

Nondispersive hole transport in a spin-coated dendrimer film measured by the charge-generation-layer time-of-flight method

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Measurements of the mobility of a first-generation (*G*1) *bis*-fluorene cored dendrimer have been performed on spin-coated samples of 500 nm thickness using the charge-generation-layer time-of-flight (TOF) technique. A 10 nm perylene charge generation layer was excited by the 532 nm line of a Q-switched Nd:YAG laser and the generated carriers swept through the dendrimer film under an applied field. We observe nondispersive hole transport in the dendrimer layer with a room-temperature mobility $\mu = 2.0 \times 10^{-4} \text{ cm}^2/\text{V s}$ at a field of 0.55 MV/cm. There is a weak field dependence of the mobility and it increases from $\mu = 1.6 \times 10^{-4} \text{ cm}^2/\text{V s}$ at 0.2 MV/cm to $\mu = 3.0 \times 10^{-4} \text{ cm}^2/\text{V s}$ at 1.4 MV/cm. These results suggest that the measurement of mobility by TOF in spin-coated samples on thickness scales relevant to organic light-emitting diodes can yield valuable information, and that dendrimers are promising materials for device applications. © 2002 American Institute of Physics. [DOI: 10.1063/1.1514400]

Organic electroluminescence (EL) has generated much interest recently due to numerous optoelectronic applications such as light-emitting diodes (LEDs) and lasers. Current peak external quantum efficiencies of organic light-emitting diodes (OLEDs) are of the order of 20%¹ and lifetimes in excess of 10 000 h have been reported.² There are three classes of organic EL materials: Small molecules, conjugated polymers, and conjugated dendrimers. Of these, the latter two are solution-processable materials, and it is believed that these offer greater flexibility for cheaper display fabrication and the possible application of such simple techniques such as ink-jet printing of displays. Polyfluorene-based polymers have shown much promise due to their high photoluminescence efficiency and color tunability^{3–5} and more recently solution-processible phosphorescent dendrimers have shown excellent emissive properties.⁶

For all classes of materials, the injection and transport of charge plays a crucial role in determining the efficiency of OLEDs. Ideally, both electrons and holes should have mobilities of similar magnitude, so that charge recombination occurs away from the electrodes which may quench luminescence. Measurements of charge mobility therefore provide important information for the development of improved materials and device structures. A high mobility is desirable for high brightness applications, field-effect transistors, and novel devices such as electrically pumped organic lasers.^{7–10} A commonly used method for studying charge transport in organic materials is the time-of-flight (TOF) technique, first developed in the 1950's.¹¹ A sheet of charge carriers is gen-

erated optically at one edge of the sample and swept through the device under an applied field, and the time for the charge-carrier packet to travel across the device is known as the transit time (t_T). Generally for solution-processable materials, this is performed on a thick sample of a few micrometres thickness to ensure that the optical density of the sample is sufficient for the photoexcited carriers to be generated within a small percentage of the device thickness. For solution-processable materials, this usually entails preparation of a drop-cast film in order to achieve the desired thickness. Hence, the charge transport measurements are made on films that are different from the spin-coated films commonly used to make LEDs. Morphology has been determined to be an important factor in determining the transport properties of solution-processable materials such as conjugated polymers,¹² and it has been shown that the effect of solvent, solution concentration, and spin-coating¹³ conditions can all have a major impact on the microscopic properties of the material. Thus, there is considerable scope for large variations between the morphology of drop-cast and spin-coated films. In addition, studies have shown that measured mobilities can depend strongly on film thickness.

An alternative approach to TOF measurements, which has often been used for amorphous semiconductors, is to employ a charge-generation layer (CGL).¹⁴ A thin layer of absorptive dye is evaporated onto a sample between the sample and the contact electrode. The excitation laser wavelength is chosen to pass through the semitransparent indium tin oxide (ITO) electrode and the sample, and is absorbed by the CGL. The resultant carriers are then swept through the device under an applied field. The advantage of this method is that the carrier generation point is well defined irrespective

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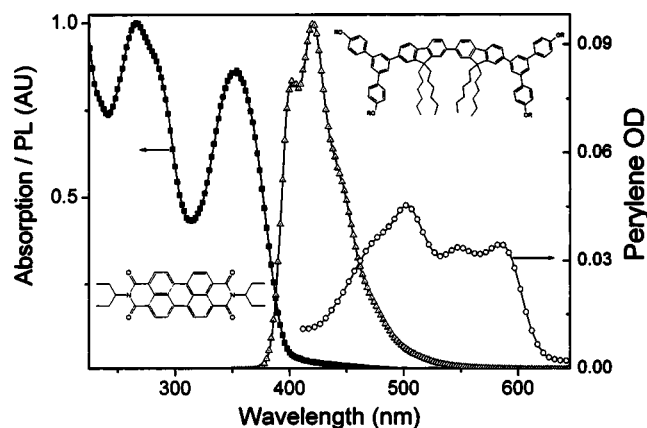


FIG. 1. The film absorption (squares), film PL (triangles), and structure of the G1 *bis*-fluorene dendrimer studied. The optical density of 10 nm of perylene used as a CGL is also shown (circles). Also shown is the structure of perylene diimide.

of optical density or thickness of the sample, allowing accurate conclusions to be drawn for materials with different absorption spectra and optical densities at the same film thickness. It can, therefore, be seen that a major advantage of the incorporation of a CGL is that mobility measurements can be performed on spin-coated films close in thickness and morphology to those found in OLED structures. Finally, the thinner structures studied here allow higher applied fields to be investigated without the use of high tension power supplies, and the practical limit of applied field is then field-induced device breakdown.

In this letter, we report charge transport measurements using a CGL on a new blue emissive conjugated dendrimer. Conjugated dendrimers consist of a light-emitting core, dendrons, and surface groups that control the processing properties. One of the great advantages of this molecular framework is that each of the components can be tuned independently to control the color of emission, degree of intermolecular interaction, and solubility as required for different applications.^{15,16} This scope for molecular engineering has recently been used to make high efficiency single-layer spin-coated dendrimer LEDs.⁶ The structures of the *bis*-fluorene cored dendrimer and perylene charge generation layer are shown in Fig. 1 (insets). The dendrimer consists of a *bis*-fluorene core with hexyl side groups attached to the 9 position of each of the fluorene units. Phenylene-based dendrons with 2-ethylhexyloxy surface groups are attached to the core. The dendrimer contains one layer of branching phenylene dendrons, making it a first-generation material. The photoluminescence (PL) and absorption spectra of a thin film are shown in Fig. 1. Two peaks can be resolved in the absorption spectra, an absorption peaking at 272 nm attributable to the biphenyl moieties within the dendron, and a feature with an absorption maximum at 352 nm arising from the *bis*-fluorene-*bis*-phenyl unit. The PL emission is in the deep blue with peaks at 401 nm and 424 nm. The optical density of a 10 nm perylene diimide dye charge transport layer is also shown. Solutions of dendrimer were made to concentrations of 45 mg/ml in chloroform, and films spun onto ITO (20 Ω/cm^2) at 700–800 rpm to yield a homogeneous film of 500–600 nm thickness. The spin-coated films were of optical quality and possessed good uniformity. A 10 nm film of

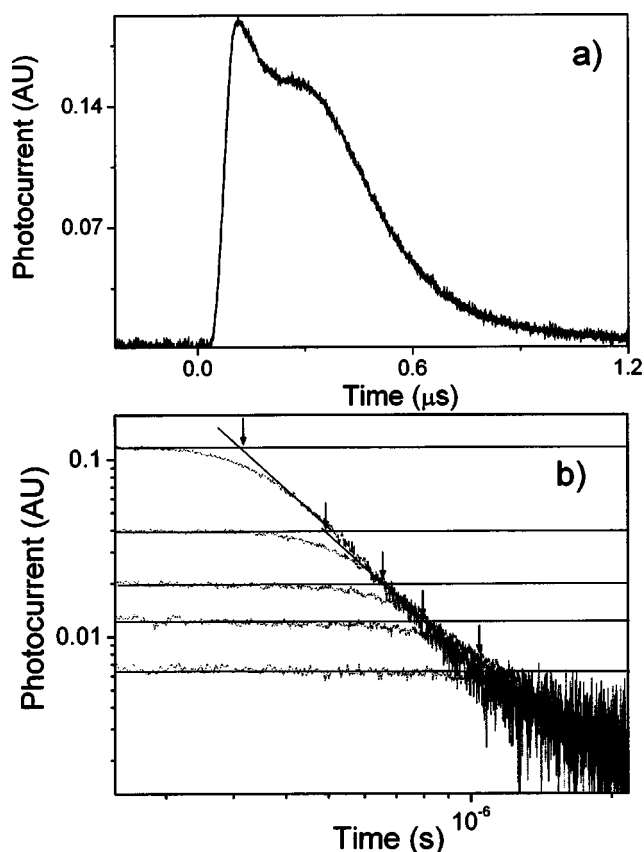


FIG. 2. (a) Typical TOF transient taken at a field of 0.71 MV/cm and (b) double-logarithmic plots of transients at applied fields of 0.34, 0.47, 0.54, 0.68, and 0.89 MV/cm. Measured on a 520 nm film.

peryene dye was then evaporated under a vacuum of 3×10^{-6} mbar to cover the whole of the device, with subsequent deposition of 100 nm of aluminum through a shadow mask, defining an active pixel area of around 5 mm². The perylene CGL was excited through the ITO and dendrimer layer using the 532 nm line of a Q-switched Nd:YAG laser. The aluminum electrode was biased positively and the photocurrent signal detected from the ITO using a 50 Ω input of a digital storage oscilloscope. The resistance–capacitance (RC) time constant of the system was less than 100 ns.

A typical transient measured at room temperature is shown in Fig. 2. It can be seen that there is an initial current peak at short times, commonly attributed to initial electronic relaxation of the charge carriers towards their intrinsic density of states distribution.^{17,18} A plateau region is observed, although at the studied device thickness it is not very apparent on a linear scale. There is then a decrease in the current at longer times as the charge-carrier packet reaches the counter electrode. The plateau region can clearly be seen in a double-logarithmic plot of the data [Fig. 2(b)], and the results are shown for a range of applied fields. The transient is clearly nondispersive, somewhat a surprise for a dendritic material, that intuitively one would assume to be rather disordered. A previous study on a family of amine-cored distyrylbenzene dendrimers showed highly dispersive behavior¹⁶ and this, coupled with photophysical measurements, suggested a highly disordered system. However, good vibronic structure in the PL emission of the fluorene-cored dendrimer is another indicator of apparent molecular scale order in this

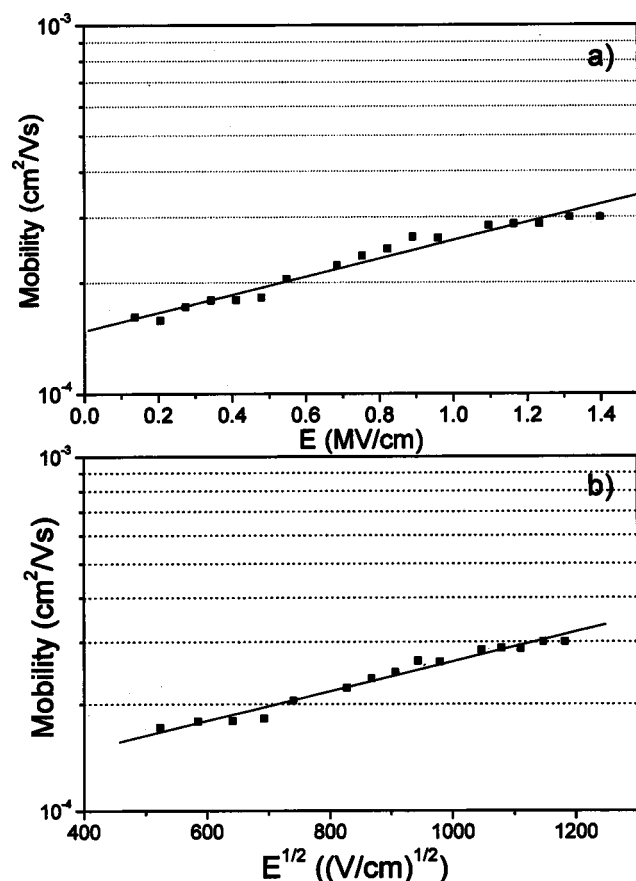


FIG. 3. Mobility of the G1 *bis*-fluorene dendrimer vs E and vs $E^{1/2}$ measured on a film of thickness 520 nm.

material. The nondispersive behavior also suggests that the dendrimer has a very high level of chemical purity. Nondispersive transport has been observed previously in poly(9,9-dioctyl fluorene) (PFO),¹⁹ but an important difference is that the measurements were made on much thicker solution-cast films, and are thus less comparable to the morphology found in an LED structure.

In order to assume a constant bias field across the sample in TOF measurements, the collected charge needs to be below 5% of the sample capacitor charge. In this experiment, the collected charge was of the order 3%–4% of the capacitor charge, partially due to the perylene layer absorbing only a small fraction of the incident laser light. The transit times are defined as the intersection between the asymptotes of the two power-law regions of the traces, and are indicated by arrows in the diagram. The mobility can then be calculated by $\mu = d^2/Vt_T$ where d is the device thickness, V is the applied voltage, and t_T is the transit time. The dependence of the mobility on the applied field [Fig. 3(a)] and the square root of the applied field [Fig. 3(b)] are shown. Good linear fits to both of these characteristic forms can be seen ($R^2 = 0.962$ and $R^2 = 0.971$, respectively). The mobility increases from $\mu = 1.6 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at 0.2 MV/cm to $\mu = 3.0 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at 1.4 MV/cm. This mobility is two orders of magnitude higher than the value of $2.2 \times 10^{-6} \text{ cm}^2/\text{Vs}$ at 0.5 MV/cm measured for MEH-PPV²⁰ and comparable to that for PFO²¹ ($3 \times 10^{-4} \text{ cm}^2/\text{Vs}$ at a field of 0.5 MV/cm). In the dendrimer, charge transport must occur by hopping between the *bis*-fluorene cores. The result

is significant as it shows that the extended conjugation of conjugated polymers is not required to achieve reasonable (i.e., suitable for OLED) mobilities in solution-processed organic semiconductors. The field dependence of the mobility is weak, similar to that measured for PFO systems,¹⁹ but in contrast to MEH-PPV.²⁰ Theoretical studies have shown that such a weak field dependence is characteristic of a system with little geometrical flexibility,²¹ and suggests that the dendrimer units are very rigid, rodlike structures.

In conclusion, we have observed nondispersive hole transport in a spin-coated film of an organic semiconductor. The results show that the CGL-TOF method is effective for the study of charge transport in films deposited by the same process used to make LEDs. We have used this technique to study a fluorene-cored conjugated dendrimer, and we measure a high mobility and low-field dependence for this system, making it attractive for electroluminescent applications.

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