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Journal of Luminescence 117 (2006) 199–208
JOURNAL OF LUMINESCENCE
www.elsevier.com/locate/jlumin

Concentration dependence of steady-state fluorescence behavior of a liquid crystal molecule E7 in ethanol

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Received 8 November 2004
Available online 5 July 2005

Abstract

The fluorescence excitation and emission spectra of a liquid crystal E7 in ethanol have been explored at a variety of concentrations from very dilute solutions ($<1.0\times10^{-7}$ mol/L) to concentrated solutions ($>1.0\times10^{-2}$ mol/L) and also for neat E7. The result showed a strong dependence of the steady-state fluorescence behavior on E7 concentration in ethanol. The photophysical behavior has been interpreted in terms of short-range and long-range intermolecular interactions and ground-state molecular association as well as spectral changes of the fluorescence excitation and emission. The short-range intermolecular interaction characterized by the fluorescence emission band with the maximum between 376 and 385 nm gradually increases with increasing E7 concentration. On the other hand, the long-range intermolecular interaction characterized by the emission band with the maximum between 347 and 362 nm gradually decreases with increasing E7 concentration. Consequently, with increasing E7 concentration in ethanol the long-range interaction effect is reduced, whereas the short-range effect is enhanced and the monomer emission completely disappears at concentrations greater than 2.83×10^{-5} mol/L.

Keywords: Liquid crystal E7; Steady-state fluorescence; Concentration dependence; Molecular interaction

1. Introduction

Polymer dispersed liquid crystal (PDLC) is a heterogeneous thin composite film that nematic liquid crystal (LC) droplets of micrometer size are uniformly dispersed in an optically transparent polymer matrix. It is very useful in light control, LC display panels, and other electro-optical applications [1,2]. The LC droplets in the PDLC film normally have bipolar director configuration [3]. In the absence of an external electric field (OFF-State), the LC droplets are randomly distributed in a matrix polymer and the refractive indices between the droplet and the polymer are mismatched. Therefore, the PDLC film is optically opaque. On the other hand, in the presence of

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doi:10.1016/j.jlumin.2005.05.009

electric field (ON-State), the droplets are aligned along with the field and their refractive indices are matched each other. Therefore, the PDLC film is optically transparent [4].

Fluorescence is very sensitive to the microenvironment change such as local viscosity and molecular interaction, association, conformation, and orientation of molecules with the fluorophore in solution. Hence, this technique has been widely used to study cure behavior, molecular interdiffusion, electronic energy transfer, charge transfer complexation in polymer systems including polyblends [5–7]. A large number of papers [8–14] reported on PDLC films have focused on their electro-optical properties, whereas only some papers on the photophysical properties of PDLC films have been reported. The photophysical behavior of a nematic liquid crystal E7, which is widely used for preparing PDLC films, should be studied prior to understanding the photophysical response of PDLC films. The photophysical properties of alkylcyanobiphenyl (*n*CB) and alkoxycyanobiphenyl (*n*OCB), where *n* is the number of methylene in the substituent, have been reported in a number of papers [15,16].

Iketa et al. [17] studied on the kinetics of excimer formation in a *n*CB liquid crystal system. They reported that the excimers are formed within picoseconds by a bimolecular process. The excimer formation was significantly enhanced in the nematic state compared with other LC states. It could also be possible by the direct excitation of molecular association in the ground state. Huang et al. [18] used the fluorescence technique to study the intermolecular interaction between mesogenic biphenyl moieties of thermotropic liquid crystalline polyester using a biphenyl model compound. Kato et al. [19] reported that the excimer fluorescence intensity from a CB mesogen in PDLC films was strongly influenced by excitation wavelength due to different molecular associations. Klock et al. [20] observed a large Stokes shift and a red-shift of the excimer fluorescence in *n*CB and *n*OCB liquid crystal molecules with increasing solvent polarity in various solutions.

Most of the fluorescence studies on liquid crystalline compounds earlier have been about the effect of temperature and solvent on the fluorescence behavior. Consequently, the objectives of this work are to investigate the fluorescence excitation and emission spectra of a liquid crystal E7 in ethanol at a variety of concentrations from very dilute solution to concentrated solution and also to understand the ground-state association and molecular interaction of E7 molecules.

2. Experimental

2.1. Materials

A thermotropic nematic liquid crystal (E7, Merck Inc.), which is widely used for processing PDLC films, was used in the present work. The E7 is a eutectic mixture composed of four different types of liquid crystals, 5CB (47 mol%), 7CB (25 mol%), 8OCB (18 mol%), and 5CT (10 mol%), as shown in Fig. 1. The 5CB is a main component of the compound. The compound has a positive dielectric anisotropy ($\varepsilon' = 18$ and $\varepsilon'' = 6$ at 1 kHz frequency), a glass transition temperature of $-65\,^{\circ}C$, and a nematic–isotropic transition temperature of 58 °C [21]. Ethanol (Spectrophotometric grade, Aldrich Chemical Co.) was used to prepare the E7 solution at various concentrations. The average molecular weight of the E7 is 346.05 g/mol, based on the mole percent of each LC component. Eleven kinds of E7 solutions in ethanol have been prepared in the range of 3.55×10^{-8}–0.1 mol/L according to the average molecular weight.

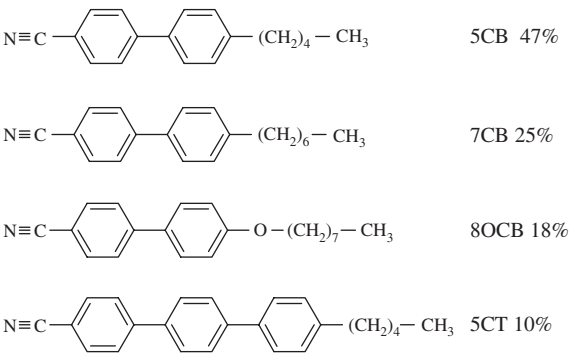

Fig. 1. Chemical structures and commercial names of four components of E7.