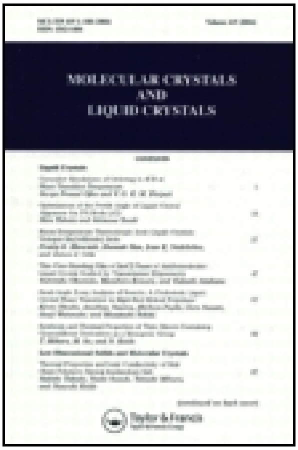

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Designing a Black Mixture by Dichroic Dyes for Liquid Crystal Devices

Boris Umanskii [a], Elena Prudnikova [a] & Sofia Torgova [a]

[a] SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B. Sadovaya 1/4, Moscow, 103787, Russia

Version of record first published: 24 Sep 2006

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 27-36
Reprints available directly from the publisher
Photocopying permitted by license only

Designing a Black Mixture by Dichroic Dyes for Liquid Crystal Devices

BORIS UMANSKII, ELENA PRUDNIKOVA and SOFIA TORGOVA

SSC RF "NIOPIK" (Organic Intermediates & Dyes Institute), B. Sadovaya 1/4, Moscow 103787, Russia

A method for choosing dichroic dyes either with positive or with negative dichroism was established, for obtaining efficient black mixtures, suitable for being dissolved in liquid crystals. The absorption spectra of many dyes have been checked: the peak maxima were spread in all the visible range of the light. The criteria for building up efficient black mixtures covering all visible range were found. Such criteria mainly concern dyes choice and dyes relative concentration. Extinction, dichroism and saturation solubility were measured for all mixtures in different liquid crystal matrices. The results appear to be very promising for application to liquid crystal devices.

Keywords: dichroic dyes; black mixtures

INTRODUCTION

The guest-host effect is the voltage-induced change of the absorption of dichroic dyes (guest), solved in the liquid crystal matrix (host). As a rule, the dichroic dye molecules have elongated form with cylindrical symmetry. The transition moments of dyes have their greater component either parallel to the long molecular axis (positive dichroism) or to the short molecular axis (negative dichroism). Positive dichroic dyes (or L-dyes) absorb the linearly polarized light, which electric field E is parallel to average long molecular axis of the dye, whereas negative dichroic dyes (or T-dyes) absorb the light, which E is perpendicular to the average long molecular axis. Usually these dyes have a narrow absorption spectrum, the maximum absorption wavelength hereafter defined as λ_{max}. The colour of the cell is basically due to the light which was not absorb by the dye.

The efficiency of dichroic dye in a given LC matrix is determined by size of an absorption A at λ_{max}, width of the absorption band and order parameter defined as $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} + 2A_{\perp})$. Here $A_{\parallel}$ and $A_{\perp}$ are the polarized absorbences parallel and perpendicular to the nematic director at λ_{max}. The dichroic ratio $R = A_{\parallel}/A_{\perp}$ also used to characterize the dichroism of the dye.

The first guest-host effect display was built up by Heilmeier and co-workers, who used host matrix consisting of a nematic liquid crystal having positive dielectric anisotropy with unidirectional planar orientation and incorporated the guest dye molecules[1,2]. Such a display requires one polarizer to reach an acceptable contrast of the optical transmission between off- and on-states. An considerable improvement of the guest-host effect from the point of view of the optical contrast was found by White and Taylor[3]. This improvement is based on the field-induced reorientation of the dichroic dye molecules, solved in the nematic matrix with a chiral dopant. The reorientation takes place during the cholesteric-nematic phase transition. Such a display does not require polarizers, but must be operate at higher voltage. The contrast of White and Taylor display can in principle be larger than in Heilmeier guest-host displays without polarizers. Moreover, the very interesting fact is that there is a very low angular dependence of the contrast of such displays.

The LC display technology based on the guest-host effect has not yet found broad application, because of a lot of drawbacks: for instance the high control voltage, the gently sloping dependence of the contrast vs. voltage giving low multiplexing ability, and eventually a contrast not so high. Nevertheless, such type of LC displays has good perspectives for the application due to the intrinsic advantages, as compared with twisted nematic displays; namely, the absence of polarizers, the wide viewing and the capability of obtaining colored images.

Furthermore, it is possible to increase the efficiency of the information mapping by means of guest-host effect, extending the working spectrum of the dichroic dyes, by composing a black mixture of dyes having the absorption peak covering almost the whole visible spectrum of the light. Thus certainly it is necessary to renounce to colored images, as in this case the switched on- and off- states will be black-and-white.

The design of a black mixture requires the solution of many problems:

a) To get a number of dyes high enough to overlap, covering the largest possible interval of the visible spectrum of the light;

b) To reach a high dichroism for all dyes to be included in the black mixture. All the dyes must be characterized by high order parameter S or contrast ratio R;

c) To get dyes with the broad absorption bands;

d) To take into account the limited solubility of any dye in any LC matrix at low temperature;

e) To control the mutual influence of different dyes included in the some mixture, to depress their solubility;

f) To get a sufficiently high absorbance of the dyes for certain concentration and certain thickness of the LC layer, the dye with lower specific absorbence should have high saturation solubility;

g) To determine with high accuracy absorbences of all dyes included in the black mixture.

EXPERIMENT

With the aim of composing black mixtures we used a large number of dichroic anthraquinone and azo dyes with positive and negative dichroism, developed in SSC RF "NIOPIK" and already covered by patents.

The polarized absorption spectra of the guest-host mixtures in the visible spectral region were obtained by using a Specord M40 (Carl Zeiss Jena) double beam spectrophotometer equipped with neutral polarizes.

The unidirectional planar orientation of the guest-host mixture was achieved by treatment of the glass surfaces of the cells with polyvinyl alcohol and by rubbing. This procedure usually provide a good planar orientation in a thin layer: *in our case it was controlled through the crossed polarizers*. *In all* experiments, the light propagation was perpendicular to the surfaces of the cells. The thickness of "sandwich" cells were 20 μm.

The absorption spectra of the dyes dissolved in the liquid crystal matrix *were recorded for two orientations*, *that is*, *with the easy axis of the liquid* crystal sell at the angles of 0^0 and 90^0 with respect to the polarization plane of the light beam. Thus the absorbence $A_{\parallel}$ and $A_{\perp}$ as function of wavelength were obtained.

RESULTS AND DISCUSSION

The main point to be taken into account for designing a black mixture are : i. the choice of suitable LC matrix, according to the possible various applications; ii. The choice a sufficient number of dichroic dyes characterized by convenient properties, as listed above. For instance, if the black mixture is prepared for outside application, the LC matrix must have a large mesomorphic range and small viscosity at low environment temperature: thus, we have to choose dichroic dyes having enough solubility in such a host.

In our experiments we used as LC matrix Merck mixtures MLC-6281 and ZLI-1840 and NIOPIK mixtures ZhKM-807 and ZhKM-3141. The main purpose was the building up of a black mixture with positive dichroism for wide temperature application suitable for MLC-6281, and a black mixture with negative dichroism suitable for ZhKM-807. The later is a mixture of cyanobiphenyls. It was selected due to the reason that dyes with negative dichroism exhibit maximum solubility and maximum contrast ratio when dissolved in such a mixture.

For the determination of the leading parameters it is necessary to obtain the polarizing absorption spectra of the dichroic dyes to be chosen in the pre-fixed LC matrices in identical conditions at the same concentration. The dyes produced by NIOPIK were used for composing black mixtures with positive dichroism and with negative dichroism. The order of magnitude of the leading parameters for a typical dyes are reported Tab.1. The polarizing spectra of some of these dyes are shown on Fig.1. and Fig.2.

TABLE I Properties of dichroic dyes

N	DYES	λ_{max} (ZhKM - 807)nm	$S = \frac{D_{//} - D_{\perp}}{D_{//} + 2D_{\perp}}$	Optical Density d=10μm, c=1% $D_{\perp}$ (negative dyes) $D_{\parallel}$(positive dyes)	Solubility at 25°C %
1	KD-266	466	-0.38(ZhKM-807) -0.37(ZLI-1840)	0.18($D_{\perp}$)	6.5(ZhKM-807) 5,7(ZLI-1840)
2	KD-36	512	-0.34(ZhKM-807) -0.34(ZLI-1840)	0.15($D_{\perp}$)	2.4(ZhKM-807) 0.6(ZLI-1840)
3	KD-261	536	-0.38(ZhKM-807) -0.37(ZLI-1840)	0.21($D_{\perp}$)	4 (ZhKM-807) 2.5(ZLI-1840)
4	KD-312	618	-0.34(ZhKM-807)	0.2($D_{\perp}$)	0.7(ZhKM-807)
5	KD-318	614	-0.31(ZhKM-807)	0.2($D_{\perp}$)	0.78(ZhKM-807)
7	KD-378	640	-0.36(ZhKM-807)	0.38($D_{\perp}$)	1.0(ZhKM-807)
8	KD-4	603	0,7(ZhKM-807) 0,72(ZLI-1840)	0,6($D_{\parallel}$)	3,9(ZhKM-807)
9	KD-8	387	0,77(ZhKM-807) 0,79(ZLI-1840)	1,6($D_{\parallel}$)	1,8(ZhKM-807) 2,7(ZLI-1840
10	KD-9	450	0,77(ZhKM-807) 0,79(ZLI-1840)	1,6($D_{\parallel}$)	1,7(ZhKM-807) 1,8(ZLI-1840)
11	KD-10	630	0,76(ZhKM-807) 0,77(ZLI-1840)	0,6($D_{\parallel}$)	3,8(ZhKM-807) 2,7(ZLI-1840)

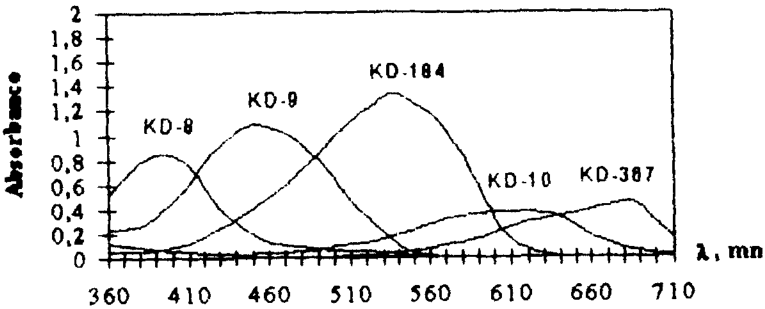

FIGURE 1 The absorbance spectra of dichroic dyes with positive dichroism

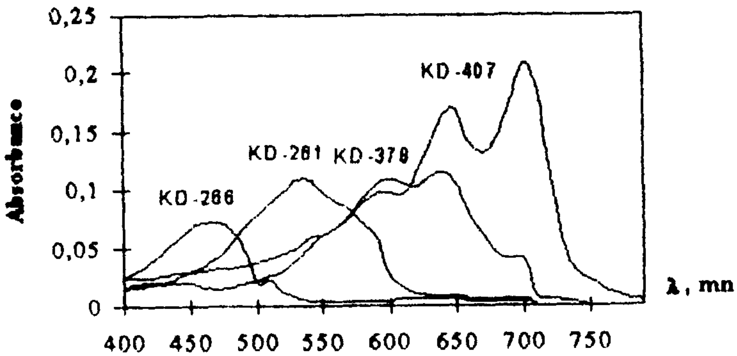

FIGURE 2 The absorbance spectra of dichroic dyes with negative dichroism

The limiting solubility of dyes in the LC matrix at low temperature was determined spectroscopically comparing the absorbencies of the dye solution in LC at room and at low temperatures.

After determination the limiting solubility of dyes at various temperatures in the prefixed LC matrix, the absorbance was measured, the widths of the absorption spectra at identical concentration was detected and the composition of a possible black mixture was calculated, according to the principle of additivity. The final structure of the black mixture was reached experimentally, by varying the dyes concentrations according to their solubilities and their absorbance at the presence of other dyes.

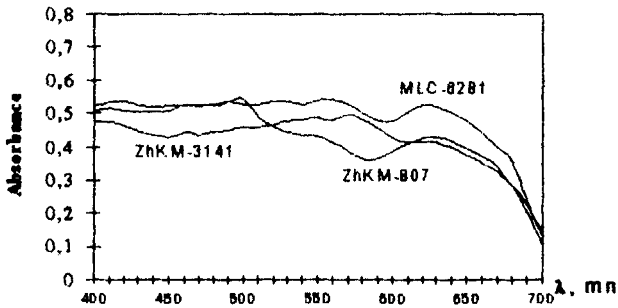

FIGURE 3 The absorbance spectra of black dichroic dyes with positive dichroism in the different LC matrices

The absorption spectrum of the black mixture with positive dichroism prepared for the LC matrix MLC-6281 is shown on Fig.3. As indicated there this mixture absorbs practically in the whole visible spectrum, curve of the absorption being sufficiently flat. The absorption spectra of some black mixture in ZhKM-807 and in ZhKM-1341 also are shown on Fig.3. As indicated in the figure, the absorption spectrum in ZhKM-807 considerably differs from the spectrum in MLC-6281, and the spectrum in ZhKM-1341 is similar to the spectrum in MLC-6281, but the solubility is about three times less, which does not exceed 1% in ZhKM-3141. The difference between the absorption spectrum of the black mixture in ZhKM-807 and the one in MLC-6281 are due to the difference of the absorption spectra of the individual dyes in these matrices (Fig.4). In turn, it is coming from the difference in the molecular structure of the LC components which define these matrices, and also from the difference of the intermolecular interaction among the LC matrices and the dichroic dyes.

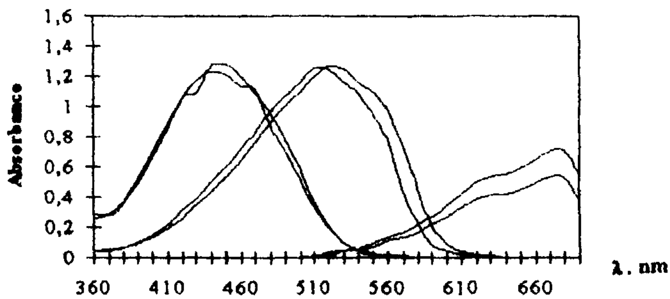

FIGURE 4 The absorbance spectra of the dichroic dyes with positive dichroism in MLC-6281 and ZhKM-807

In a similar way the black mixture with negative dichroism for ZhKM-807 was obtained. Its spectrum is shown on Fig.5. As indicated the black mixture with negative dichroism is considerably worth with respect to the black mixture with positive dichroism, namely, it has a narrower absorption range, significantly less absorbance and dichroic ratio. It is due to a number of reasons. The narrower absorption band is due to the composition of this black

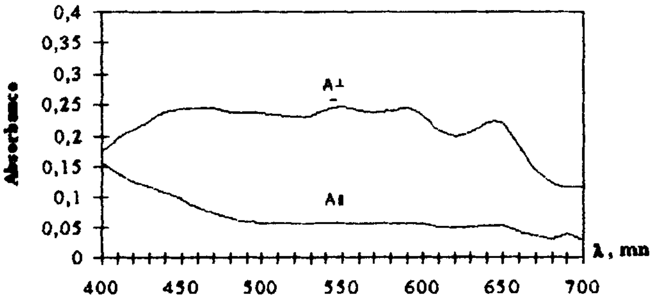

FIGURE 5 The absorbance spectra of the black mixture with negative dichroism

mixture, which consists only of anthraquinone dyes of T-type [4]. The position of the absorption band of these dyes can be varied only by changing various substitutes. The small dichroism is determined by the nature of the dyes with negative dichroism, which contrast ratio between the on and off state without polarizers in ideal case does not exceed 2. Therefore the application of dichroic dyes with positive dichroism allows us to obtain higher operating performances of LC-devices, with respect to the case when dyes with negative dichroism are used. Though in some cases, when a positive display mode[5] is required i.e. with black numerals on light background) dichroic dyes with negative dichroism find their application too.

CONCLUSION

In this paper the principles of designing black mixtures with positive and negative dichroism for liquid crystals are established. It is shown that to obtain high effective black mixtures, it is necessary to combine a sufficiently large number of individual dichroic dyes, well soluble in the prefixed LC matrix. It is characterized by high absorbance and by sufficiently large absorption spectra, covering as a whole all the visible range. It is shown, that for various LC matrices the optimum compositions of black mixture be different. Two black mixtures, one with positive dichroism, suitable for MLC-6281 and the other with negative dichroism, suitable for ZhKM-807 were built up.

Acknowledgments

The authors are grateful to Pr. A.Strigazzi for useful discussions. One of the authors, B.A.U. fully acknowledges the support of the Organizing Committee of 16^{th} and 17^{th} ILCC, which allowed him to attend Strasbourg Conference.

References

[1] G.H. Heilmeier and L.A. Zanoni, *Appl. Phys. Lett.*, **13**, 91 (1968).
[2] G.H. Heilmeier, J.A. Castellano and L.A. Zanoni, *Mol. Cryst. Liq. Cryst.*, **8**, 293 (1969).
[3] D.L. White and G.N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
[4] A.V. Ivashchenko, *Dichroic Dyes for Liquid Crystal Displays* (CRC Press, London Tokyo, 1994), p. 147.
[5] C. Tani, T. Ueno, S. Naemura, T. Mimitsuka, F. Ogava, T. Onozava, Y. Takekawa and K. Ota, *Nec Research & Development*, No. 61, 42 (1981).