Influences of oligomer length on carrier-transport properties of oligofluorenes

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(Received 9 April 2004; accepted 23 June 2004)

In this letter, carrier-transport properties of a homologous series of oligofluorenes with C9 diaryl substitution have been examined. These substituted oligofluorenes possess stable amorphous states, ambipolar carrier-transport properties, and processability to thin films for a range of oligomer lengths, rendering feasible investigating dependence of carrier transport on oligomer length in disordered systems. It is found that carrier mobilities of these oligofluorenes show a clear decreasing trend with the oligomer length. Such findings are in contrast with previous observations for crystalline oligomers and impose certain implications in carrier transport of conjugated polymers and oligomers. © 2004 American Institute of Physics. [DOI: 10.1063/1.1784031]

Organic materials with extended π-conjugation, such as conjugated polymers and monodisperse conjugated oligomers, have been intensively pursued in recent years due to applications in photonics and optoelectronics. Conjugated oligomers have a number of advantages over polymers, such as well-defined structures, absence of chain defects, and ease of purification and characterization. In addition, oligomers generally possess more predictable and reproducible properties, facilitating systematic investigation of structure–property relationship and optimization. There thus exists general interest in conjugated oligomers as model systems for conjugated polymers or as a distinct class of materials themselves.

One general strategy in the science of fully conjugated polymers has been to study the trend of properties with oligomer (conjugation) length, which through extrapolation usually would provide invaluable information for understanding characteristics and mechanisms in conjugated polymers. Such a strategy has proved successful in certain aspects, such as electronic structures and photophysical properties. For carrier transport properties that are of both fundamental and practical interest, it however poses certain challenges because linear conjugated oligomers in films generally have a strong tendency to crystallize. Although there exist sporadic reports or carrier-transport properties as a function of oligomer lengths in crystalline states of few conjugated oligomers, e.g., oligothiophenes, polycenes, oligophenylene, etc., they however give no representation of the generally amorphous (disordered) situation in polymer films. Homologous series of conjugated oligomers having stable amorphous states, appropriate carrier-transport properties, and processability to thin films, therefore would be valuable to such studies.

As such, our recent findings that introducing diaryl substituents on C9 of terfluorenes leads to enhanced morphological stability of the amorphous phase and that ter(9,9-diaryfluorene)s exhibit intriguing nondispersive ambipolar carrier-transport properties strongly suggest that homologues of oligo(9,9-diaryfluorene) may be ideal candidates for such studies. In this letter, we present the systematic examination of oligomer-length-dependent carrier-transport properties in glass-forming (i.e., amorphous) oligo(9,9-diaryfluorene).

Structures of oligofluorenes under investigation are shown in Fig. 1, and a few properties of these homologues are listed in Table I. These oligofluorenes were synthesized by Suzuki coupling reactions and details of syntheses and characterization will be reported elsewhere. For the present purpose, it suffices to mention that their molecular structure were validated with elemental and spectroscopic analyses. The backbone of these oligofluorenes contains two to four fluorene units (corresponding to compounds B2, B3, and B4, respectively). The rigid and bulky spiro-linked 2,2′-biphenyl substituents are introduced on C9 to provide spatial hindrance between chromophores, which suppresses the tendency to crystallization and gives the whole homologues sufficient thermal and morphological stability in thin films. As such, these oligofluorenes retain glass-forming properties down to the backbone length of only two fluorene units and all exhibit high glass transition temperatures (>170°C, Table I). The lowest-energy absorption bands of these oligofluorenes, which is characteristic of the lowest π–π* transition of the central oligofluorene chromophores, show consistent redshift in the peak wavelength with the backbone length (Table I), as expected from the increase of conjugation length.

Charge transport in oligofluorene films was characterized by the time-of-flight (TOF) transient photocurrent tech-
nique using the sample structure of glass substrate/Ag (30 nm)/oligofluorene (μm thick)/Al (150 nm). Thich oligofluorene films (1–3 μm) for TOF measurements were prepared by vacuum deposition at a rate of ~0.5 nm/s onto the semitransparent Ag contact (30 nm), using materials carefully purified by temperature-gradient sublimation. All three oligofluorenes form homogeneous films with vacuum deposition, and the amorphous nature of vacuum deposited oligofluorene films were confirmed by featureless x-ray diffraction patterns. Ag and Al were chosen as blocking contacts for the TOF samples due to their poor carrier-injection capability for the present oligofluorenes. All material layers were deposited by thermal evaporation in a vacuum chamber with a base pressure of <10⁻⁵ Torr. The amount (mass) of materials deposited was monitored with the quartz crystal microbalance and the thicknesses of films were confirmed by profilometry or ellipsometry, from which one can further deduce the density of materials in thin films.

In the TOF mobility measurement, a frequency-tripled Nd:YAG laser (355 nm, ~10 ns pulse duration) was used for pulsed illumination through the semitransparent Ag. This wavelength is around the absorption peaks of oligofluorenes (~330–360 nm, Table I) and gives a large absorption coefficient of ~10⁵ cm⁻¹, ensuring the penetration depth of the illumination (~100–200 nm) and the sheet of photogenerated carriers to be thin enough in comparison with the thickness of the organic layer. The TOF measurements were performed in a 10⁻⁵ Torr vacuum chamber. Under an applied dc bias, the transient photocurrent was recorded with a digital storage oscilloscope. The intensity of illumination was adjusted to keep the photogenerated charges less than 5% of the sample capacitor charge, avoiding space-charge-induced nonuniform distribution of electric field during the drift of carriers. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of τ. With the applied bias V and the sample thickness D, the applied electric field E is then V/D, and the carrier mobility is given by $\mu = D/t_\tau E = D^2/(Vt_\tau)$.

All three oligofluorenes exhibit nondispersive ambipolar carrier-transport characteristics. For instance, Figs. 2(a) and 2(b) show representative TOF transients of holes and electrons, respectively, for B2 at room temperature. 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 by the carriers reaching the collection electrode (Al), where they are discharged. The appearance of a plateau indicates the charge carriers have attained a constant drift velocity and hence nondispersive carrier transport.

The carrier transit time $t_\tau$ 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. 2). 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 by the carriers reaching the collection electrode (Al), where they are discharged. The appearance of a plateau indicates the charge carriers have attained a constant drift velocity and hence nondispersive carrier transport.

Hole and electron mobilities thus determined for all materials are shown as a function of $E^{1/2}$ in Figs. 3(a) and 3(b), respectively. Among these oligofluorenes, the shortest B2 exhibits the highest hole mobility of up to $5 \times 10^{-3}$ cm²/V s, and the highest electron mobility of up to $3 \times 10^{-3}$ cm²/V s, which also represents the highest electron mobility ever reported for amorphous organic solids. The field-dependence of mobilities in Fig. 3 follows the universal Poole-Frenkel relationship: $\mu \propto \exp(\beta E^{1/2})$, where $\beta$ is the decay parameter.
Poole-Frenkel factor.$^{13-20}$ Such relationship is often observed in disordered organic systems and could be attributed to effects of energetic and positional disorder on the hopping conduction in disordered organic solids.$^{13-20}$ The negative field dependence of mobility in B4 is less usual but similar phenomena were also observed previously and were ascribed to larger influence of positional disorder than energetic disorder.$^{14,18-23}$

To manifest the dependence of the carrier mobility on the backbone length, the hole and electron mobilities of the homologues near a certain electric field are shown as a function of the oligomer length in Fig. 4. Mobilities of both carriers clearly decrease with the backbone length. This is quite in contrast with those previously reported for conjugated oligomers in crystalline states, in which either the opposite dependence or no clear dependence of carrier mobility on oligomer length was observed.$^{7-11}$ In the crystalline state, molecules with the definite conformation are arranged (aligned) in an ordered manner, and there are cases showing that along certain preferential orientations for carrier transport the spacing between molecules remains rather constant with the oligomer length.$^{9}$ Correspondingly, the (mass) density remains similar or even slightly increases with the oligomer length.$^{9}$ As such, more extended conjugated systems are expected to cause enhanced intermolecular interaction and carrier transport. In disordered systems like the present cases, however, locations, orientations, and conformations of molecules are with distributions. The results here therefore imply that for misaligned (disordered) oligomer chains, the progressive delocalization of frontier molecular orbitals with increased oligomer length does not benefit interchain interaction and carrier transport. Instead, longer oligomers could lead to larger variation of molecular conformation and consequently larger disorder, impeding carrier transport. In addition, we have found that the (mass) density of vacuum-deposited amorphous oligofluorene films tends to decreases with oligomer length (inset of Fig. 4). It indicates less dense molecular packing and less efficient space filling for longer oligomers, which would also render carrier transport more difficult. With well-defined conjugation length and better-controlled characteristics of the oligomeric systems, the trend observed here may represent an intrinsic limit to carrier transport in disordered polycrystalline and other similar conjugated polymers. The fundamental origin of such phenomena, according to the present results, is strongly associated with inherent disorder in polymers. In real cases, other extrinsic issues in polymeric systems could lead to even inferior transport properties, as indicated by generally lower carrier mobility and lack of nondispersive electron transport in conjugated polymers.$^{16-29}$

In summary, we have examined carrier-transport properties of a homologous series of glass-forming oligofluorenes, and found that both hole and electron mobilities decrease with the oligomer length. Such findings are in contrast with previous results for crystalline oligomers and impose certain implications in carrier transport of conjugated polymers and oligomers.

The authors would like to acknowledge financial support from National Science Council of the Republic of China.

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