Mesomorphic behaviors and photoconductive properties of binary systems composed of electron donor and acceptor mesogens

To cite this article: Sang-Hee Han et al 2006 Sci. Technol. Adv. Mater. 7 62

View the article online for updates and enhancements.

Related content
- Photoconductive Properties of MEH-PPV/CuS-Nanoparticle Composites
  Jin Hui, Hou Yan-Bing, Tang Ai-Wei et al.
- Influence of Deposition Conditions on Properties of a SiGe:H Prepared by Microwave-Excited Plasma CVD
  Takeshi Watanabe, Kazufumi Azuma, Masahiro Tanaka et al.
- Photoconductive Properties of Organic Films Based on Porphine Complex Evaluated with Image Pickup Tubes
  Satoshi Aihara, Kazunori Miyakawa, Yuji Ohkawa et al.

Recent citations
- Photoelectrochemical Photocurrent Switching and Related Phenomena
- Magnetic field effects on electro-photoluminescence of photoinduced electron transfer systems in a polymer film
  Kamlesh Awasthi and Nobuhiro Ohta
- Mesomorphic Schiff's base ether with dimethylamino end group
  Sie-Tiong Ha et al.
Mesomorphic behaviors and photoconductive properties of binary systems composed of electron donor and acceptor mesogens

Sang-Hee Han a, Hirohisa Yoshida b, Fumiyasu Iwahori a, Jiro Abe a,*,

a Department of Chemistry, and The 21st Century COE Program, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan
b Department of Applied Chemistry, Tokyo Metropolitan University, 1-1 Minami-Ohsawa, Hachioji, Tokyo 192-0397, Japan

Received 2 September 2005; received in revised form 25 September 2005; accepted 9 November 2005
Available online 30 January 2006

Abstract

Mesomorphic behaviors and photoconductive properties in the binary mixture composed of electron donor (R10D) and acceptor (R10A) mesogens were investigated in three different phases, i.e. crystalline, liquid crystalline and isotropic liquid phases. Optoelectronic properties for R10DA (R10D:R10A = 50:50 mol%) were compared with those of the individual R10D and R10A in the different phases. The magnitude of the short-circuit photocurrent in the ITO/R10DA/ITO symmetrical sandwich cell showed the effective improvement in SmA phase compared with one in crystalline phase. These experimental results imply that optoelectronic properties of mesogenic materials could be affected not only by the molecular ordering but also by the enhancement of the electrical contact at interface between the ITO electrode and the LC layer through the course of the phase transitions. This photocurrent behavior for the binary mixture provided considerable potentials useful for photoconductive switches under the short-circuit condition. This binary mixture gives a new insight into understanding the processes of the photoinduced charge carrier generation and transport under short-circuit condition through the variation of the orientational order of molecules in each phase.

Keywords: Binary mixture; CT complex; Optoelectronic properties; Photoconductive switches

1. Introduction

Liquid crystalline (LC) materials have been promising candidates for potential applications of numerous areas. The highly ordered structures arising from the self-organizing nature of LC materials afford the optical signal processing [1–3], electrooptical information storage, and the photoinduced charge transport [4]. With respect to charge carrier transport properties in photoexcited molecules, the photoconductivity and charge carrier mobility have been studied extensively for discotic and calamitic types of LCs, e.g. in triphenylene, phthalocyanine, 2-phenylbenzothiazole and naphthalene derivatives [4–8]. These LCs show the superior photoconductivity and fast charge carrier mobility independent of electric field and temperature compared with those of conventional amorphous or disordered organic materials. Mesomorphic charge transfer (CT) complexes have also been studied on several discotic as well as calamitic LCs and a few of them have been investigated in terms of photo/electronic conductivity [9–12]. However, the photoinduced charge carrier transport as well as energy migration in the CT complexes formed by electron donor–acceptor interaction between calamitic mesogens have been little published.

Recently, we have reported that the optoelectronic properties by means of charge trapping/detrapping effects in the binary mixture composed of electron donor and acceptor mesogens [13]. We noticed that the efficient optoelectronic properties in liquid crystalline phase may be related to the capability of photoinduced charge carrier transport and the molecular alignment formed in the mixture of donor and acceptor molecules. Especially, to fabricate optoelectronic devices with desirable properties and the enhanced efficiency for organic photoconductive materials, it is so important to understand the process of the photoinduced charge carrier generation and transport within thin layer. The photocarrier generation in organic photoconductive materials usually occurs as follows: the formation of bound electron–hole pairs generated from photoexcited molecules, and then dissociation of this exciton into free electrons and holes with the aid of electric field [14].

The introduction of molecular orientation and ordering is one of the promising approaches from the intention of
improving the photocarrier generation and the dissociation of the electron–hole pairs. Furthermore, the binary mixture composed of electron donor and acceptor molecules can enhance the efficiency of the charge carrier generation due to the large π-orbital overlap between them [15,16]. Therefore, the ability to transport photoinduced charge carriers and the highly ordered molecular alignment in the mesogenic mixture formed by the two components are significant factors in obtaining the efficient charge generation and the enhanced carrier mobility, as described in our recent publication [13]. We have demonstrated that the smectic LC mixtures could be applied for interesting and useful optoelectronic applications such as photoconductive switches and photodiode, in which high performance was attained through the exploitation of intermolecular and mesoscopic ordering. In this article, we would like to describe the mesomorphic behavior and the formation of CT complexes of the mesogenic compounds N-(4-decylxobenzylidene)-4-dimethylaminoaniline (R10D) as an electron donor and N-(4-decylxobenzylidene)-4-nitroaniline (R10A) as an electron acceptor (Fig. 1(a)). We will present significant optoelectronic properties of the binary mixture in different phases and discuss how its photoconductive characteristics under short-circuit condition are affected by the variation of the orientational order of molecules in each phase.

2. Experimental

2.1. Reagents and preparation

4-Nitroaniline, 4-hydroxybenzaldehyde, 4-dimethylaminoaniline, and 1-bromodecane (Tokyo Kasei Kogyo Co., Ltd) were used without further purification. N-(4-hydroxybenzylidene)-4-dimethylaminoaniline (1) [17], N-(4-hydroxybenzylidene)-4-nitroaniline (2) [17], N-(4-decylxobenzylidene)-4-dimethylaminoaniline (R10D) and N-(4-decylxobenzylidene)-4-nitroaniline (R10A) were prepared as shown in Scheme 1. All the syntheses were monitored by TLC (CHCl₃:hexane = 9:1) during the reactions. Binary mixtures were prepared by dissolving the appropriate ratios of R10D and R10A in benzene. Evaporation of the solvent and drying in vacuum yielded binary mixtures as colored solid.

2.2. N-(4-decylxobenzylidene)-4-dimethylaminoaniline (R10D)

To a solution of 1 (1.0 g, 4.2 mmol) in 2-butanone (50 ml), 1-bromodecane (2.8 g, 12.5 mmol) and K₂CO₃ (1.8 g, 12.7 mmol) were added. The reaction mixture was refluxed...
for 5 h with stirring. The resultant yellow solution was filtered, and the solvent was removed under reduced pressure. Recrystallization from ethanol gave the analytically pure sample of \textbf{R10D} (1.2 g, 3.2 mmol, yield: 76%). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 8.54 (s, 1H, –CH=N–), 7.81 (d, 2H, \(2^J=8.6\) Hz, H–Ar), 7.21 (d, 2H, \(3^J=9.2\) Hz, H–Ar), 7.02 (d, 2H, \(3^J=8.6\) Hz, H–Ar), 6.75 (d, 2H, \(3^J=9.2\) Hz, H–Ar), 4.03 (t, 2H, \(3^J=6.4\) Hz, –O–CH\(_2\)—), 2.92 (s, 6H, N–(CH\(_3\))\(_2\)), 1.73 (m, 2H, –O–CH\(_2\)--CH\(_2\)—), 1.30–1.59 (m, 6H, –(CH\(_2\))\(_3\)—) and 0.86 (t, 3H, \(3^J=7.0\) Hz, –CH\(_3\)). Anal. Calcd for C\(_25\)H\(_36\)N\(_2\)O: C \(78.90\), H \(8.90\), N \(7.36\); found: C \(78.95\), H \(9.46\), N \(7.37\).

2.3. \textit{N-(4-decxyloxybenzylidene)-4-nitroaniline (R10A)}

Compound 2 (0.8 g, 3.3 mmol), 1-bromodecane (2.2 g, 9.9 mmol) and K\(_2\)CO\(_3\) (1.4 g, 9.9 mmol) were refluxed in 50 ml of 2-butanol in 100 ml two-necked round-bottom flask equipped with a reflux condenser. After 5 h, the resultant yellow solution was filtered, and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from ethanol. The light yellow solid of \textbf{R10A} was obtained (0.9 g, 2.4 mmol, yield: 68%). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\): 8.57 (s, 1H, –CH=N–), 8.26 (d, 2H, \(3^J=8.9\) Hz, H–Ar), 7.90 (d, 2H, \(3^J=8.6\) Hz, H–Ar), 7.40 (d, 2H, \(3^J=8.9\) Hz, H–Ar), 7.08 (d, 2H, \(3^J=8.9\) Hz, H–Ar), 4.05 (t, 2H, \(3^J=6.4\) Hz, –O–CH\(_2\)—), 1.72 (m, 2H, –O–CH\(_2\)--CH\(_2\)—), 1.25–1.42 (m, 6H, –(CH\(_2\))\(_3\)—) and 0.85 (t, 3H, \(3^J=6.9\) Hz, –CH\(_3\)). Anal. Calcd for C\(_{23}\)H\(_{30}\)N\(_2\)O: C \(72.22\), H \(7.85\), N \(7.32\).

2.4. Characterization

Molecular alignment on the phase transition behavior was evaluated by an Olympus model BX-51 polarizing optical microscopy (POM) equipped with an Imoto hot stage and thermocouple (Imoto ES100P with an accuracy of ±0.1 °C) and X-ray diffractometer. Powder X-ray diffraction (XRD) analyses were performed on an MXP-18 (MAC Science Co., Ltd) diffractometer using Cu K\(_{\alpha1}\) radiation (\(\lambda=0.15405\) nm). Thermodynamic properties for phase transition of the binary mixtures were explored by means of differential scanning calorimeter (DSC: Seiko I&E DSC-6200) with heating and cooling rates of 5 °C/min. To examine the formation of CT complex, the reflection spectra in the region from 300 to 800 nm were measured using a multichannel spectrometer (Soma Optics, Fastevert S-2600).

A symmetrical sandwich type cell of ITO electrode was fabricated in the same way as previously reported [8,10]. The photoconductive cells were prepared using ITO-coated glass (area, 1 cm\(^2\), 20 Ω) electrodes separated by silica spacers with ~2 μm diameter in parallel and glued together with epoxy cement as shown in Fig. 1(b). Mesogenic molecules (\textbf{R10D}, \textbf{R10A} and binary mixtures) were capillary-filled into the cell space in isotropic liquid phase (130 °C). Then, the cell was then carefully cooled down to room temperature and two opening edges of the glasses are sealed with epoxy cement. To reduce the influence of oxygen and moisture absorbed in the cells, all cell preparations were carried out under a reduced pressure and an inert (nitrogen) atmosphere with exclusion of light. Microscopic observation of the cells revealed that the resulting mesophase of the mesogenic molecules were formed to have polydomain structures, in which the homogeneous alignment stayed stable under applied voltage range of −1 V to 1 V, although the surfaces of ITO electrodes were not rubbed to obtain homogeneous alignment.

For the steady-state photocurrent measurements, which involved the transport characteristics of photogenerated charge carriers, a xenon-lamp (100 W) equipped with a band-pass filter was used as light source. All photocurrent measurements were carried out in the atmosphere condition, the sample cell was placed on a hot stage and the illumination light intensity at UV irradiation ranging from 300 to 400 nm was held constant of 18.5 mW/cm\(^2\) using the power meter. The \(J\)–\(V\) characteristics of the photocurrent and dark current were recorded with an Advantest model R6245 source measurement.

3. Results and discussion

3.1. Mesophase characterization

The mesomorphic behavior and the significant thermal stability of \textbf{R10D}, \textbf{R10A} and binary mixtures were characterized by a combination of the techniques consisting of POM, DSC and XRD. Table 1 summarizes the phase transition temperatures and associated enthalpy and entropy changes of \textbf{R10D}, \textbf{R10A}, and binary mixtures. \textbf{R10D} on cooling shows only a monotropic nematic phase (N) over the narrow temperature ranges from 88.5 to 94.9 °C, while \textbf{R10A} on both heating and cooling displays an enantiotropic smectic C phase (SmC) over the widest temperature ranges from 61.4 to 94.2 °C and from 42.9 to 92.3 °C, respectively. In contrast, \textbf{R10DA} (\textbf{R10D}:\textbf{R10A}=50:50 mol%) formed by mixing the two components exhibits an enantiotropic smectic A phase (SmA) over relatively wide temperature ranges from 105.6 to 123.0 °C on heating and from 88.1 to 121.3 °C on cooling, respectively. The entropy changes of transition from isotropic phase to mesophase for \textbf{R10D}, \textbf{R10A} and \textbf{R10DA} are 4.5, 6.3 and 15.2 J K\(^{-1}\) mol\(^{-1}\), respectively. \textbf{R10DA} on cooling shows the most stable liquid-crystalline phases as proved by the highest isotropic-SmA phase transition temperature (121.3 °C), the relatively wide temperature range of the SmA phase (33.2 °C) and the highest values of the isotropic-SmA phase transition entropy change (15.2 J K\(^{-1}\) mol\(^{-1}\)) compared with those of other binary mixtures. Its thermal stability and the induction of a smectic mesophase would be caused by intermolecular interactions between the electron donor and acceptor mesogens [18–20]. These thermal behaviors are similar to those of the previously reported materials with shorter alky chain [17]. Fig. 2(a) and (b) show a binary phase diagram for the mole fraction of \textbf{R10D} on heating and cooling cycle. When the mole fraction of \textbf{R10D} is in the range between 10 and 70 mol%, binary mixtures show the enantiotropic SmA phase which is not appear in the individual \textbf{R10D} and \textbf{R10A}. On the other hand, \textbf{R10DA}(91) exhibits a monotropic N phase.
in the narrow temperature range from 94.1 to 100.4 °C on cooling. Furthermore, binary mixtures in the range between 10 and 50 mol% of R10D show the two-phase region (K1) with coexisting the crystalline phase and SmA phase on heating or cooling because of the non-mixing behavior between R10D and R10A. Interestingly, the temperature range of the induced SmA phase in 10 mol% of R10D is much wider than that in 70 mol% on heating and cooling cycle. This indicates that the formation of the induced SmA phase as increasing the mole concentration of R10A is probably related to the variation of electron donor–acceptor interaction. Moreover, if the interactions between two different molecules are stronger than those between two identical ones, the mesophase–isotropic transition curve should be expected to become convex upwards [17]. The induced mesophase in binary mixture formed by two different components is more thermally stable than those in mixtures of the same type. Its enhanced mesophases and thermal stability are consistent with the binary phase diagrams in Fig. 2. In this phase diagrams both on heating and cooling, the SmA-isotropic transition curves for binary mixtures are seen to have convex curves.

The molecular alignment behavior of the mesophases induced by intermolecular interactions between two components was explored by POM on the cooling. Fig. 3 shows optical textures of R10D, R10A, and R10DA sandwiched within untreated glass slides or two pieces of ITO-coated glass. R10D displays only the typical Schlieren texture corresponding to the nematic phase on cooling from the isotropic state. R10A appears to be a broken-fan texture, which are characteristic of the SmC phase, rather than the fan texture. R10DA exhibits the focal conic fan texture, similar to that observed for conventional SmA phase [21]. Microscopic observation of R10DA within two pieces of ITO-coated glass also shows the typical fan texture. This indicates that the thin film of R10DA in the SmA phase is formed to have polydomain structures, in which homogeneous alignment stayed stable under bias voltage as shown in Fig. 3(d).

To prove the identification of the smectic phases, powder X-ray diffraction measurements were carried out for R10A and the mixture R10DA on the second cooling. Fig. 4(a) shows the results of small angle powder X-ray diffraction measurements for R10A and R10DA at 90 °C. These XRD patterns below

Table 1
Thermal properties of R10D, R10A and binary mixtures

| Compound designation | R10D/R10A (mol%)* | Heating (°C)/cooling (°C)b | ΔH (kJ/mol)c | ΔS (J/K/mol)c |
|----------------------|--------------------|-----------------------------|--------------|---------------|
| R10D                 | 100:0              | K 104.8 I                   | –            | –             |
|                      |                    | K 88.5 N 94.9 I             | 1.6          | 4.5           |
| R10A                 | 0:100              | K 61.4 SmC 94.2 I           | 2.3          | 6.3           |
|                      |                    | K 42.9 SmC 92.3 I           | 2.3          | 6.3           |
| R10DA(19)            | 10:90              | K 59.0 K1 80.5 SmA 101.7 I  | 3.5          | 9.3           |
|                      |                    | K 38.6 K1 47.3 SmA 101 I    | 3.4          | 9.2           |
| R10DA(37)            | 30:70              | K 58.4 K1 92.9 SmA 117.1 I  | 5.0          | 12.9          |
|                      |                    | K 38.8 K1 76.5 SmA 115.7 I  | 5.2          | 13.5          |
| R10DA                | 50:50              | K 59.2 K1 105.6 SmA 123 I   | 5.8          | 14.5          |
|                      |                    | K 88.1 SmA 121.3 I          | 6.0          | 15.2          |
| R10DA(73)            | 70:30              | K 106.2 SmA 114.6 I         | 3.7          | 9.58          |
|                      |                    | K 92 SmA 115.4 I            | 4.6          | 11.9          |
| R10DA(91)            | 90:10              | K 102.8 I                   | –            | –             |
|                      |                    | K 94.1 N 100.4 I            | 1.9          | 5.2           |

ΔH, enthalpy change from mesophase to isotropic; ΔS, entropy change from mesophase to isotropic.

* The ratio of R10D and R10A.

** Transition temperature (°C) determined by the DSC measurement at a scanning rate of 5 °C/min on the second heating and cooling scans.

* Measured by DSC.

Fig. 2. Binary phase diagrams for the mixtures of R10A (on left) and R10D (on right): (a) the second heating scan; (b) the second cooling scan. K and K1, crystalline phase; SmC, smectic C phase; SmA, smectic A phase; N, nematic phase; I, isotropic phase.
the smectic–isotropic transition temperature show a sharp scattering peak at small angles region and a broad halo around \(2\theta = 20^\circ\) at wide angles region corresponding to the smectic character of the mesophases [17]. The small angle \(2\theta\) values for R10A and R10DA are 4.88 and 2.86°, which associate with smectic layer spacings of 18.1 and 30.9 Å, respectively. In the case of the individual electron donor and acceptor mesogens, as shown in Fig. 4(b), the calculated molecular lengths employing the MM2 energy minimization parameters are approximately 26.5 and 25.9 Å for R10D and R10A, respectively. On the basis of the results for these X-ray diffractions and the fully extended molecular conformations, Fig. 4(c) illustrates the proposed model of a smectic layer structure for R10DA. The layer spacing of R10A is shorter than the calculated molecular length, which is consistent with a tilted bilayer structure with the tilt angle of 46° in the SmC phase. However, the molecular packing of R10DA may have a bilayer structure resulting from the electron donor–acceptor interactions in the SmA phase, in which alkyl chains are highly interdigitated and heading groups of R10D and R10A overlapped partially [17]. The head-to-head molecular alignment of R10DA should provide the effective contact of the aromatic \(\pi\)-systems of the donor and acceptor. This molecular arrangement should promise a possible charge carrier transport ability.

3.2. Formation of charge transfer complex

CT interactions between electron donor and acceptor molecules should be usually confirmed by the observation of a CT absorption band in an electronic absorption spectrum. The color of R10DA is reddish brown in both crystalline and LC phases, but those of R10D and R10A are only yellow. The persistence of color in the solid and LC states should be considered as the additional evidence for the molecular complexing in R10DA induced by the electron donor–acceptor mesogens. Fig. 5 shows reflection spectra of R10D, R10A, and R10DA measured in the crystalline, liquid crystalline and isotropic phases. CT interactions between donor and acceptor mesogens in the crystalline and liquid crystalline phases of R10DA are manifested by the appearance of weak broad absorption band in the 450–600 nm region of their electronic spectra. These observations can be considered as the direct evidence for the formation of CT complex in R10DA between R10D and R10A [17]. On the other hand, this CT absorption band is also detected in isotropic phase and its intensity decreased with increasing the temperature. These results suggest that the CT interaction on molecular-scale region is maintained in the isotropic phase in which the positional and orientational order vanish generally.

3.3. Optoelectronic properties

Steady-state current density–voltage (\(J–V\)) characteristics of photocurrent and dark current for the ITO/R10D/ITO, ITO/R10A/ITO and ITO/R10DA/ITO cells in the crystalline phase are shown in Fig. 6. The photoresponse for R10A is clearly observed under UV irradiation, while the photocurrent of R10D is very small. In particular, when light was turned on and off, the photocurrent response curve for R10DA showed the reversible switching on the applied voltage, as shown in Fig. 6(b). The magnitude of the observed photocurrent showing a larger increase for positive voltages in the ITO/R10DA/ITO
cell also exhibits noticeable values compared with those of the individual R10D and R10A cells. This indicates that R10DA can be made more efficient charge generation due to the large overlap between donor and acceptor mesogens. Its photoconductive behavior is interpreted in terms of the various mechanisms for transport characteristics of photogenerated or injected charge carriers. The slight rectification of photocurrent observed for R10DA is mainly caused by the positive charged carriers in the extrinsic and/or intrinsic conduction process due to the mobility difference of the photogenerated charge carriers. In addition, the electric conduction process through the electron injection from the R10DA layer into the illuminated ITO electrode under UV irradiation takes place only at the interface between the mesogenic molecules and the positive electrode.

Fig. 7 shows typical J–V characteristics of photocurrent and dark current for the ITO/R10D/ITO, ITO/R10A/ITO and ITO/R10DA/ITO cells in the LC phase (90 °C). The dark current for the cells in the LC phases is about three orders of magnitude larger than that in the crystalline phase. This large dark current is tentatively explained by the following reasons: (i) the contribution of the charge carries provided by the thermal
excitation from the shallow or deep trapping sites; (ii) the contribution of a small amount of accumulated impurities at grain boundaries of polycrystalline. The increase of molecular motion in the vicinity of the interface on heating scanning can also induce the improvement of the interfacial contact for the electric or ionic conduction at the interface. In these LC phases of R10D, R10A and R10DA, the electric conduction as charge hopping may be dominant due to the very viscous smectic phase in which the charged mesogenic molecules themselves could not easily migrate, although there still remains the possible ionic conduction as increasing the temperature. On the other hand, the photocurrent behavior in the LC phase is different from that in the crystalline phase. The difference between the photocurrent and dark current for R10DA is fairly smaller compared with the crystalline phase. This would be related to the charge carrier trapping and recombination process with increasing the temperature. Under irradiation, the charge trapping process would be promoted by increasing the temperature and the promotion leads to a decrease in the mobility of charge carriers [22]. Therefore, the increase in the electron-hole recombination probability will cause the reduction of the difference between the photocurrent and dark current. The observed photocurrent for the R10DA cell in LC phase shows a significant improvement relatively to the photoresponse of the R10D and R10A cells as described in the crystalline phase. The magnitude of photocurrent for R10A and R10DA in the smectic phase, which generally depends on an efficiency of charge generation and a mobility of charge carriers [14], also exhibits larger values than that of R10D in the nematic phase. This implies that the variation of molecular ordering in each phase could have a substantial influence on the photoconductivity. These results are probably due to the high-quality LC thin film and the self-organized molecular alignment in the smectic phase as described in the previous study [13].

Fig. 8 shows photocurrent responses as a function of time obtained from the ITO/R10D/ITO, ITO/R10A/ITO and ITO/R10DA/ITO cells in the crystalline phase (90 °C). A steady-state photocurrent (I) was measured at a constant applied bias voltage of −0.5 V (Fig. 8(a)), while the short-circuit photocurrent (ISC) was observed at zero bias voltage under

![Fig. 6. (a) Steady-state current density–voltage curves (J–V) of photocurrent and dark current for the ITO/R10D/ITO and ITO/R10A/ITO cells at room temperature. (b) J–V curves of photocurrent and dark current for the ITO/R10DA/ITO cell at room temperature.](image)

![Fig. 7. Steady-state current density–voltage curves (J–V) of photocurrent and dark current for the ITO/R10D/ITO, ITO/R10A/ITO, and ITO/R10DA/ITO cells in the LC phase (90 °C).](image)

![Fig. 8. (a) Photocurrent (I) under a constant bias of −0.5 V with UV irradiation. (b) Short-circuit photocurrent (ISC) as a function of time for the ITO/R10D/ITO, ITO/R10A/ITO and ITO/R10DA/ITO cells at room temperature under a periodic irradiation with UV light.](image)
The observed photocurrent behavior for binary mixture shows significant optoelectronic properties. The magnitude of $I$ and $I_{SC}$ for R10DA exhibits superior values compared with that of the individual R10D and R10A under identical experimental conditions. This enhanced $I$ and $I_{SC}$ for R10DA may be attributed to the increase in the concentration of photogenerated charge carriers induced by the large overlap between the two components. These optoelectronic properties of $I$ and $I_{SC}$ could offer a potential possibility in optoelectronic devices such as the photoconductive switches and photodiode. This photocurrent mechanism in binary mixture is probably performed by the electron or hole transfer reaction from the photoinduced ITO electrode to the mesogenic molecule, which was associated with the extrinsic conduction process. Furthermore, spike current responses were observed for the cells when the light was turn on. This spike current would be caused by the variation of dielectric constant in the photoexcited mesogenic molecule during light irradiation [23].

As for the photocarrier generation and charge transport properties in the fluid phase, we have also investigated the $J$–$V$ characteristics and the $I_{SC}$ for the cells above the mesophase–isotropic transition temperature, which is accompanied by a sudden change of viscosity. In contrast to a very viscous smectic phase, ionic species (ionic impurities or carriers) can be easily transferable in the isotropic liquid phase owing to the lower viscosity. In fact, the observed photocurrent and dark current for the cells in the isotropic liquid phase (130 °C) was larger than those in the LC phases as shown in Fig. 10(a). For the photoconductive behavior in the fluid phase, it would be
supposed that the amounts of photo-induced charge carriers should be largely decreased due to a rapid electron–hole pair recombination caused by the reduction of the carrier mobility. However, the difference between the photocurrent and dark current in the isotropic liquid phase decreased slightly smaller than one in the LC phase. Therefore, the above results are probably due to the dominant contribution of a possible ionic conduction.

Fig. 10(b) also shows the anodic $I_{SC}$ as a function of time for the cells with UV irradiation in the isotropic liquid phase. The considerable increase of $I_{SC}$ for all cells relatively to the LC phase was observed unexpectedly in the isotropic liquid phase. Although carrier recombination takes place at the interface, electron injection under UV irradiation might still occur from the excited state of LC molecules in the vicinity of the interface into the irradiated ITO electrode because the differential charge transfer at the interface is maintained in isotropic liquid phase [22]. However, the substantial contribution to the increase of $I_{SC}$ might be attributed to the charge-transfer reactions between the accumulated ionic species near the interface and the illuminated ITO electrode. The nature of ionic species is not yet apparent in the present materials. Further investigations and evaluation of carrier mobility are needed before conclusion can be drawn about the conduction mechanism for the photo-induced charge carriers in the isotropic liquid phase.

3.4. Temperature dependence of photocurrent and dark current

Fig. 11 shows Arrhenius plots of the steady-state photocurrent and dark current as a function of temperature for R10DA under the constant applied bias voltage and short-circuit conditions. The $J_d$ gradually increased with increasing the temperature (Fig. 11(a)), while no significant increase in the $J_{SCd}$ was observed over the whole temperature range (Fig. 11(b)). Temperature dependence of the $J_d$ in the crystalline phase obeyed the Arrhenius’s equation. On the assumption that a thermally activated hopping mechanism for each phase, the values of the activation energy ($E_{ac}$) calculated by the Arrhenius plots were 1.01, 0.02 and 0.12 eV for the crystalline, the SmA and isotropic phase, respectively. The $E_{ac}$ of R10DA in the crystalline phase is larger than the representative value of 0.75 eV usually seen along the best conducting direction in organic CT salts. This seems to be due to the additional contribution through the thermal excitation and/or a small amount of accumulated impurities as mentioned previously. However, the value of the $E_{ac}$ in the SmA phase is very small in comparison with that in the crystalline and isotropic phases. This should provide another support for the electronic conduction such as charge hopping in the SmA phase, rather than the ionic conduction. The $J_p$ and $J_{SCP}$ continuously increased with increasing the temperature and reached to a plateau region. In the SmA region, it remained constant over a temperature range of 15 °C, then gradually increased at the temperature where the liquid crystal to isotropic phase transition occurred. This indicates that the photocurrent behavior is strongly influenced by the variation of the molecular ordering at phase transition point as increasing the temperature. Furthermore, the current density ratio ($J_{SCP}/J_{SCd}$) under a short-circuit condition increases in the SmA and isotropic phases compared to that ($J_p/J_d$) under the constant applied bias voltage. Especially, the $J_p/J_d$ shows the marked values in the SmA phase. These complexities for conduction behavior may be due to the relationship between the molecular ordering and dynamics for R10DA on heating.

Thus, these results indicate that the photoconductivity of R10DA is severely related to the orientational order of molecules and interactions between donor and acceptor mesogens in each phase.

4. Conclusion

In this work, we examined the mesomorphic and optoelectronic properties for R10D, R10A, and R10DA in different phase. Optoelectronic properties for the cells are strongly influenced by the variation of phase transition as increasing the temperature. The magnitude of the observed photocurrent for R10DA cell in each phase exhibits noticeable values compared with those of the individual R10D and R10A cells. We found...
that efficient photoconductive properties of R10DA are related to the large overlap between donor and acceptor mesogens. R10DA in the SmA phase also led to a large improvement of the optoelectronic properties compared with the individual R10D and R10A because of the molecular ordering and the enhanced electrical contact at interface between the ITO electrode and the LC layer. On the other hand, as for optoelectronic properties of R10DA in the isotropic liquid phase, it is thought that the ionic conduction, rather than the electronic conduction is dominant due to the better molecular motion on heating. It is found that this binary mixture can be a good candidate for high-performance photoconductive switches and provide a new insight into the comprehension for the processes of the photoinduced charge carrier generation and transport under short-circuit condition through the variation of the orientational order of molecules in each phase.

Acknowledgements

This work was partially supported by a Grant-in-Aid for the 21st Century COE Program (Aoyama Gakuin University) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] G.P. Wiederrecht, B.A. Yoon, M.R. Wasielewski, High photorefractive gain in nematic liquid crystals doped with electron donor and acceptor molecules, Science 270 (1995) 1794–1797.

[2] G.P. Wiederrecht, B.A. Yoon, W.A. Svec, M.R. Wasielewski, Photorefractivity in nematic liquid crystals containing electron donor–acceptor molecules that undergo intramolecular charge separation, J. Am. Chem. Soc. 119 (1997) 3358–3364.

[3] M.J. Fuller, M.R. Wasielewski, Photorefractivity in nematic liquid crystals using a donor–acceptor dyad with a low-lying excited singlet state for charge generation, J. Phys. Chem. B 105 (2001) 7216–7219.

[4] D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, K. Siemensmeyer, K.H. Etzbachi, H. Ringsdorf, D. Haarer, Fast photoconduction in the highly ordered columnar phase of a discotic liquid crystal, Nature 371 (1994) 141–143.

[5] P.G. Schouten, J.M. Warman, M.P. de Hass, M.A. Fox, H.L. Pan, Charge migration in supramolecular stacks of peripherally substituted porphyrins, Nature 353 (1991) 736–737.

[6] M. Funahashi, J. Hanna, Fast hole transport in a new calamatic liquid crystal of 2-(4′-heptyloxphenyl)-6-dodecylthiobenzothiazole, Phys. Rev. Lett. 78 (1997) 2184–2187.

[7] N. Boden, R.J. Bushby, J. Clements, Mechanism of quasi-one-dimensional electronic conductivity in discotic liquid crystals, J. Chem. Phys. 98 (1993) 5920–5931.

[8] H. Monobe, S. Mima, T. Sugino, Y. Shimizu, Mesomorphic and photoconductive properties of a mesogenic long-chain tetraphenylporphyrin nickel (II) complex, J. Mater. Chem. 11 (2001) 1383–1392.

[9] K. Ohta, H. Hasebi, H. Ema, M. Moriya, T. Fujimoto, I. Yamamoto, Discotic liquid crystals of transition metal complexes: 11. The first π-acceptor in discotic columnar liquid crystals obtained from octasubstituted bis(diphenylethane-1,2-dithiolene)nickel complexes, Mol. Cryst. Liq. Cryst. 208 (1991) 21–32.

[10] F.D. Saeva, G.A. Reynolds, L. Kaszczuk, Liquid-crystalline cation-radical charge-transfer systems, J. Am. Chem. Soc. 104 (1982) 3524–3525.

[11] P. Davidson, A.M. Levelut, H. Strzelecka, V. Gionis, Nature of the mesophase of a conducting charge transfer complex: neither discotic nor calamitic, J. Phys. Lett. 44 (1983) 823–828.

[12] V. Gionis, H. Strzelecka, M. Veber, R. Kormann, L. Zuppiroli, Liquid crystalline organic conductors: studies in crystalline and mesomorph phase, Mol. Cryst. Liq. Cryst. 137 (1986) 365–372.

[13] S.-H. Han, H. Yoshida, M. Fujiwara, Y. Nobe, F. Iwashori, J. Abe, Optoelectronic memories based on photoconductive binary liquid crystal composed of electron donor and acceptor molecules, Electrochemistry 73 (2005) 41–43.

[14] K.-Y. Law, Organic photoconductive materials: recent trends and developments, Chem. Rev. 93 (1993) 449–486.

[15] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Efficient photodiodes from interpenetrating polymer networks, Nature 376 (1995) 498–500.

[16] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer photovoltaic cells: enhanced efficiencies via a network of internal donor–acceptor heterojunctions, Science 270 (1995) 1789–1791.

[17] S.-H. Han, H. Yoshida, Y. Nobe, M. Fujiwara, J. Kamizori, A. Kikuchi, F. Iwashori, J. Abe, Molecular alignment and thermal stability of liquid-crystalline phases in binary mixtures of electron donor and acceptor, J. Mol. Struct. 735/736 (2005) 375–382.

[18] K. Araya, Y. Matsunaga, Liquid crystal formation in binary systems: II. Induction of nematic and smectic phases by electron donor–acceptor interaction between the p-dimethylamino and p-nitro derivatives of N-benzylideneaniline, Bull. Chem. Soc. Jpn 53 (1980) 3079–3084.

[19] Y. Kosaka, T. Kato, T. Uryu, Synthesis and the smectic mesophase of copolymers containing a mesogenic (carbazolylmethyl)eneaniline group as the electron donor and a (4′-nitrobenzylidene)aniline group as the electron acceptor, Macromolecules 27 (1994) 2658–2663.

[20] J.W. Park, C.S. Bak, M.M. Labes, Effects of molecular complexing on the properties of binary nematic liquid crystal mixtures, J. Am. Chem. Soc. 97 (1975) 4398–4400.

[21] G.W. Gray, J.W. Goodby, Smectic Liquid Crystal: Textures and Structures, Leonard Hill/Haydon and Son, Inc., Glasgow/Philadelphia, 1984.

[22] C.-Y. Liu, H.-L. Pan, H. Tang, M.A. Fox, A.J. Bard, Effect of structural interaction between the p-dimethylamino and p-nitro derivatives of N-benzylideneaniline, Bull. Chem. Soc. Jpn 53 (1980) 3079–3084.

[23] A. Aoki, Y. Abe, T. Miyashita, Effective photoinduced electron transfer in hetero-deposited redox polymer LB films, Langmuir 15 (1999) 1463–1469.