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PRELIMINARY COMMUNICATION

Persistence of ordering in 4-*n*-pentyl-4′-cyanobiphenyl above the nematic–isotropic transition as detected by picosecond time-resolved fluorescence spectroscopy

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The orientational ordering of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) was explored with the aid of picosecond, time-resolved fluorescence spectroscopy by monitoring the time dependence of excimer formation of the mesogen at various temperatures. It was found that in the nematic phase the excimer is formed with high efficiency, while in the isotropic phase the excimer formation was less effective. Immediately after pulse excitation the time-resolved fluorescence spectra revealed that short range ordering persists just above the N–I transition, although the macroscopic order had disappeared.

Fluorescence spectroscopy is a powerful tool for investigating microscopic environments because of the rich information content of this method [1, 2]. The fluorescence is extraordinarily sensitive to the microenvironment around the fluorophore, which is the reason for the high utility of fluorescence spectroscopy. In most cases, a probe molecule is incorporated into the system of interest just by doping or by covalent attachment [3]. The location sites of the probe molecule is of primary importance since the information which we can obtain is related to the location site. Unfortunately, however, it is very difficult to control the location site because it is determined by the affinity of the probe with the microsites of the system. Another problem associated with the fluorescence probe method is the perturbation of the organization of the system by the introduction of the probe. This is a serious, but unavoidable problem encountered when we use an extrinsic probe since this is just a foreign molecule in the system. To prevent the perturbation by the probe molecule, we are encouraged to use an intrinsic probe, but few molecules or groups are in fact available which fulfil the requirements of a fluorescence probe, such as high fluorescence quantum yield, low chemical reactivity towards the system, high photochemical stability and clear photophysical properties [3]. In a research programme on the characterization of molecular aggregate systems by the fluorescence spectroscopic method, we have started to study the dynamic properties of liquid crystals by this method. This is a preliminary report on the characterization of liquid crystals by time-resolved fluorescence spectroscopy in which we have used a picosecond

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† Deceased.

time-correlated single photon counting method to follow the dynamic nature of liquid crystals.

4-*n*-Pentyl-4′-cyanobiphenyl (5CB) was chosen as the mesogen, because cyanobiphenyls form a family commonly used in display devices and exhibit clear fluorescent behaviour, thus they can act as the intrinsic probe. Furthermore, cyanobiphenyls were found to form excimers, which could provide us with additional information on orientational ordering [4]. In fact, excimer formation in liquid crystal systems is a topic of current interest relating to how the morphology of the chromophores in the ground state affects excimer formation. In this respect, the kinetic behaviour of excimer formation in liquid crystals has been extensively investigated by Anderson *et al.* [5], where the excimer-forming chromophores (not mesogens) were dissolved in a liquid crystal host and so aligned. From the viewpoint of the characterization of liquid crystals, these excimer forming molecules may be regarded as extrinsic probes.

The first example of an intrinsic excimer in a liquid crystal was reported by Sabramanian *et al.* [4]. They studied the emission properties of 4-*n*-dodecyl-4′-cyanobiphenyl by steady-state fluorescence measurements and found that excimer formation was strongly dependent on the mesophase. Time-resolved measurements of the intrinsic excimer in liquid crystals were first conducted by Yamazaki *et al.* who showed with time-resolved fluorescence spectra that the excimer is formed by a bimolecular process in 4-*n*-octyloxy-4′-cyanobiphenyl [6].

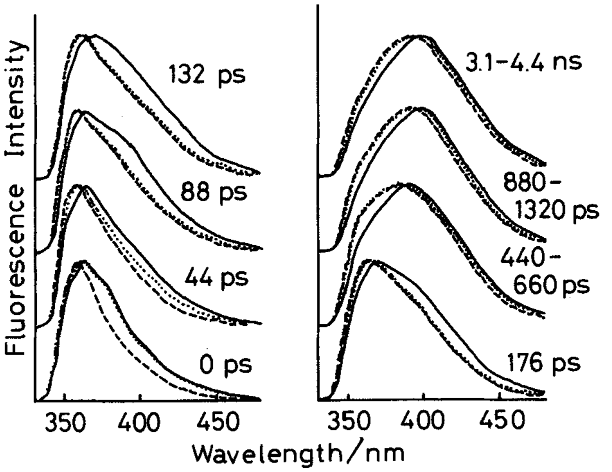
Here we report the excimer formation behaviour of 5CB studied by steady-state and time-resolved fluorescence spectroscopy, and discuss its orientational ordering just above the nematic–isotropic transition.

Liquid crystal and phase transition behaviour were examined with an Olympus model BHSP polarizing microscope equipped with a Mettler hot stage, model FP-80 and FP-82. Thermodynamic data were obtained with a differential scanning calorimeter (SEIKO I&E SSC-5000) operated at a heating rate of 2°C/min. The nematic to isotropic transition temperature (T_{NI}) of 5CB was 35·3°C.

Steady-state fluorescence spectra (corrected) were measured on a Hitachi F-4000 fluorescence spectrometer. The time-resolved fluorescence measurements were performed with a picosecond time-correlated single photon counting system, the details of which have been reported elsewhere [7]. Briefly, a synchronously pumped, cavity-dumped dye laser (Spectra Physics 375B and 344S) operated with a mode-locked Nd : YAG laser (Spectra Physics 34600 and 3240) with an excitation pulse source with a pulse width of 4 ps (FWHM). We obtained a frequency-doubled pulse for the excitation of the samples through a KDP crystal (Inrad 531). Fluorescence from the samples was detected at right angles to the excitation pulse through a monochromator (JASCO CT-25C) with a microchannel-plate photomultiplier (Hamamatsu R1564U-01). Signals from the photomultiplier were amplified (HP 8447D), discriminated (Ortec 583) and used as a stop pulse for a time-to-amplitude converter (Ortec 457). A start pulse was provided from a fast photodiode (Antel AR-S2) monitoring a laser pulse through a discriminator (Ortec 436). Data were stored in a multichannel analyser (Canberra 35 Plus) and then transferred to a microcomputer (NEC 9801) where the decay analysis was performed. The instrument response function of the whole system was 60 ps FWHM. Fluorescence spectra of 5CB in the neat phase or in concentrated solutions were measured with front face excitation and front face measurement of emission with 1 mm quartz cells in the presence of air. The temperature of the samples was controlled by means of a JASCO HTV cell coupled with a temperature-controlling unit, which was well calibrated.

In dilute solution in 2-propanol ($1{\cdot}7 \times 10^{-6}$ M), 5CB showed a fluorescence spectrum with a maximum at 335 nm, while in concentrated solution 5CB exhibited a new peak at 380 nm with a shoulder at 335 nm. By analogy with the fluorescence spectra of 4-*n*-octyloxy-4′-cyanobiphenyl [4], the peak at 335 nm can be ascribed to monomer fluorescence and the peak at 380 nm to excimer emission. In the neat phase 5CB exhibited similar fluorescence spectra to that of the concentrated solution both in the nematic and in the isotropic phases, although the maximum in the excimer fluorescence was slightly shifted to a longer wavelength in the nematic phase. As a measure of the efficiency for excimer formation, the ratio of the fluorescence intensity at 450 nm (excimer fluorescence, I_D) to that at 330 nm (monomer fluorescence, I_M), I_D/I_M was taken and this ratio was measured at various temperatures. It was found that the excimer was formed with high efficiency in the nematic phase as demonstrated by the high I_D/I_M values and an abrupt decrease in the ratio was observed at a temperature close to the N–I transition. The high efficiency of excimer formation in the nematic phase can be interpreted in terms of the favoured spatial orientation adopted by the chromophores in this phase. In the nematic phase, the mesogenic chromophores are aligned parallel to each other in the ground state, which enables the chromophores to attain face-to-face configuration, essential to the excimer formation, quite easily. On the other hand, in the isotropic phase, the chromophores are oriented rather randomly, thus the efficiency of excimer formation is reasonably lower than that in the nematic.

Interesting results were obtained from the time-resolved fluorescence measurements. In the figure we show the time-resolved fluorescence spectra of 5CB at various temperatures; at 35·0°C (N), 38·0°C (I) and 45·0°C (I). The numbers in the figure denote the time elapsing after the excitation pulse. The time zero was taken at the channel in the multichannel analyser when the instrument response function showed its maximum value. It can be recognized that immediately after the excitation pulse monomer emission was predominant at all the temperatures, as evidenced by the clear maxima around 350 nm in addition the excimer emission grew with time and, in the



Time-resolved fluorescence spectra of 5CB at various temperatures. ——, at 35·0°C; ···· at 38·0°C; – – –, at 45·0°C. The numbers in the figure show the delay time after the excitation pulse and the range of times at the later time indicates the time range in which the signals were accumulated to construct the spectra. The spectra have been normalized at the maximum emission intensity, $\lambda_{ex} = 310$ nm.

spectra taken at the longest time region, the emission maxima were clearly shifted to a longer wavelength region (~410 nm). This means that the excimer is formed by a bimolecular process between the excited 5CB and 5CB in the ground state.

It is of particular interest to note that the time-resolved spectra obtained for $t = 0$ varied depending on the temperature. It seems reasonable to assume that the time-resolved spectra at $t = 0$ reflect the number of preformed sites for excimer formation, where two relevant chromophores are already in the face-to-face arrangement in the ground state, so that once excited the pair forms the excimer directly without a reorientation process. In the nematic, the 5CB molecules are, on average, aligned parallel to each other, thus the number of such preformed sites is expected to be high. On the other hand, in the isotropic phase the orientation of the molecules is essentially random, and so the number of preformed sites is assumed to be low. The time-resolved fluorescence spectra at $t = 0$ support this view. At 35·0°C, 5CB is nematic and the emission intensity at ~400 nm was significantly higher than that measured at 45·0°C where 5CB is isotropic. The significant finding of the present study is that the emission intensity at $t = 0$ measured at 38·0°C was higher than that in the isotropic phase in the excimer emission wavelength region. This result strongly suggests that although there is no macroscopic order at 38·0°C where 5CB is isotropic some microscopic order such as pair-like aggregates persists above the transition.

X-ray diffraction studies on molecular packing in the N and S_A phases of the cyanobiphenyls reveal that they have a preferred local structure based on a head-to-tail overlapping core packing in which the cyanobiphenyl moieties are oriented antiparallel and the alkyl chains extend in opposite directions [8, 9]. Because of the strong longitudinal correlations in these compounds, such a local structure may remain above T_{NI}, although the long range order disappears. Persistence of such short range order has already been demonstrated for cholesterics [10, 11]. If we assume such a local structure above T_{NI} of 5CB, the concentration of the 5CB pairs would decrease with increasing temperature since thermal movement of the mesogens will destroy the local structure. Thus, at temperatures far above T_{NI} no local structure will remain, which is in good agreement with the time-resolved spectra obtained at 45·0°C.

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