Ambipolar carrier transport properties in a built-in donor–acceptor discogen

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Carrier transport in the hexagonal columnar mesophase of a discogen with a built-in dipole moment in the core—hexaalkoxydibenzo[a,c]phenazine (HDBP-3) was investigated. The temperature and field dependences of bipolar carrier mobilities up to the order of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in the homeotropically aligned HDBP-3 have been revealed by time-of-flight (TOF) measurement. One-dimensional hopping model was used to discuss the effect of built-in donor–acceptor molecular dipole in the core. The calculation of charge transfer integral also supported the results of mobility measurement. The donor–acceptor molecular dipole in the discogen not only stabilized the mesophase but also contributed to the nondispersive ambipolar nature and substantially enhanced the electron transport in HDBP-3.

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1. Introduction

Discotic liquid crystals (DLCs) consisting of a disc-shaped rigid aromatic core surrounded by flexible side chains that form highly ordered structures in the columnar mesophase have attracted attention because of their potential in optoelectrical applications. Mesogenic groups of DLCs that lay face to face in stacks have been shown to transport carrier charges efficiently in columns [1–5]. The high mobility $>0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ of the DLCs mentioned is comparable to those of organic poly-crystals, such as pentacene [6] and oligothiophene [7]. Therefore, DLCs are considered versatile functional materials in field effect transistors [8] and photovoltaic devices [9–12] because of their excellent charge transport capability. Although DLCs can attain high carrier mobility, they typically do not have long-range supramolecular assemblies and can exhibit one or more phase transitions within a narrow temperature range. Because the carrier mobility of DLCs often diminishes with disordered columns and abruptly changes between phases, DLCs with enhanced order through core interaction and a single mesophase over a wide temperature range are desirable for practical applications. To extend the mesophase range, Ong et al. proposed hexaalkoxydibenzo[a,c]phenazines (HDBPs) derivatives with six long alkoxy chains. The mesophase range of HDBPs is up to 80°C [13]. The built-in donor acceptor region in the core of HDBPs enhances the intermolecular interaction among the disks by inducing a lateral dipole. The strong intermolecular interactions between disks have been shown to make conditions favorable for the long-range order in columns [13]. Ambipolar carrier transport has been reported in triphenylene-based DLCs, which contain symmetric cores [1,2,4,14]. Furthermore, good ambipolar charge transport properties have been found in donor–acceptor systems, such as those in the blends of phthalocyanine and fullerene [15]. These reports prompted us to elucidate the charge transport properties of HDBPs, which contain a built-in donor–acceptor region in the core.

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and exhibit a wide mesophase range. This study investigated the charge carrier transport properties of a homeotropically aligned hexaalkoxydibenzophenazine-based DLC, named HDBP-3, by using time-of-flight (TOF) measurements. The effect of the built-in donor-acceptor molecular dipole on carrier transport was also discussed in the aspect of both experimental measurement and theoretical simulations.

2. Experimental

The chemical structure of the discotic hexaalkoxydibenzophenazine HDBP-3 is shown in Fig. 1a. The details regarding their synthesis and characterization have been reported in previous studies [13]. The HOMO and LUMO energy level for HDBP-3 was estimated to be $-5.36 \text{ eV}$ and $-2.73 \text{ eV}$, respectively by cyclic voltametry (CV) measurements [16]. According to the characterization with differential scanning calorimetry and variable temperature X-ray diffraction, HDBP-3 exhibits a wide Col$_h$ mesophase range between 65 and 140 °C [13]. The molecular arrangement in the mesophase of HDBP-3 was examined by polarized light microscopy. Fig. 1b shows a photo of a micrometer-thick HDBP-3 sample (placed between two glass slides) at 120 °C taken under a polarized microscope equipped with a heating/cooling stage. A typical birefringent fan texture of the Col$_h$ mesophase was clearly observed. Small domains and domain boundaries in the unaligned sample hindered the observation of non-dispersive carrier transports in the TOF mobility measurement. To realize homeotropically aligned (i.e., with the column axes normal to the substrate) and defect-free films, we proceeded as follows. The patterned indium-tin-oxide (ITO) glass substrates (110 nm, 15 Ω/sq) were cleaned in an ultrasonic bath. The cleaned glass substrates were then immersed in a 1 mM octadecyltrichlorosilane (OTS) solution for 30 min to form a self-assembly monolayer (SAM) onto them. The substrates were then sonicated in turn with toluene, ethanol, and DI water prior to being dried in a stream of filtered nitrogen gas. The substrates were then modified by oxygen plasma buffing. With this treatment, the surface free energy is increased and the DLC alignment tends to be homeotropical [17]. The plasma-treated and SAM-coated substrates were then placed on top of each other, and were separated by approximately 5 μm diam silica rod-shaped spacers, as shown in Fig. 1c. HDBP-3 was placed into the cell at 160 °C by capillary flow in a dry nitrogen environment. The temperature of the cell was taken down at a rate of $-0.01 \text{ °C/min}$ from 160 °C once the molecules were inside the cell. The cell was then encapsulated under dry nitrogen to avoid the degradation of HDBP-3. To investigate the charge transport properties in discotic liquid crystals, the TOF technique is used under normal atmospheric pressure. The schematic illustration of the TOF measurement system is depicted in Fig. 2. A frequency-tripled Nd:YAG laser (355 nm, 6.5 ns pulse duration) was used for pulsed illumination through a transparent ITO electrode. This wavelength was approximately the absorption peak of HDBP-3, thereby giving a large absorption coefficient of the order of $10^5 \text{ cm}^{-1}$, ensuring that the penetration depth of the illumination (approximately 100–200 nm) and that the sheet of photogenerated carriers was thin enough compared to the thickness of the HDBP-3 cell. The intensity of illumination was adjusted to keep the photogenerated charges less than 5% of the sample capacitor charges, avoiding a space-charge-induced non-uniform distribution of the electric field during the drift of the carriers. The transient photocurrent under an applied DC bias was recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, the selected carriers (holes or electrons) were swept across the sample with a transit time of $t_T$. With the applied bias $V$ and sample thickness $D$, the applied electric field $E$ was $V/D$, and the carrier mobility was given by $\mu = D/(t_T \cdot E) = D^2/(V \cdot t_T)$. The sample thickness $D$ of the HDBP-3 cell was accurately measured from the interference pattern obtained by an ultraviolet–visible spectrometer. The mobilities of HDBP-3 under different temperature were also measured to understand the effect of the built-in donor-acceptor molecular dipole on carrier transport.

3. Results and discussion

Fig. 3a shows a photo of an aligned LC cell of HDBP-3 taken under a polarized microscope at 120 °C. Upon alignment, the mono-domain homeotropic alignment of HDBP-3 was achieved. Fig. 3b shows the conoscopic figure of the aligned HDBP-3 cell, which provides further confirmation regarding the homeotropic alignment.

Fig. 4a and b shows representative TOF transients of the holes and electrons for HDBP-3 measured at an applied field of $1.2 \times 10^5 \text{ V/cm}$ and $1.4 \times 10^5 \text{ V/cm}$ at 120 °C, respectively. In all of these curves, the short initial spike in the transient, limited by the time resolution of the measurement setup, was first followed by a constant-current plateau and then by a sharp reduction. The final falloff of
the current was caused by the carriers reaching the collection electrode, where they were discharged. The appearance of a current plateau indicated that the charge carriers had attained a constant drift velocity and were non-dispersive ambipolar carrier transports [18–20]. Carrier mobility was unambiguously evaluated from the intersection point of the two asymptotes to the plateau and the tail sections in a double logarithmic representation (inset of Fig. 3). The transit time was in the order of microseconds. A slow transit following a fast transit attributed to the ionized impurities in the liquid crystal is frequently found when liquid crystal is contaminated with chemical impurities [4]. To verify the existence of ionic transport, the transient photocurrent measurement was extended down to the 10 ms range. No clear transit was present, and the photocurrent became extremely small and noisy in the 10 ms range. Therefore, we could not determine whether a slow transit was present.

Fig. 5 shows the field dependence of both the hole and electron mobilities of HDBP-3 in Colh phase. HDBP-3 under homeotropic alignment showed both hole and electron mobilities up to the order of 10^{-3} cm^2 V^{-1} s^{-1} for the fields from 9.4 \times 10^4 to 2.2 \times 10^5 V/cm and for the temperature from 40 °C to 120 °C. At a field of 2.2 \times 10^5 V/cm and 40 °C \mu^+ = 8 \times 10^{-4} cm^2 V^{-1} s^{-1} and at 120 °C \mu^+ = 1.5 \times 10^{-3} cm^2 V^{-1} s^{-1}. The electron mobilities are about 2.3 times as high as the hole mobilities. The charge carrier mobility is often assumed to be proportional to the square of the charge transfer integral that describes the transport of a charge between two adjacently stacked molecules. Thus, the ambipolar nature and a superior electron transport compared to hole transport of HDBP-3 may be further substantiated from the parameter of the charge transfer integral. Here, only charge transfer integrals between the occupied molecular orbitals (HOMO and HOMO – 1) and unoccupied molecular orbitals (LUMO and LUMO + 1) of HDBP-3 molecules in the antiparallel conformation, and with a stacking distance of 3.5 Å between adjacent molecules are considered. Furthermore, the nitrogen atoms between the two stack molecules are prevented from over-lapping to prevent repulsion. All energetic results are calculated with the M06 density functional and 6–31G(d,p) basis set and geometries optimized by the B3LYP density functional with the 6–31G(d,p) basis set and the convergence criterion of 10^{-8} Hartree [21,22]. The calculations were performed with the Gaussian 09 code. The transfer integral of a given system is related to

![Fig. 2. The schematic illustration of TOF measurement.](image)

![Fig. 3. (a) Photo of the homeotropically aligned LC cell of HDBP-3 (sandwiched between two SAM coated ITO glass slides) taken under the polarized microscope at 120 °C. (b) Conoscopic figure of the sample in (b).](image)

![Fig. 4. Representative TOF transients for the homeotropically aligned HDBP-3 sample (D = 5 μm): (a) hole, E = 1.4 \times 10^5 V/cm and (b) electron, E = 1.2 \times 10^5 V/cm. The insets of (a) and (b) are the double logarithmic plots of (a) and (b), respectively.](image)
Fig. 5. Electric field dependence of the (a) hole and (b) electron mobilities for HDBP-3 in the Col₄ phase.

Fig. 6. Frontier orbitals including LUMO + 1, LUMO, HOMO, and HOMO + 1 energy levels of HDBP-3.
the energetic splitting of electronic levels, which is attributed to segment interaction. We calculated the charge transfer integral employing the Koopmans' theorem in conjunction with Hartree-Fock model (HF-KT), in which transfer integral values were calculated as half of the energy splitting between HOMO (LUMO) and HOMO – 1 (LUMO + 1) for hole (electron) transfer of the π–π stacking complex [23]. Fig. 6 shows the frontier orbitals including LUMO + 1, LUMO, HOMO, and HOMO – 1 energy levels of HDBP-3. The theoretical calculated transfer integral for HDBP-3 as hole and electron are $1.41 \times 10^{-2}$ eV and $7.73 \times 10^{-2}$ eV, respectively. The calculated theoretical transfer integrals also show HDBP-3 as a better electron acceptor which correlate to the experimental data for charge mobility. The value of the transfer integral for electron transport is approximately five times of that for hole transport, reflecting the ambipolar nature of HDBP-3.

Because ambipolar carrier mobility was attributed to the presence of the pyrazine ring (nitrogen containing ring) in HDBP-3, we next performed similar theoretical calculation on a all carbon analog, the benzo[a,c]anthracene, and assuming having similar stacking geometry. Fig. 7 shows the frontier orbitals including LUMO + 1, LUMO, HOMO, and HOMO – 1 energy levels of the benzo[a,c]anthracene. Interestingly, the theoretical calculated transfer integral for benzo[a,c]anthracene as hole and electron are $1.5 \times 10^{-1}$ eV and $1.40 \times 10^{-2}$ eV respectively. Here, benzo[a,c]anthracene is an excellent hole transport, but a
very poor electron transport. The vast difference between hole and electron properties (11 times) for benzo[a,c]anthracene, thus preferentially behaves only as hole.

For the discussion of the temperature dependence for HDBP-3, it is worth mentioning a dipolar discogen, HAT6-NO$_2$ [24], which was designed by Iino et al. The temperature dependence of the mobility of HAT6-NO$_2$ was much stronger than nonpolar triphenylene DLC because of the strong dipole induced by the nitro end-group [24]. However, the temperature dependence of mobility for HDBP-3, which with a built-in dipole in the core, was much weaker than it for HAT6-NO$_2$. To further understand the effect of the built-in dipole in the core, the field and temperature dependence of mobilities in Fig. 5 are fitted to the one-dimensional hopping transport equation established by Bleyl et al. [25].

$$\mu = \mu_0 \exp \left[ -\frac{0.9 \sigma}{kT} \right]^2 \exp \left[ \frac{\sigma}{CkT} - \Sigma \right] \sqrt{E}$$

where $E$ is the electric field, $T$ is the absolute temperature, $k$ is the Boltzmann constant, $\mu$ is the mobility, $\mu_0$ is the prefactor mobility, and the parameter $\sigma$ describes the width of the Gaussian energy disorder. The values of $\mu_0$ and $\sigma$ are $2.1 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ and 62 meV for hole, and $8.2 \times 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ and 70 meV for electron, respectively. It is quite interesting while compared these values with those obtained by Iino et al. by an equivalent treatment of HAT6-NO$_2$ [24]. For this discogen, which with a polar nitro substituent, the values of $\mu_0$ and $\sigma$ are $8.6 \times 10^{-1}$ cm$^2$V$^{-1}$s$^{-1}$ and 102 meV. The energy disorder of HDBP-3 is much smaller than HAT6-NO$_2$, which indicates the position of the molecular dipole has significant effect on charge transport. The molecular dipole in the core compared to it in the substituent place is much favorable to charge transport.

4. Conclusion

In summary, the charge carrier transport properties of homeotropically aligned HDBP-3 were investigated using a time-of-flight measurement. In the C$_{60}$ mesophase, HDBP-3 exhibited excellent ambipolar and non-dispersive charge transport. Carrier mobility was up to $10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$. As anticipated, hexaalkoxydibenzo[a,c]phenazine with a built-in dipole enforced better columnar stacking, which is favorable to charge transport. The excellent ambipolar charge transport properties and a wide mesophase range of HDBP-3 make it a great candidate for application in organic optoelectronic devices.

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