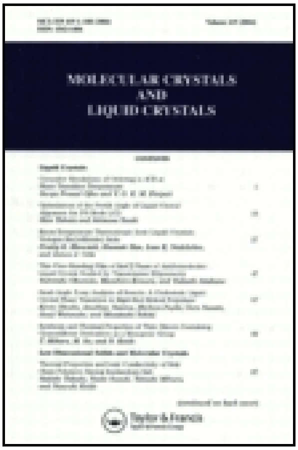

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The Spectral Properties of New Types of Fluorescence Dyes in Nematic Liquid Crystals

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The Spectral Properties of New Types of Fluorescence Dyes in Nematic Liquid Crystals

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The spectral properties of the new class of fluorescent dyes in isotropic and anisotropic (liquid crystals) solvents have been investigated. The main purpose of these investigations was to get some information on these dyes in order to utilize them in colored liquid crystal displays. These dyes align well in nematic liquid crystals and have high fluorescence yield, therefore the authors tried to apply one of them in two various types of liquid crystal displays.

Keywords: liquid crystal, "guest-host" effect, absorption and fluorescence spectra, display device

1. INTRODUCTION

In 1968 Heilmeier and Zanoni[1] first reported the "guest-host" effect in nematic liquid crystals using the dye methyl red as a "guest". In the next year Heilmeier *et al.*[2] reported in somewhat more details of the "guest-host" cells with the dye indophenol blue as a "guest". But these dyes did not give good pleochroism and a large color change upon the application of an electric field. Ever since, the use of aligned nematics as orienting matrices for studying the spectral properties of dissolved dyes have been well documented.[3-7]

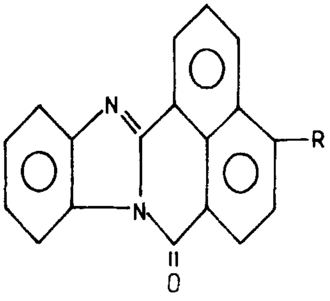
Sackmann[8,9] first measured not only the polarized absorption but also polarized fluorescence of various pleochroic fluorescent dyes in nematic liquid crystals and found that the long molecular axes of the dye molecules align parallel to those of the liquid crystal molecules. He has also shown that this technique is useful for obtaining the orientation of the transition moments of oriented "guest" molecules. On the other hand as have been shown by Uchida *et al.*[4,10] and Larrabee[11] the polarized absorption and fluorescence of "guest" in aligned nematic liquid crystals can be utilized in colored liquid crystal display devices. In colored liquid crystal displays (LCDs) good color switching and a large viewing angle should be obtainable, meaning in practice that good pleochroic dyes must be found. The characteristics of color switching depend on dichroic properties of dyes, dye concentration and the applied voltage. But in the case of fluorescent dyes an excellent character for color switching can be obtained if the quantum fluorescence yields of dyes are high. Therefore, in order to check the usefulness of the fluorescent dyes in LCD devices their basic spectral parameters (the absorption and fluorescence maxima, the quantum fluorescence yield and the extinction coefficients) first in isotropic solvents and next in liquid crystals should be measured.

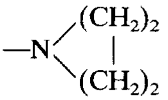
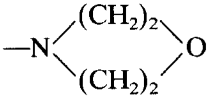
In this paper, therefore, the authors show and describe the spectral properties of a new class of fluorescence dyes in two kinds of isotropic solvents and in nematic liquid crystals. Next, the possibility of application of these dyes in LCDs have been presented.

2. MATERIALS AND METHODS

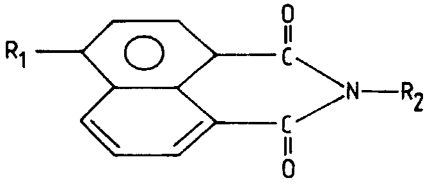
The following fluorescent dyes were used:

1.



Dyes	R
R 823	NH_2
R 825	$NHCH_2CH_2CH_3$
R 827	$N(CH_3)_2$
R 829	
R 831	

2.



Dyes	R_1	R_2
R 719 N	$N(CH_3)_2$	CH_2CH_3
R 764	$N(CH_3)_2$	p-$C_6H_4CH_3$
R 800	$NHCH_2CH_2OCH_3$	CH_2CH_3

These dyes were synthesized and chromatographically purified.[12] For the isotropic solvents benzene (nonpolar) and acetone (polar) were used. The room temperature nematic liquid crystals 5CB and 6CB as the orienting matrices were used.

The absorption spectra were measured with the SPECORD M40 spectrophotometer (Carl Zeiss Jena). The experimental arrangement for the fluorescence spectra measurements was described elsewhere.[13] The quantum fluorescence yield (Φ) of investigated dyes in isotropic solvents have been calculated using the following equation:[14]

$$\Phi = \Phi_0 \frac{1 - 10^{-A_0}}{1 - 10^{-A}} \frac{\int_0^\infty F\, d\lambda}{\int_0^\infty F_0 d\lambda}, \qquad (1)$$

where Φ_0—the quantum fluorescence yield of standard,
A_0, A—the absorbances of standard and investigated dye in maximum of absorption wavelength, respectively,
$\int_0^\infty F\,d\lambda$, $\int_0^\infty F\,d\lambda$—the integrals of fluorescence spectra of standard and investigated dye, respectively.

As a standard we have taken fluorescein of 10^{-6}M/l concentration in 0.1 M NaOH. The quantum fluorescence yield of fluorescein at 20°C is $\Phi_0 = 0.92$.[14]

All spectral measurements of investigated dyes dissolved in nematic liquid crystals have been carried out in "sandwich" cells. Homogenous alignment of the liquid crystals and dye molecules in these cells were achieved by evaporation of an SiO_x thin layer onto cell windows at an angle 30° to the surface.[15]

From the absorption measurements of dyes in nematic liquid crystals the absorption order parameters S_A have been evaluated using the following formula:[16–18]

$$S_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} \frac{1}{1 - \frac{3}{2}\sin^2\beta}, \tag{2}$$

where $A_\parallel$ and $A_\perp$ denote parallel and perpendicular components of absorption and β is an angle between the vector of absorption transition moment and the "long axis" of the dye molecule.

If $\beta = 0°$ the equation (2) is reduced to the following equation:[19]

$$S'_A = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}, \tag{3}$$

However, for the new types of fluorescent dyes studied in this paper the angles β are still unknown. Therefore we used the equation (3) in order to estimate the orientation of dyes dissolved in liquid crystal matrices, although the symmetry group of these dyes is not high enough to fix $\beta = 0°$.

Similarly we evaluated the orientation of dyes in liquid crystals from the fluorescence emission measurements using the following equations:[19]

a) for unpolarized excitation

$$S'_F = \frac{F_\parallel - F_\perp}{F_\parallel + 2F_\perp}, \tag{4}$$

b) for polarized excitation

$$S'_F = \frac{\sqrt{F_\parallel} - \sqrt{F_\perp}}{\sqrt{F_\parallel} + 2\sqrt{F_\perp}}, \tag{5}$$

where $F_\parallel$ and $F_\perp$ denote parallel and perpendicular components of emission intensities.

These equations hold only for $\gamma = 0°$, where γ is an angle between the vector of emission transition moment and long molecular axis.

3. RESULTS AND DISCUSSION

3.a Isotropic solvents

The basic spectral parameters: absorption and fluorescence maxima (λ_{max}), extinction coefficients (ϵ), halfbandwidths (δ), quantum fluorescence yields (Φ) and Stokes shifts ($\bar{\nu}_A - \bar{\nu}_F$) for both groups of dyes in benzene (nonpolar solvent) and acetone (polar solvent) are given in Table I whereas in Figure 1 the absorption and fluorescence spectra of R 800 and R 825 in two solvents are shown. In all absorption and fluorescence measurements the dye concentrations were 10^{-5} M/l and 10^{-6} M/l, respectively.

As can be seen from Table I the spectral parameters of both groups of dyes are quite similar to one another but when the polarity of solvent increases then the absorption and emission spectra are shifted towards longer wavelength. It could be simply explained in terms of solute–solvent interactions.[20,21] The dual fluorescence of R 825 and R 829 in benzene have been the subject of considerable controversies,[22–24] therefore two questions:

1) why does dual fluorescence occur,
2) what kind of mechanism is responsible for the observed dual fluorescence, remain still open.

For all investigated dyes, except for R 719 N and R 764 dissolved in acetone, the quantum fluorescence yield are very high. A small fluorescence yield of R 719 N ($\Phi = 0.14$) and R 764 ($\Phi = 0.17$) in acetone may be caused by the molecular interactions between the carbonyl groups C=O of these dyes and acetone molecules (CH_3COCH_3). In these two cases the oxygen in acetone's molecular structure may act as a fluorescence quencher.

TABLE I

The values of spectral parameters of investigated dyes in isotropic solvents.

Dyes Code	Benzene						
	Absorption			Fluorescence			
	λ_{max} [nm]	$\epsilon \cdot 10^4 \left[\frac{1}{M \cdot cm}\right]$	δ [nm]	λ_{max} [nm]	Φ	δ [nm]	$\tilde{\nu}_A - \tilde{\nu}_F\,[cm^{-1}]$
R 825	429; 450	1.34	61.5	481; 500	0.98	59.0	2520; 2220
R 827	427	1.76	76.0	490	0.61	59.5	3011
R 829	444; 467	1.53	67.0	490; 515	0.48	60.0	2114; 1996
R 831	409;	1.13	67.5	490.5	0.79	59.0	4041
R 719N	405	1.04	70.3	494	0.64	63.0	4448
R 764	400	1.08	72.4	494	0.63	67.0	4757
R 800	417	1.60	64.7	490	0.73	76.0	3573

Dyes Code	Acetone						
	Absorption			Fluorescence			
	λ_{max} [nm]	$\epsilon \cdot 10^4 \left[\frac{1}{M \cdot cm}\right]$	δ [nm]	λ_{max} [nm]	Φ	δ [nm]	$\tilde{\nu}_A - \tilde{\nu}_F\,[cm^{-1}]$
R 823	431; 446	1.20	69.0	495	0.87	70.0	2999; 2219
R 825	434; 454	1.11	62.0	500	0.97	64.0	3041; 2026
R 827	434	1.75	74.0	510	0.46	62.0	3434
R 829	431	1.94	79.0	500	0.54	67.0	3201
R 831	411	1.57	71.0	500	0.61	55.0	4330
R 719N	413	1.01	76.0	500	0.14	78.0	4213
R 764	412	1.10	68.5	510	0.17	72.0	4664
R 800	429	1.66	69.4	504	0.40	68.0	3469

R 823 does not dissolve in benzene

3.b Liquid crystals

In this chapter we would like to answer the following question: will the investigated dyes be able to apply in colored liquid crystal displays or not?

The spectral measurements which have been presented in the previous chapter indicate that both these groups of dyes absorb and fluoresce in the spectral region 405–515 nm and have high fluorescence yield which are very profitable to their application in colored liquid crystal displays. One should still check the solubility and the orientation of these dyes in nematic liquid crystals.

The absorption and fluorescence maxima (λ_{max}), Stokes shifts $(\tilde{\nu}_A - \tilde{\nu}_{F\parallel})$, $(\tilde{\nu}_A - \tilde{\nu}_{F\perp})$ and the S'_A and S'_F values for investigated dyes

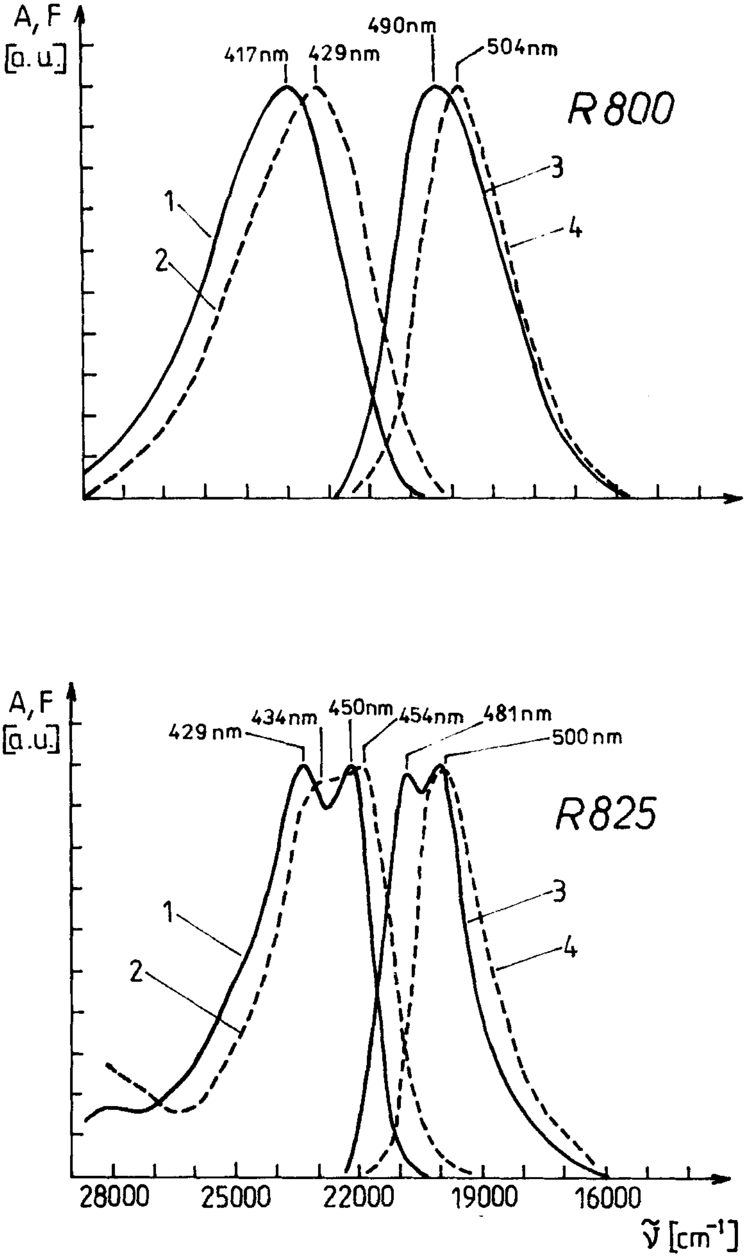


FIGURE 1 Absorption (curves 1, 2) and fluorescence (curves 3, 4) spectra of R 800 and R 825 in benzene (solid curves) and acetone (dashed curves). The dyes concentrations were 10^{-5} M/l and 10^{-6} M/l for absorption and fluorescence measurements, respectively.

TABLE II

The values of spectral parameters of investigated dyes in nematic liquid crystals. The thickness of the samples $d = 10$ μm.

Dyes Code	6CB						
	Absorption		Fluorescence				
	$\lambda_{\max}$ [nm]	S'_A	$\lambda_{\max}$ [nm]		S'_F	$\tilde{\nu}_A - \tilde{\nu}_{F_\parallel}$ [cm^{-1}]	$\tilde{\nu}_A - \tilde{\nu}_{F_\perp}$ [cm^{-1}]
			$F_\parallel$	$F_\perp$			
R 823	440; 455	0.35	490	487	0.36	2319; 1570	2194; 1445
R 827	450	0.30	505	501	0.31	2421	2262
R 829	455; 480	0.33	510	508	0.33	2371; 1226	2293; 1148
R 831	420	0.28	505	502	0.26	4008	3889
	5CB						
R 719N	424	0.29	518	514	0.24	4280	4130
R 764	427	0.36	515	512	0.33	4002	3888
R 800	432	0.26	512	508	0.23	3617	3463

dissolved in nematic liquid crystals 5CB and 6CB are given in Table II. The dye's solubility in these two liquid crystal matrices were very good up to $5 \cdot 10^{-2}$ M/l. As can be seen from Table II the absorption and emission maxima of these dyes in nematic liquid crystals in comparison with isotropic solvents (Table I) are slightly shifted towards longer wavelengths. The dyes R 719 N and R 764 emit more strongly in 5CB than in acetone. It may be caused by the particular type of interactions between the cyano group C≡N of 5CB and the dye molecules.

For practical reasons ("guest-host" effect) it is important to choose dyes with a high ability of orientation in a liquid crystal matrix. This ability strongly depends on dye structure,[25] molecular interactions between dye and liquid crystal molecules[26] as well as on the surface interactions between liquid crystal molecules and the cell surface.[27] In liquid crystal "guest-host" cells with fluorescent dyes the surface interactions can be revealed on the basis of comparison of values S_A and S_F.[27] Our previous observations indicate that if $S_F > S_A$ then surface interactions are present—owing to the specific dipole–dipole interactions between SiO_x layer, liquid crystal and dye molecules. In this paper, however, as can be seen from Table II, $S'_F \leq S'_A$ which suggest that strong surface interactions in our liquid crystal cells does not occur.

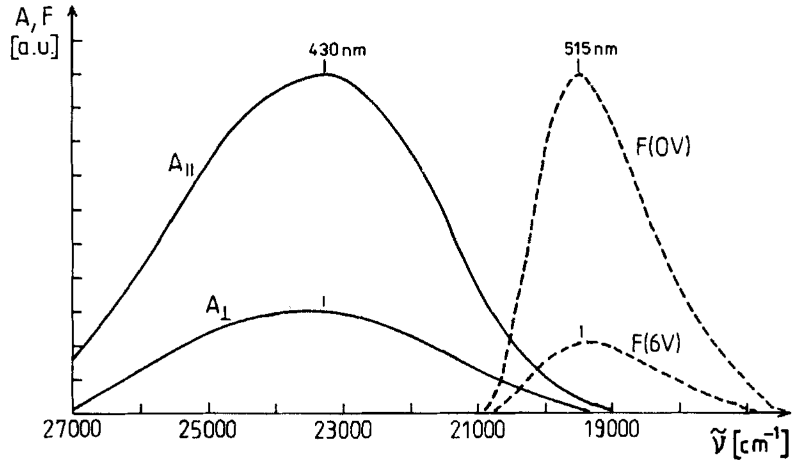


FIGURE 2 The polarized components of absorption spectra ($A_\parallel$, $A_\perp$) and fluorescence spectra in "off" (U = 0V) and "on" (U = 6V) states for R 764 in E18 ($C = 2.5 \cdot 10^{-2}$ M/l). The cell thickness was d = 10 μm.

4. APPLICATION

The results presented in Table II indicate that the values of S'_A and S'_F of all investigated dyes are not very high in comparison with azo- and antra-quinone dyes,[28,29] what probably is due to the fact that $\beta \neq 0°$ and $\gamma \neq 0°$. However, because of their high quantum fluorescence yield in isotropic solvents we have decided to check the usefulness of these dyes in a colored liquid crystal display. We chose the dye R 764 because it had the best orientation in 5CB. R 764 has also been dissolved in nematic mixture E18 (BDH) which is often used in liquid crystal displays. In Table III the absorption and fluorescence maxima (λ_{max}) as well as the values of S'_A and S'_F of R 764 in E18 are shown. The quantum fluorescence yield of R 764 in E18 has been estimated in relation to quantum fluorescence yield of this dye in benzene. The value obtained was $\Phi = 0.31$, which is high, in comparison with, for example, Φ of methine dyes ($\Phi = 0.13$).[24]

We have used two types of liquid crystal displays. The first one consisted of: liquid crystal cell of 10 μm thickness with dye R 764 dissolved in E18 and an external neutral polarizer. The light incident on the cell (λ = 436 nm) was linearly polarized by the external polarizer in which the electric vector was parallel to the molecular alignment of the liquid crystal long axes. The dye fluorescence was observed on the other side of the cell. The dye concentration

TABLE III

The absorption and fluorescence maxima and the values of S'_A and S'_F of R 764 in E18

	λ_{max} (nm)	S'
Absorption	430	$S'_A = 0.43$
Fluorescence	$F_\parallel = 513$ $F_\perp = 511$	$S'_F = 0.42$

($C = 2.5 \cdot 10^{-2}$ M/l) was adjusted so that the degree of coloration was as large as possible. The changes of fluorescence intensities at $U = 6$V ac voltage and frequency of 1 kHz were measured. In Figure 2 the absorption and fluorescence spectra of R 764 in E18 at $U = 0$V and $U = 6$V are shown. The ratio of fluorescence intensities in $\lambda_{max} = 515$ nm is $F_{off}/F_{on} = 4.72$. This result indicates that the change of fluorescence intensities by on–off control of the applied voltage is large and in LCD a light sign on a green fluorescent background can be observed.

The second type of liquid crystal display consisted of two liquid crystal cells (C_1 and C_2) and external neutral polarizer (Figure 3). The cell C_1 contained the fluorescence dye R 764 in E18 (pointers in

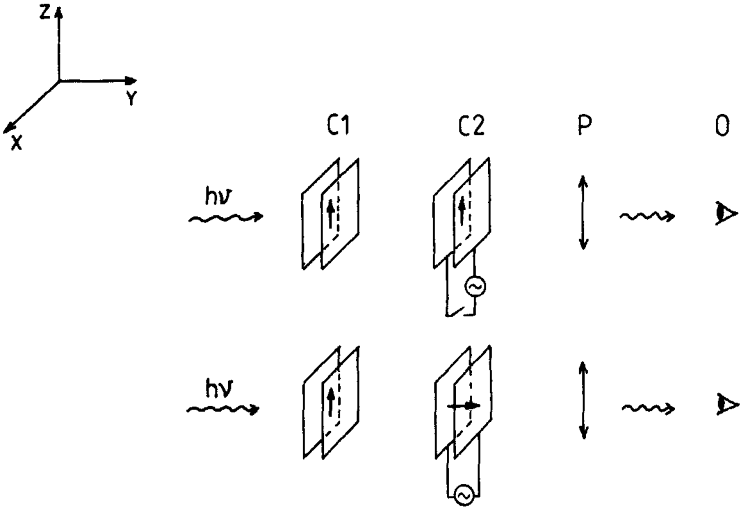
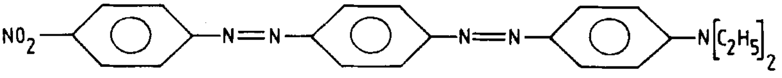


FIGURE 3 The mutual arrangement of C_1 and C_2 cells and external neutral polarizer P in liquid crystal display.

Figure 3 show the directions of liquid crystal and dye molecules alignment) and the cell C_2 contained the pleochroic dye red I in E18. The chemical structure of red I is as follows:



In Figure 4 the polarized absorption components of red I ($C = 1.4 \cdot 10^{-2}$ M/l) in E18 and normalized fluorescence spectrum of R 764 in E18 are shown. The R 764 fluorescence spectrum is covered by the red I absorption spectrum. Thus the emission of R 764 is absorbing by red I and the display has a red color when the ac applied voltage is in the "off" state. In the "on" state the voltage applied to the cell C_2 (Figure 3) orients the liquid crystal and red I molecules to the direction of electric field (because of positive dielectric anisotropy of liquid crystal) and then the emitted light from the first cell (C_1) can be observed. In this type of display one can also obtain the intensive green fluorescent sign on the red background. The ratio of fluorescence intensities in the "on" and the "off" states is $F_{on}/F_{off} = 7$, therefore the second type of our liquid

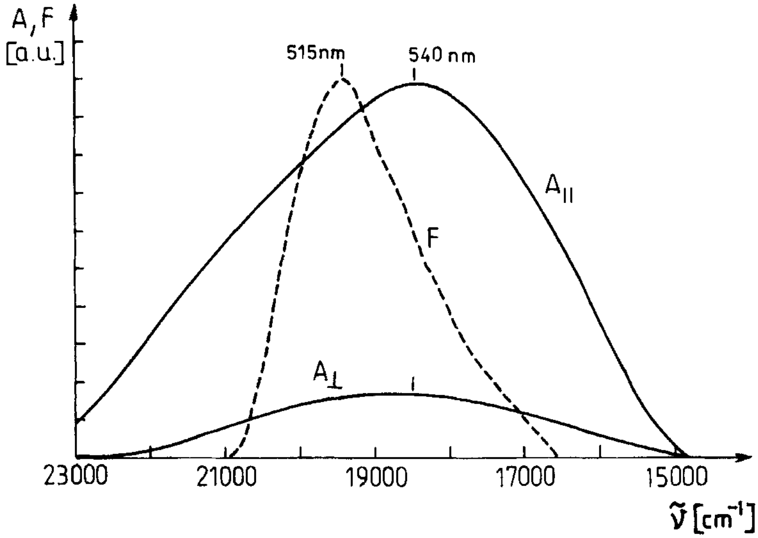


FIGURE 4 The polarized components of absorption spectra ($A_{\parallel}$, $A_{\perp}$) for the dye red I in E18 ($C = 1.4 \cdot 10^{-2}$ M/l) and fluorescence spectrum of R 764 in E18 ($C = 2.5 \cdot 10^{-2}$ M/l). The thickness of the samples were $d = 10$ μm.

crystal display give the better perceived contrast with respect to the first one.

Acknowledgments

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