Anisotropic ambipolar carrier transport and high bipolar mobilities up to $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in aligned liquid-crystal glass films of oligofluorene

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By taking advantage of the rich morphological characteristics of oligofluorenes and the mesophase-mediated molecular assembly/alignment, we studied carrier-transport properties of solid-state oligofluorenes in different morphologies and orientations. Compared to the amorphous phase, the uniaxially aligned liquid-crystal glass of oligofluorenes could give up to 100-fold enhancement in bipolar carrier-transport mobilities, bringing both hole and electron mobilities to nearly $0.1 \text{ cm}^2/\text{V s}$. Furthermore, significant anisotropic bipolar transport, i.e., preferential bipolar carrier transport along the oligomer chain direction is observed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2801360]

There exists increasing demands in organic semiconductors with high carrier mobilities in the broad context of organic electronics.^{1–11} Charge transport in condensed organic systems, in addition to intrinsic characteristics of molecules themselves, strongly depends how molecules are assembled (i.e., morphologies).^{1–11} More ordered molecular assembly promotes larger overlap of orbitals between molecules, facilitating intermolecular charge transfer.^{1–11} Although mobilities exceeding that of amorphous Si have been achieved with single-crystalline and polycrystalline organic materials, difficulties associated with film processing and reproducibility/uniformity remain,^{1–4} particularly for electronic/optical applications requiring large areas and homogeneity. Therefore, embedding ordering in molecular thin films yet also giving a homogeneous nature is highly desired.

One distinctive recent approach of achieving such characteristics in an organic material is through formation of vitrified liquid-crystalline films [e.g., liquid-crystal (LC) glasses], in which mesophase-mediated molecular ordering at elevated temperature is frozen into the solid state by cooling across the glass transition temperature (T_g) of the material.^{5–11} With the aid of alignment techniques, monodomain LC assembly/alignment is feasible over large areas. Such a concept was previously demonstrated with the aligned LC glass of polyfluorenes, resulting in an enhancement of hole mobility from $<10^{-3} \text{ cm}^2/\text{V s}$ in the amorphous phase to nearly $10^{-2} \text{ cm}^2/\text{V s}$ in the aligned LC glass.⁷ Later, similar enhancement in carrier mobility was also reported for various polymer and oligomer systems that can be processed into LC glasses.^{7–11} In particular, Chen *et al.* found that in aligned LC glasses of carefully purified oligofluorenes, not only enhanced hole mobility but also enhanced electron mobility over $10^{-2} \text{ cm}^2/\text{V s}$ could be achieved, giving effective bipolar transport characteristics.¹¹

The somewhat ordered/aligned conjugated systems very often exhibit anisotropic carrier-transport characteristics, i.e., showing strong dependence on orientations with respect to molecular axes.^{3,8,10} Yet, in Chen's studies of aligned oligofluorene LC glasses, only carrier transport perpendicular to molecular chains was studied. In this work, by taking advantage of the distinctive feature that molecular assembly/orientations of LC materials can be manipulated through different surface treatments, we report the anisotropic bipolar carrier transport of aligned oligofluorene LC glasses. In particular, very high mobilities of nearly $10^{-1} \text{ cm}^2/\text{V s}$ for both holes and electrons, close to the electron mobility of amorphous Si, were observed for carrier transport along the direction of molecular chains.

In this study, an ethyl-substituted tetrafluorene E4 (inset of Fig. 3), which possesses a nematic LC phase at $190\text{--}230^\circ\text{C}$ and a reasonably high T_g of $\sim 134^\circ\text{C}$, was used.¹¹ With fast enough cooling, the molecular ordering and morphology in the LC phase of E4 could be preserved as the LC glass at the room temperature without suffering crystallization. The charge-transport characteristics of E4 films were investigated by the time-of-flight (TOF) transient photocurrent technique, as detailed in the previous reports.^{12–15}

To investigate the influences of morphologies and molecular orientations on carrier transport, E4 films in TOF samples were prepared into three types of configurations (Fig. 1): the amorphous film, the homogeneously (horizontally) aligned LC glass film, and the homeotropically (vertically) aligned LC glass film. The amorphous E4 sample (prepared by vacuum deposition) and the homogeneously (horizontally) aligned LC glass sample were prepared by previously reported methods,¹¹ while preparation of the homeotropic sample is described as follows. To induce vertical molecular alignment to a larger extent, E4 was sandwiched between two substrates coated with the vertical alignment layer (polyimide based, Nissan Chemical Industries, Ltd.), using glass-rod spacers ($\sim 22 \mu\text{m}$) to control the cell gap.

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Amorphous Homogeneous Homeotropic

	Glass	Glass
	(Semi)transparent electrode	(Semi)transparent electrode
Al (150 nm)	Horizontal alignment layer	Vertical alignment layer

Ag (30 nm)	Horizontal alignment layer	Vertical alignment layer
Glass	(Semi)transparent electrode	(Semi)transparent electrode
	Glass	Glass

FIG. 1. The schematic illustrations of three sample configurations for TOF studies of E4: the amorphous film, the homogeneously (horizontally) aligned LC glass film, and the homeotropically (vertically) aligned LC glass film.

The alignment film was prepared by first spin coating a precursor on the substrate (either a glass or a glass precoated with the indium tin oxide), followed by baking at 220 °C for 1 h to achieve full imidization. The resulting alignment film (40 nm) subjected to no further processing (e.g., rubbing) could induce homeotropic (vertical) alignment of E4 molecules. When the E4 sample (sandwiched between two glass/polyimide slides) was right heated to the LC temperature (220 °C), the threaded texture typical of nematic LCs could be observed [Fig. 2(a)] under the polarized microscope (with crossed polarizers). Upon annealing at 220 °C, a nearly monodomain uniaxial alignment of E4 molecules, as shown in Fig. 2(b), was achieved. By rapidly cooling the aligned sample to room temperature (~ -60 °C/min), the molecular alignment mediated by fluidic nematic mesomorphism was preserved and an uniaxially aligned and uniform glassy nematic film was obtained, as shown in Fig. 2(c). The dark images in Figs. 2(b) and 2(c), which were taken with crossed polarizers and were invariant with in-plane rotation of the sample, clearly indicate the vertical alignment of molecules. As a further confirmation, we measured the transmission of the vertically aligned E4 cell sandwiched between two crossed polarizers as a function of the in-plane rotation angle. The low transmission across all angles (Fig. 3) again confirms vertical alignment of molecules.

All the amorphous films and the aligned glassy nematic films of E4 exhibit nondispersive ambipolar carrier-transport characteristics. As an instance, Figs. 4(a) and 4(b) show representative TOF transients of holes and electrons, respectively, for the homeotropically aligned LC glass of E4 at room temperature. In these curves, the short initial spike in the transient, limited by the time resolution of the measurement setup, is followed first by a constant-current plateau and then by a drop. The final falloff of the current is caused

FIG. 2. (a) Photo of a micrometer thick E4 sample (sandwiched between two glass/polyimide slides) taken under the polarized microscope when right heated to 220 °C. (b) Photo of the vertically aligned LC cell of E4 taken under the polarized microscope at 220 °C. (c) Photo of the sample in (b) taken after rapidly cooling (~ -60 °C/min) to room temperature.

FIG. 3. The transmission (measured with the He-Ne laser, 632.8 nm) of the vertically aligned E4 cell sandwiched between two crossed polarizers as a function of the in-plane rotation angle. Inset: the molecular structure of E4.

by the carriers reaching the collection electrode, where they are discharged. The appearance of a plateau indicates the charge carriers have attained a constant drift velocity and hence nondispersive carrier transport.^{5-7,11-15} The carrier transit time t_T needed for determining the mobility can be unambiguously evaluated from the intersection point of the asymptotes to the plateau and the tail sections in the double logarithmic representation (insets of Fig. 4). Hole and electron mobilities thus determined for all the amorphous and the nematic glass films are shown as a function of $E^{1/2}$ in Figs. 5(a) and 5(b), respectively. The field dependence of mobilities in Fig. 5 follows the universal Poole-Frenkel relationship, $\mu \propto \exp(\beta E^{1/2})$, where β is the Poole-Frenkel factor,^{7,11-16} as often observed in somewhat disordered organic systems.^{7,11-16}

The homeotropically aligned glassy nematic film shows a hole mobility up to $0.9 \times 10^{-1} \text{ cm}^2/\text{V s}$ and an electron mobility up to $1.0 \times 10^{-1} \text{ cm}^2/\text{V s}$ for fields from 8×10^4 to $2.3 \times 10^5 \text{ V/cm}$. If not limited by the time resolution of the current measurement setup, even higher mobilities may be observed at higher fields. Nevertheless, these values

FIG. 4. Representative TOF transients for the vertically aligned E4 sample ($\sim 22 \mu\text{m}$): (a) hole, $E = 1.3 \times 10^5 \text{ V/cm}$ and (b) electron, $E = 1.6 \times 10^5 \text{ V/cm}$. The insets of (a) and (b) are double logarithmic plots of (a) and (b), respectively.

FIG. 5. (a) Hole mobilities and (b) electron mobilities vs $E^{1/2}$ for E4 in the amorphous state, the homogeneously aligned LC glass state, and in the homeotropically aligned LC glass state.

already represent the highest mobilities ever reported for fluorene-based materials. The homogeneously aligned glassy nematic film shows a hole mobility up to $2.0 \times 10^{-2} \text{ cm}^2/\text{V s}$ and an electron mobility up to $2.3 \times 10^{-2} \text{ cm}^2/\text{V s}$ for fields from 1.0×10^5 to $3.0 \times 10^5 \text{ V/cm}$. The amorphous film shows a hole mobility up to $1.9 \times 10^{-3} \text{ cm}^2/\text{V s}$ and an electron mobility up to $2.7 \times 10^{-3} \text{ cm}^2/\text{V s}$ for fields from 1.6×10^5 to $7.1 \times 10^5 \text{ V/cm}$. Under a similar field (e.g., $E = 2.3 \times 10^5 \text{ V/cm}$), the homeotropically aligned film shows room-temperature mobilities about five times larger than those of the homogeneously aligned film and nearly two orders of magnitude (~ 80 – 100 times) larger than those of the amorphous film.

Significantly higher TOF carrier mobilities in the vertically aligned LC glass than in the horizontally aligned LC glass indicate preferential carrier transport parallel to the chain direction of oligofluorenes to that perpendicular, i.e., anisotropic carrier transport in the uniaxially aligned oligofluorenes. It is interesting to note that although anisotropic hole transport was previously reported for both polyfluorene or oligofluorene films with mesophase-induced molecular alignment (in the field-effect transistor configuration),¹⁰ yet anisotropic electron transport was not reported before. Also compared to the hole mobilities of polyfluorenes or oligofluorenes measured with the field-effect configuration,¹⁰ TOF hole mobilities (either amorphous, parallel or vertical to the molecular chains) observed here for oligofluorenes in general are one to two orders of magnitude higher. Such differences are most possibly associated with various extrinsic issues involved in the field-effect measurement, such as the source/drain contacts and the interface with the gate insulator, etc.^{2–4,8} In TOF measurements, carriers are photogenerated and drifted inside the bulk materials, not involving issues of carrier injection and interfaces and rendering the TOF results more straightforward and intrinsic.

The anisotropy of charge transport in aligned LC glasses of E4 is worthy of further considerations. Charge transport

within the oligomer backbone is faster than interchain hopping between adjacent oligomer chains. However, the oligomer length ($\sim 3 \text{ nm}$) is much smaller than the separation between the two TOF electrodes ($\sim 22 \mu\text{m}$). Therefore, for both vertically and horizontally aligned cases, the rate-limiting step is still the interchain hopping. According to previous theoretical treatments, at low electric fields (e.g., $\sim 10^5 \text{ V/cm}$), the interchain hopping rate is rather independent of the direction of the electric field with respect to the oligomer chain direction (at least to the first order).¹⁷ This implies that the mobility anisotropy detected by two different molecular alignments may be roughly interpreted in terms of the differences in average distances that charge carriers diffuse per interchain hopping step, which correspond to the length of $\sim 3 \text{ nm}$ and the width of $\sim 0.5 \text{ nm}$ for the E4 molecule under the two alignment configurations.

In summary, by taking advantage of the rich morphological characteristics of oligofluorenes (e.g., amorphous phase, LC phase, LC glass phase, etc.) and the mesophase-mediated molecular assembly/alignment, we studied carrier-transport properties of solid-state oligofluorenes in different morphologies and orientations. Compared to the amorphous phase, the uniaxially aligned LC glass of oligofluorenes could give up to 100-fold enhancement in bipolar carrier-transport mobilities, bringing both hole and electron mobilities to nearly $0.1 \text{ cm}^2/\text{V s}$. Furthermore, significant anisotropic bipolar transport, i.e., preferential bipolar carrier transport along the molecular chain direction to that perpendicular, is observed in the uniaxially aligned LC glass.

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