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CIRCULARLY POLARIZED FLUORESCENCE SPECTRA OF CHOLESTERIC LIQUID CRYSTALS CONTAINING AROMATIC CHROMOPHORES

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Circularly polarized fluorescence (CPF) spectra of guest aromatic molecules embedded in host cholesteric liquid crystals were measured. Such chromophores as tetracene and pyrene showed frequently oscillating CPF spectra which were interpreted in terms of the alternative direction of the fluorescence polarization of vibronic transitions.

The direction of fluorescence polarization is one of the essential quantities for the understanding of the electronic structure of fluorescent molecules.[1] The polarization has been measured for aromatic molecules dispersed in anisotropic media, such as uniaxially stretched polymers, single crystals, and nematic liquid crystals,[1] or by a photoselective excitation technique.[2] In this communication a facile and sensitive technique is presented which is based on a circularly polarized fluorescence (CPF) due to the chirality of cholesteric liquid crystals (CLC).

Cholesteric liquid crystal consists of a helical pile of quasi-nematic layers in which molecules are oriented along a particular direction (optical axis).[3] When a chromophore was embedded in a CLC, the helical pile of dichroic layers induces very intense circular dichroism (CD) and emits CPF. CPF in CLC has been reported and its sign and intensity are quantitatively related to the orientation of chromophores in the quasi-nematic layer.[4-7] However, no CPF spectrum, i.e., CPF as a function of fluorescence wavelength has been reported so far.

The guest/host technique using CLC may be advantageous in determining the orientation of the absorption or fluorescence transition moment as follows: (1) CLC is easy to handle and when it was formed as a capillary film of ca. 10 μm thichness between a pair of glass plates, its helix axis orients spontaneously normal to the glass surfaces.[3-8] (2) Since the helix pitch and even the helix sense

can be controlled by temperature, the CD and CPF spectra can be measured under the conditions of different chiralities. (3) CD and CPF signals induced by CLC are very intense and easy to detect.

Commercial CLC-forming compounds were used without further purification or sometimes recrystallized. Cholesteryl 3-(1-pyrenyl)propionate (Pyr-2) and cholesteryl 3-(9-anthryl)propionate (Ant-2) were prepared from the corresponding ω-arylalkanoic acids.[9] CLC was formed as a thin capillary film of ca. 10 μm thickness between a pair of quartz plates and kept at a constant temperature. Fluorescence spectra were measured on a Hitachi MPF-4 instrument. The exciting light was introduced at an incident angle of 56° to the normal of the plate. The CPF instrument of JASCO FCD-1F was used.[9] In this case, the exciting light was introduced perpendicularly to the front surface and the fluorescence was detected from the opposite surface. The CPF spectra were represented with the Kuhn's dissymmetry factor, $g_e = 2(I_L - I_R)/(I_L + I_R)$, as an ordinate, where I_L and I_R represent the intensities of left- and right-circularly polarized fluorescence, respectively.

Figure 1 shows fluorescence (bottom) and CPF (top) spectra of Pyr-2 (1 mol%) in a liquid-crystalline mixture of cholesteryl nonanoate (34.5 mol%) and cholesteryl chloride (64.5 mol%) at different temperatures. It is known that the mixture forms a left-handed helix below T_n = 43°C, a right-handed one above the T_n, and a compensated nematic phase at $T = T_n$.[6,7] In a left-handed CLC, a positive CPF signal is expected for a fluorescence transition which is polarized perpendicularly to the optical axis in a quasi-nematic layer. The inverse is ture for the right-handed helix or for the transition with parallel polarization.[6,7] Therefore, the CPF spectrum of Figure 1 suggests that the 0-0 peak observed at 378 nm which is polarized along the short axis of pyrenyl group,[10,11] is oriented perpendicularly to the optical axis. At longer wavelengths, an oscillation was observed in the CPF spectrum which may indicate the alternation of the direction of the fluorescence polarization from one vibronic peak to another. The polarization observed in Figure 1 shows a qualitative agreement with the assignment by Bree and Vilkos.[11] For example, the peak at 397 nm, located away by 1266 cm^{-1} from the 0-0 peak has been assigned to the totally symmetric vibration (a_{1g}), thus the B_{2u} symmetry of pure electronic transition is kept unchanged. Actually the vibronic peak shows a positive CPF peak, indicating that the transition moment

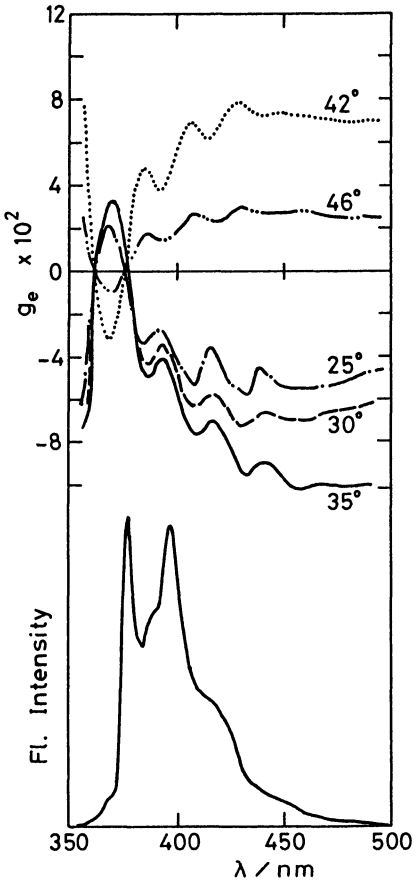

Figure 1. Fluorescence (bottom) and CPF (top) spectra of cholesteryl 3-(1-pyrenyl-propionate (1 mol%) dispersed in a liquid crystalline mixture of cholesteryl nonanoate (34.5 mol%) and cholesteryl chloride (64.5 mol%). Temperatures are indicated in the figure. Excitation wavelength was 320 nm.

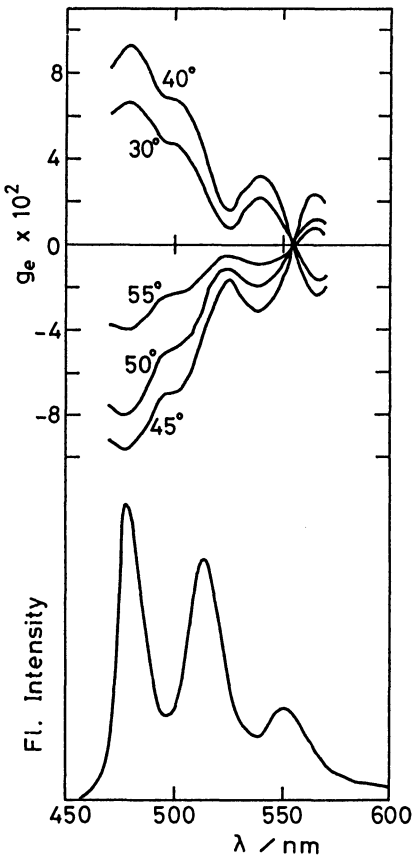

Figure 2. Fluorescence (bottom) and CPF (top) spectra of tetracene (0.5 mol%) dispersed in the same cholesteric liquid crystal as used in Figure 1. Excitation wavelength was 260 nm.

is polarized along the short axis of the pyrenyl group. A similar CPF spectrum with less oscillation was observed for pyrene (1 mol%) doped in the same CLC.

The fluorescence and CPF spectra of tetracene (0.5 mol%) in the same CLC are shown in Figure 2. The 0-0 peak observed at 478 nm, which is polarized along the short axis of tetracene,[12] exhibits a positive CPF peak at lower temperatures than T_n. This indicates that the tetracene molecule is oriented in the quasi-nematic layer with its long axis along the optical axis. The CPF spectrum again oscillates from one vibronic peak to another, suggesting the alternation of the direction of fluorescence polarization. The fundamental transition of tetracene is allowed and belongs to B_{2u} symmetry. The oscillation therefore indicates that the fluorescence transition moment of tetracene consists of a vectorial sum of a

pure electronic term having B_{2u} symmetry and of vibrational terms having a_{1g} or b_{1g} symmetry, which results in a parallel or a perpendicular polarization to the short axis, respectively. A similar oscillation of the fluorescence polarization has been detected in the photoselective fluorescence polarization spectrum of tetracene in ethanol at -180°C.[12]

Anthracene embedded in the CLC showed a CPF spectrum without the fine structure of the vibronic peaks, whereas the CPF spectrum of Ant-2 in the CLC indicated a small contribution of vibrational term. The sign of CPF spectrum at the 0-0 peak of anthracene indicated that the molecules are oriented with their long axis parallel to the optical axis. An inverse CPF spectrum was observed for Ant-2 indicating that the long axis of the anthryl group is perpendicular to the optical axis. It is therefore evident that the orientation of the anthryl group of Ant-2 is fixed by the cholesteryl group.

In the case of 9,10-diphenylanthracene doped in the CLC, positive CPF signals were observed at $T < T_n$, indicating that the molecules are oriented with their long axis parallel to the optical axis. No oscillation was observed, however, in the CPF spectrum and it was almost flat over the whole fluorescence region. The absence of the oscillation indicates that the fluorescence transition moment of diphenylanthracene is purely electronic.

To conclude, the direction of fluorescence transition moment of chromophores embedded on CLC was determined by the CPF spectroscopy. Quantitative discussion on the CPF spectrum requires the order parameter of aromatic molecules in CLC.[13]

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