

Spectral properties and orientational order of tetrafluoro-pentenyl-perylene dye in uniformly aligned liquid-crystalline films

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ABSTRACT

The spectral properties of 3,4,9,10-tetra-(2,2,3,3,4,4,5,5,5-tetrafluoro-pentenyl)-perylene in low-molar-mass liquid crystals, 4-*n*-heptyl-4'-cyanobiphenyl, 4-*n*-octyl-4'-cyanobiphenyl, and *trans*-4-(4-heptylcyclohexyl)-benzotrile, are investigated using electronic absorption and fluorescence methods. The experiments reveal the presence of the bands in the spectra characteristic of perylene precursor. Subsequently, the orientational order parameters of the fluorescent dye molecules in the calamitic liquid crystals are determined from the absorption and fluorescence anisotropies. The investigations show that the orientational distribution of the dye molecules in the liquid-crystalline films is anisotropic which make such systems technologically applicable in optoelectronics. However, the relatively low order parameters values for the tetrafluoro-pentenyl-perylene are a drawback in utilization of this dye as a fluorescent probe for determination the orientational order parameters of liquid crystal molecules.

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1. Introduction

Perylene derivatives are well known dyes characterized by efficient fluorescence emission and well defined polarization of the electronic transitions in the molecule [1–3]. By the reason of their high photostability, yellow to orange color, and efficient fluorescence, perylenes are very attractive from technological point of view. When dissolved in liquid crystals they do not react chemically with the host nor destabilize significantly the mesophase. Therefore perylene derivatives can be used in passive and active guest–host liquid crystal displays [4–7]. The applications in OLEDs and OFETs technologies are also possible [8,9]. If mixed with fatty acids or liquid crystals the non-amphiphilic perylenes can form Langmuir or Langmuir–Blodgett films [10,11]. Perylene derivatives were proposed for application as probes in the experimental studies of molecular orientational order in thermotropic low-molar-mass liquid crystals and liquid-crystalline polymers, and also in lyotropic liquid crystals and lipid membranes [12,13].

In this paper the investigations of the orientational order of the tetrafluoropentenyl substituted perylene molecules, characterized by a high molecular point group symmetry, dissolved in calamitic liquid crystals, are reported. Due to the presence of highly polarized bands in the electronic absorption and the fluorescence spectra, the orientational order parameters of the dye in the liquid crystals are determined from the absorption and fluorescence

anisotropies. Based on the results, the usefulness of the perylene derivative as a probe in the investigations of molecular orientational order in uniaxial liquid crystal phases is discussed.

2. Experimental

The investigated compound 3,4,9,10-tetra-(2,2,3,3,4,4,5,5,5-tetrafluoro-pentenyl)-perylene (TTFPP), presented in Fig. 1, was synthesized and chromatographically purified in the Institute of Dyes, Łódź University of Technology, Poland. The general scheme of the perylene derivatives synthesis is described in [14].

Low-molar-mass liquid crystals, 4-*n*-heptyl-4'-cyanobiphenyl (7CB), 4-*n*-octyl-4'-cyanobiphenyl (8CB), and *trans*-4-(4-heptylcyclohexyl)-benzotrile (PCH7), were synthesized and chromatographically purified in the Institute of Chemistry, Military University of Technology, Poland, based on the procedures described in the literature [15,16]. The chemical structures and the phase transition temperatures of these mesogens are given in Fig. 2. Above the room temperature, the liquid crystals form nematic (N) mesophase in a sufficiently large temperature range. In the case of 8CB, apart from N, the smectic (SmA) mesophase is also observed. Monotropic N and SmA mesophases formed by supercooling an isotropic liquid are found for PCH7. The transition temperatures are in agreement with the data found in LiqCryst® 5.0 database.

The mixtures of TTFPP with 7CB, 8CB, and PCH7 were prepared by heating the liquid crystals up to the temperature above the clearing point and intense stirring. The possible dye recrystalliza-

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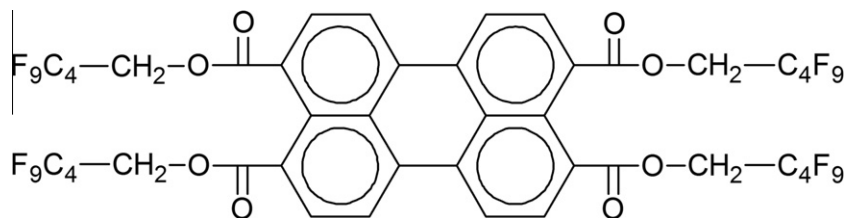


Fig. 1. Molecular structure of TTFPP dye.

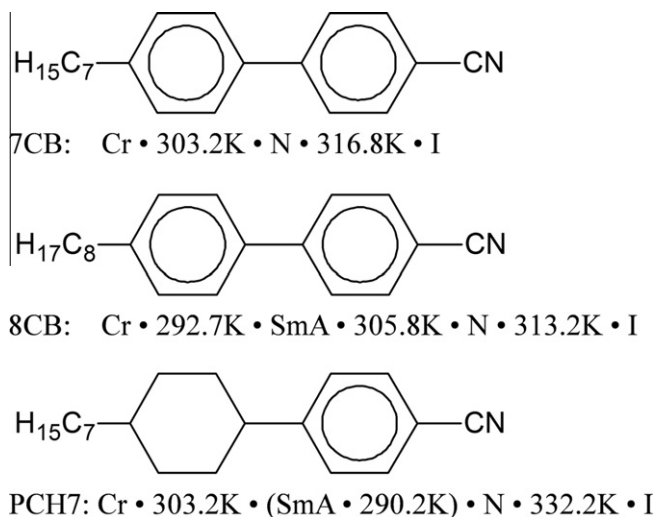


Fig. 2. Molecular structures and phase transition temperatures of 7CB, 8CB, and PCH7 liquid crystals.

tion in the mesophase was checked under polarizing microscope. By design the TTFPP was dissolved in the liquid crystals at the greatest possible concentration at which the recrystallization in the mesophase did not occur. The molar fractions (MF) of TTFPP in 7CB, 8CB, and PCH7 were found as equal to 2.2×10^{-3} , 5.0×10^{-4} , and 1.5×10^{-4} , respectively. The maximum solubility of the dyes was in correlation with the molecular structure and the mesophase type of particular liquid crystal. Namely, the maximum concentration of TTFPP was found for 7CB performing as nematic in the whole mesophase range and having the molecular structure based on the biphenyl core. The lowest MF was characteristic of PCH7 having the benzene group in the core replaced with the cyclohexane ring.

The cells for spectroscopic investigations were built of two, 1 mm in thick, microscope glass plates covered with polyimide orienting layers. The plates were separated with 10 μm in thick Teflon spacers. The mixtures were introduced into the cells by using capillary effect. As a result, thin layers of liquid crystals with the dye dissolved into them, characterized by uniform planar molecular alignment in N and SmA phases, were obtained. The quality of the molecular alignment was checked under polarizing microscope. For spectroscopic investigations the samples without defects in liquid-crystalline layer and characterized by perfect macroscopic uniaxial symmetry, were selected.

The spectral properties of TTFPP in the liquid crystals were investigated in the temperature range of the mesophase, and, additionally, at some selected temperature points just above the N–I phase transition. The samples were maintained at the required temperature by means of a self-made oven designed for spectroscopic investigations. The temperature was controlled and stabilized with the accuracy of $\pm 0.1\text{K}$ by using Model 9700 Temperature Controller (Scientific Instruments, Inc.). Components

of polarized absorption (parallel and perpendicular to the axis defining the direction of uniform alignment of liquid crystal molecules in the sample) were recorded in the wavelength range from 360 nm to 600 nm by means of spectrophotometer Cary 400 (Varian, Inc.) equipped with dichroic polarizers. Four components of polarized fluorescence were recorded by using a computer-controlled photon-counting spectrophotometer build in our laboratory. The experimental setup details are found in [17]. The TTFPP molecules were excited with the 435.8 nm line from a high-pressure mercury lamp. The registration of the fluorescence spectra was conducted in a so named parallel configuration for which the incident and the emitted light beams were parallel to each other. Maximum values for the components of polarized absorption (absorbances) and polarized fluorescence were taken for calculation of the order parameters of the TTFPP molecules in the mesophase.

3. Theory

The physical characteristics of substances can be derived from the individual features of constituting molecules. From the point of view of statistical theories, the relationship between micro- and macro-parameters can be established if the distribution function of a given system is known. For uniaxial N or SmA liquid crystals the orientational distribution function, reflecting the symmetry of the mesophase in the state of equilibrium, is given by the following formulae [18]:

$$f(\theta) = \sum_{L=0}^{\infty} \frac{4L+1}{2} \langle P_{2L} \rangle P_{2L}(\cos \theta), \quad (1)$$

where θ is the angle between the long molecular axis and the symmetry axis of the system, $P_{2L}(\cos \theta)$ are the even Legendre polynomials, and $\langle P_{2L} \rangle$ – the statistical averages which define the order parameters.

The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ parameters can be calculated by integration of the Legendre polynomials, respectively:

$$\langle P_2 \rangle = \int_0^{\pi} \frac{1}{2} (3 \cos^2 \theta - 1) f(\theta) \sin \theta d\theta, \quad (2)$$

$$\langle P_4 \rangle = \int_0^{\pi} \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3) f(\theta) \sin \theta d\theta. \quad (3)$$

A wide variety of spectroscopic methods was derived to determine the orientational order parameters in uniaxial liquid crystals [19]. Dissolving fluorescent dye in liquid crystal, the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ can be determined by using simultaneously the electronic absorption and fluorescence measurements. Assuming free rotational diffusion of the probe molecule around its symmetry axis in uniaxial liquid crystal and, additionally, considering the electronic absorption and fluorescence transition moments being parallel to the molecular symmetry axis, the following equations can be derived [20,21]:

$$r_A = \langle P_2 \rangle, \quad (4)$$

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