show the polarized absorption spectra of nematic solutions of NR and NB in different alternating electric field strengths (5 kHz). It can be seen that the intensity of the spectra (without change of its shape) decreases as the voltage increases. The ELD measurements indicate that the transitions are of $\pi-\pi^*$ type (i.e. parallel transitions), which is the only electric-dipole-allowed transition in the visible range.

4. Conclusions

The solvatochromic behavior for NB in nematic solutions is higher than those observed for the ordinary isotropic solutions indicating strong molecular interactions between the dye molecules and liquid crystalline matrix. In contrast, the absorption spectra of NR in the anisotropic hosts were blue shifted compared to polar protic solvents. However, like NB, the absorption band of NR in the liquid crystals is also red shifted as compared to the dye spectrum in non-polar solvents.

The ion–dipole interactions as well as dipole–dipole forces are expected to contribute significantly to the cationic dye, NB, spectra in liquid and liquid crystal solutions, while the van der Waals (steric and dispersive) interaction has a major effect on the absorption spectra of NR in low-polar anisotropic environment. Due to the high polarizable structure of the dyes and the nematic hosts, there is an extra $\pi-\pi$ interaction between their aromatic systems, which can give extra solvent effect on the spectral properties of the dyes in nematic environments.

Positive dichroic ratios ($R > 1$) are found for the dyes in liquid crystalline solutions. The LD and ELD measurements indicate that the transitions are of $\pi-\pi^*$ type (i.e. parallel transitions), which is the only electric-dipole-allowed transition in the visible range. It should be noted that the $\pi-\pi^*$ transition is a parallel transition, i.e. during the $\pi-\pi^*$ transition a net displacement of charge occurs parallel to the molecular plane.

Although the present fluorescence measurements provide qualitative information on the emission behavior and the influence of anisotropic surrounding on the emission properties of the dyes in the nematic hosts, a deeper fluorescence studies in nematic hosts, for the interpretation of the important photophysical features of this laser dye, is required.

References

[1] Schafer FP, editor. Dye lasers. Berlin: Springer; 1990.
[2] Jose J, Burgess K. Tetrahedron 2006;62:11021.
[3] Kubinyi M, Grofcsik A, Papai I, Jones WJ. Chem Phys 2003;286:81.
[4] Blanchard GJ, Cihal CA. J Phys Chem 1988;92:5950.
[5] Blanchard GJ. J Phys Chem 1991;95:5293.
[6] Ghoneim N. Spectrochim Acta Part A 2000;56:1003.
[7] Thomas JK. J Phys Chem 1987;91:267.
[8] Dutta AK, Kamada K, Ohta K. J Photochem Photobiol A Chem 1996;93:57.
[9] Dutta AK, Kamada K, Ohta K. Chem Phys Lett 1996;258:81.
[10] Nakashima K, Liu YS, Zhang P, Duhamel J, Feng J, Winnik MA. Langmuir 1993;9:2825.
[11] Sackett DL, Wolf J. Anal Biochem 1987;167:228.
[12] Sackett DL, Knutson JR, Wolff J. J Biol Chem 1990;265:14899.
[13] Klinkner AM, Bugelski PJ, Waites CR, Louden C, Hart TK, Kerns WD. J Histochem Cytochem 1997;45:743.
[14] Greenspan P, Fowler SD. J Lipid Res 1985;26:781.
[15] Viseu TMR, Hungerford G, Coelho AF, Ferreira MIC. J Phys Chem B 2003;107:13300.
[16] Basting D, Ouw D, Schaefer FP. Opt Commun 1976;18:260.
[17] Sarkar N, Das K, Nath DN, Bhattacharyya K. Langmuir 1994;10:326.
[18] Michl J, Thulstrup EW. Spectroscopy with polarized light. Wiley-VCH Book; 1995.
[19] Ghanadzadeh A, Zanjanchi MA. Spectrochim Acta Part A 2001;57:1865.
[20] Ghanadzadeh A, Zanjanchi MA, Tibandpay R. J Mol Struct 2002; 616:167.
[21] Bauman D, Chrzumnicka E, Dabrowski R, Jadzyne J. Z Naturfosch 1998;53a:813.
[22] Iwanaga H, Naito K, Effenberger F. Liq Cryst 2000;27:115.
[23] Ghanadzadeh A, Tajalli H, Zirack P, Shirdel J. Spectrochim Acta Part A 2004;6:2925.
[24] Ghanadzadeh A. PhD thesis, Aston University, Birmingham, UK; 1995.
[25] Dabrowski R, Jadzyn J, Czerkas S, Dziaduszek J, Walczak A. Mol Cryst Liq Cryst 1999;332:332.
[26] Reichardt C. Solvents and solvent effects in organic chemistry. 2nd ed. VCH; 1988.
[27] Cser A, Nagy K, Biczok L. Chem Phys Lett 2002;360:473.
[28] Kim HH, Song NW, Park TS, Yoon M. Chem Phys Lett 2006;432:200.
[29] Khoshsima H, Ghanadzadeh A, Tajalli H. Liq Cryst 2006;33:747.
[30] Raj D. Mater Chem Phys 1996;43:204.
[31] Marrucci L, Paparo D, Vetrano MR, Colicchio M, Santamato E. J Chem Phys 2000;113:10361.