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Photophysical and photoconductive properties of a carbazolyl derivative with a mesogen group of alkoxycyanobiphenyl in mesophases

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Abstract

4-Cyano-4′-(1-(*N*-carbazolyl)-*n*-octyloxy)biphenyl (8OCBCz), where the hydrogen atom of a well-known mesogen 4-cyano-4′-*n*-octyloxybiphenyl (8OCB) is substituted with one carbazolyl (Cz) chromophore, was synthesized, and the photophysical and photoconductive properties of its neat form and its binary mixtures with 4-cyano-4′-*n*-decyloxybiphenyl (10OCB) were investigated. The 8OCBCz exhibited intermolecular exciplex fluorescence in concentrated solutions. When 8OCBCz was quenched from its molten state, it formed an amorphous state, which exhibited exciplex fluorescence and transient photocurrent signals of both the positive and negative charge carriers. However, their mobilities could not be determined because of the strongly dispersive signals. The mixtures exhibited smectic A (Sm A) and nematic (N) mesophases. These mesophases and the isotropic phase exhibited exciplex as well as monomer fluorescence. The exciplex formation mechanism in the Sm A mesophase differed from those in the N and isotropic phases. The transient photocurrent signals for both the positive and negative charge carriers were also observed for the binary mixtures. Ionic conduction was suggested for the N and isotropic phases, whereas electronic conduction was suggested for the Sm A mesophase. The ionic carrier species were proposed.

Keywords: Carbazolyl compounds; Alkoxycyanobiphenyls; Mesophase; Exciplex fluorescence; Transient photocurrent

1. Introduction

Liquid crystals (LCs) are one of the important organic materials that have been extensively investigated because of their electro-optical characteristics and their application to display devices. Recently, the photoconductive properties of LCs have attracted attention [1,2] because it was found that columnar discotic LCs and the smectic mesophase of calamitic LCs exhibit a rapid electronic transport. The fluorescence properties of mesogens have attracted considerable attention with respect to the relationship among the photophysical property, phase transition, and molecular ordering in various mesophases. In particular, the fluorescence properties of alkyl- and alkoxy-cyanobiphenyls (abbreviated as *n*CB and *n*OCB, respectively), which are widely known as representative mesogens and have been extensively investigated for technical applications as electro-optical LC devices, were effectively examined in solution as well as in bulk neat forms [3–5]. In addition, to reveal the photophysics in ordered molecular assemblies, excimer and exciplex formations were investigated in cholesteric mesophases, where the fluorescent chromophore itself was either a cholesteric mesophase-forming substance or not [6–10]. Recently, to apply luminescent mesogens and LC materials to display and electroluminescent (EL) devices, photo-emission and EL properties of mesogens doped with fluorescent chromophores, mesogens having electron- and/or hole-transporting segments, and so on have been investigated [11].

Poly(*N*-vinylcarbazole) (PVCz) is widely known as one of the amorphous polymeric materials possessing highly photoconductive properties; further, amorphous neat films of its dimeric model compounds exhibit high photoconductivity as well [12,13]. In addition to their photoconductive properties, the photophysical properties of these polymeric and dimeric compounds have also been investigated in their amorphous solid state, including luminescence [14–17] and transient absorption measurements [18–21]. Furthermore, PVCz and its related

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polymeric and monomeric compounds were also investigated from the viewpoint of their application to organic EL devices [22]. Therefore, compounds containing Cz chromophores are interesting materials for physicists, chemists, and material scientists.

By combining the recent studies of LCs on their photoconductive and fluorescence properties with the unique characteristics of Cz compounds with respect to their photophysical and hole transport properties, mesogens comprising Cz chromophores are an interesting class of materials for material chemists. We synthesized a mesogen including one Cz chromophore, 4′-*n*-octylphenyl carbazole-2-carboxylate, and reported its absorption and fluorescence spectra, FT-IR spectra, and picosecond transient absorption spectra [23]. However, the temperature range of the LC phase of this mesogen was remarkably high. Sisido and co-workers synthesized Cz chromophores that were covalently linked to a cholesteric group [10]. These cholesteric Cz compounds did not exhibit a cholesteric mesophase by themselves; however, this mesophase was observed in their 1:1 mixture with other cholesteric mesogens. The fluorescence properties of these mixtures were investigated with regard to their cholesteric and isotropic phases. In addition, cholesteryl methyl terephthalate (CMT) was synthesized and the exciplex formation was investigated in the cholesteric mesophases comprising the cholesteric Cz compounds as a donor and CMT as an acceptor [9]. It was concluded that a constraint on the orientation of these chromophores in the cholesteric mesophase plays an important role in the exciplex formation.

In the present study, we focused on the smectic (Sm) and nematic (N) mesophases containing Cz chromophores and synthesized 4-cyano-4′-(1-(*N*-carbazolyl)-*n*-octyloxy)biphenyl (8OCBCz), where one Cz chromophore is covalently linked to the well-known mesogen, 4-cyano-4′-*n*-octyloxybiphenyl (8OCB). This was performed in order to enable the doping of the net concentration of Cz chromophores such that it was more than that in the case of a mixture of free Cz molecules with mesogens. We now investigate the fluorescence and photoconductive properties of both 8OCBCz amorphous neat films and a binary system of 8OCBCz/10OCB (4-cyano-4′-*n*-decyloxybiphenyl) in Sm, N, and isotropic (I) phases. The characteristic of the present system is that a mesogen acts as an acceptor by itself, which differs from the cholesteric system proposed by Sisido et al. [9].

2. Experimental

First, carbazole was synthesized from 1,2,3,4-tetrahydrocarbazole. The 8OCBCz was synthesized from the carbazole and 4-cyano-4′-(1-bromo-*n*-octyloxy)biphenyl, which was synthesized from 4-cyano-4′-hydroxybiphenyl and 1,8-dibromooctane. Further, *N*-ethylcarbazole (ECz) was synthesized from the carbazole and iodoethane. The 8OCB was synthesized from 4-cyano-4′-hydroxybiphenyl and 1-iodooctane. These compounds were identified by means of their IR and NMR spectra. The 10OCB (BDH chemicals) was used as received. Tetrahydrofuran (THF) (Dotite, Spectrosol) and dichloromethane (Dotite, Spectrosol) were used without further purification. For optical measurements, the bulk sample was sandwiched between two quartz plates with a polyimide spacer (thickness, 12.5 μm). The solution samples were contained in a 10 mm quartz cell. For the time-of-flight (TOF) measurement, the sample was sandwiched between two ITO glass plates with a polyimide or Teflon spacer (thickness, 12.5 or 25 μm, respectively). The surfaces on the quartz and ITO glass plates were not rubbed mechanically to establish self-organized sample structures.

A polarized optical microscope (Olympus, BX50) equipped with a Instec STC200D hot stage was used to observe the phase transitions and textures. A differential scanning calorimeter (Seiko Instruments DSC220C) was used to determine phase transition temperatures. The visible and ultraviolet absorption spectra were measured with a JASCO V-550 spectrophotometer. Steady-state fluorescence spectra were measured with a Hitachi F-4500 fluorescence spectrometer. Time-resolved measurements were performed using a two-dimensional streak camera (Hamamatsu Photonics C4780) as a detector and a N_2 gas laser (Usho KEC-150, 20 Hz, and FWHM of *ca.* 0.6 ns) as an excitation light source. All of the fluorescence spectra were not corrected for detector sensitivity.

In the TOF measurements, a N_2 laser pulse light (FHWM, *ca.* 8 ns) was irradiated on the cell set in a cryostat with a vacuum or N_2 gas purge. An induced transient current was amplified by a preamplifier (NF corporation 5307) and recorded using a digital oscilloscope (LeCroy 9362C).

3. Results and discussion

3.1. Absorption and fluorescence spectra of 8OCBCz in solution

Fig. 1 shows the absorption and fluorescence spectra of 8OCBCz, ECz, 8OCB, and an equimolar mixture of ECz and 8OCB in a dilute THF solution. The absorption spectrum of 8OCBCz is very similar to that of the mixture of ECz and 8OCB, which indicates no interaction between Cz and cyanobiphenyl (CB) groups in the ground state. As shown in Fig. 1(a), an excitation wavelength of 292 nm excites mainly the CB chromophore in 8OCBCz. However, the fluorescence spectrum of 8OCBCz excited at 292 nm is similar to that of ECz, whereas the fluorescence spectrum of the mixture excited at 292 nm is similar to that of 8OCB. These results indicate the occurrence of intramolecular energy transfer from the CB to Cz chromophores in 8OCBCz.

The fluorescence spectra of 8OCBCz in a dichloromethane solution were examined as a function of the concentration (Fig. 2(a)). With an increase in the concentration of 8OCBCz, a new fluorescence appears in longer wavelengths and its relative intensity to the Cz monomer fluorescence increases. This phenomenon is also observed for the solution of equimolar mixtures of ECz and 10OCB (Fig. 2(b)). This new fluorescence is attributed to an exciplex formed between the Cz and CB chromophores. Further, a similar concentration dependence was observed for the fluorescence spectra with the excitation of the Cz chromophore at 337 nm. These results indicate that 8OCBCz