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High charge-carrier mobilities in blends of poly(triarylamine) and TIPS-pentacene leading to better performing X-ray sensors

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ABSTRACT

A new class of X-ray sensor – in which there is a blend of poly(triarylamine) (PTAA) and 6,13-bis(triisopropylsilylethynyl) (TIPS)-pentacene in the active layer of a diode structure – has been developed. The crystalline pentacene provides a fast route for charge carriers and leads to enhanced performance of the sensor. The first time-of-flight charge-carrier mobility measurement of this blend is reported. The mobility of PTAA and TIPS-pentacene in a 1:25 molar ratio was found to be 2.2×10^{-5} $cm^2 V^{-1} s^{-1}$ (averaged for field strengths between 3×10^4 and 4×10^5 $V cm^{-1}$), which is about 17 times higher than that obtained in PTAA over the same range of field strengths. This higher mobility is correlated with a four-fold increase in the X-ray detection sensitivity in the PTAA:TIPS-pentacene devices.

1. Introduction

Numerous electronic devices, including field effect transistors [1], light-emitting diodes [2], photovoltaic cells [3], and radiation sensors [4,5], have in recent years employed organic materials as the active component. These devices share one common feature in that their efficiency depends strongly on the transport of charge carriers. The performance of electronic devices using typical semiconducting polymers is limited by the relatively low charge-carrier mobility of the active material (in the range from 10^{-5} to 10^{-2} $cm^2 V^{-1} s^{-1}$) [6–9] in comparison to conventional materials. To achieve a higher level of performance, there is a need for a material that provides the good film formation and ease of processing offered by conjugated polymers but that also possesses a high charge-carrier mobility.

Small molecule organic semiconductors, such as 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene, have been found to exhibit a very high charge carrier mobility (>1 $cm^2 V^{-1} s^{-1}$) [10,11] because the molecules arrange into a well-organized polycrystalline structure [12,13]. However, difficulties in the solution processing of TIPS-pentacene, stemming from the anisotropy of crystal formation [14], restricts its use in large-area deposition. Blending conjugated polymers with TIPS-pentacene, which brings together their advantageous properties to create a composite with good film formation and processability coupled with high charge-carrier mobility, is a logical tactic to address the materials' limitations. Blends of conjugated polymers and small molecules, such as poly(triarylamine) (PTAA) and TIPS-pentacene, have previously been studied in relation to field-effect transistor applications [15], and a better performance was observed in this type of device when blends were used. But whether *diode* structures – as employed in solar cells, LEDs, and sensors – could benefit from the use of polymer/small molecule blends is still the subject of investigation.

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Radiation sensors are an emerging application for semiconducting polymers [16]. The use of polymers – in the place of conventional inorganic semiconductors – opens up the possibility for large-area fabrication of sensors using low-cost, wet processing techniques, such as spin-casting, spray-casting, ink-jet or roll-to-roll printing [17]. Radiation sensors made from polymers exhibit greater mechanical flexibility in comparison to inorganic solids [5]. Furthermore, the elemental composition of most polymers (C, H, N and O) makes them an ideal candidate for dosimeters in medical applications, in which the detector requires a "human tissue-equivalent" interaction with radiation. (The average atomic number of muscle tissue is 7.4 [18].) Although radiotherapy and medical applications would benefit greatly from the improved accuracy of tissue-equivalent dosimeters, there are currently no low-cost, large-area devices with tissue-equivalence available.

Here, we present the first-ever measured charge transport properties of PTAA:TIPS-pentacene blends using a time-of-flight (TOF) photocurrent measurement technique. We correlate the raised mobility of the device with a four-fold increase in the X-ray detection sensitivity. Our results point to benefits in using TIPS-pentacene/polymer blends in applications that require high charge transport, such as light-emitting diodes, solar cells, and light sensors, to raise their performance to a higher level.

2. Materials and methods

The sensors employ layers (*ca.* 10 μm thick) of the polymer/molecule blend in a diode geometry. The details of the device preparation can be found elsewhere [19,20]. Briefly, slides of ITO-coated glass (Delta Technology Ltd., USA (CB-60IN)) were cleaned with acetone and deionised water. A 3 wt.% solution of PTAA (with an average molecular weight of 31 kg/mol) was prepared in toluene (99.99% purity, Sigma–Aldrich). Various concentrations TIPS pentacene (Sigma–Aldrich) were then added to the solution. It was homogenized for 10 min by stirring. Five different solutions were made: pure PTAA and PTAA blended with TIPS-pentacene with PTAA:TIPS molar ratios of 1:1, 1:10, 1:17 and 1:25. The solutions were spin-cast at 50 rpm for 30 s onto a clean substrate to provide a single layer of polymer. The films were dried under atmospheric conditions. Vacuum annealing was then performed at 100 °C for 12 h at pressure of 10^{-3} mbar, ensuring the temperature was kept below the solid-to-solid phase transition temperature of TIPS-pentacene at 124 °C [21]. Then, the thickness and average surface roughness of the active layer was measured using profilometry (Dektak Veeco). The device fabrication was completed by thermal evaporation of thin aluminum contacts on top of the active layer to create a Schottky contact.

A Leica DM 2500P microscope was employed to take polarized optical images. For energy dispersive X-ray analysis, an electron beam (Hitachi S-3200N electron microscope) with accelerating voltage of 20 kV and an X-ray detector (silicon drift detector, Oxford Instruments) was used.

For TOF measurements, an Al contact thickness of 50 nm and area of 9.6 mm^2 was deposited by thermal evaporation. The sample was held in a vacuum-tight steel box and was illuminated through the semi-transparent Al electrode. The 10 ns, 355 nm pulse of a Nd:YAG laser (Surelite Lasers, Continuum) was chosen to induce the optical excitation of the charge carriers. The intensity of the laser was attenuated by a neutral density filter in order to minimize the space-charge effect. To limit charge injection, the device was operated under a reverse bias by applying a negative voltage to the ITO electrode through a blocking resistor (10 kΩ). The resulting photocurrent pulses were recorded using a digital oscilloscope with a 50 Ω input terminal (Tektronix TDS 3032). Signal averaging and dark current subtraction were carried out to improve the quality of the data. The TOF experiments were performed in the dark, at room temperature, and under vacuum (3×10^{-1} mbar).

For X-ray photocurrent measurements, Al top contacts with a thickness of 100 nm and an area of 25 mm^2 were deposited via thermal evaporation. To prevent oxidation, the sensors were dip-coated in molten paraffin wax to create a barrier coating. The sensors were irradiated by 17.5 keV Kα X-rays from a molybdenum target X-ray tube (XF50 11, Oxford instruments, UK). While operating in a reverse bias, the sensor was exposed to the X-ray beam through the metal top electrode. The induced photocurrent was then measured using a voltage source-picoammeter (487, Keithley Instruments, UK). The dark current was subtracted from the measured X-ray photocurrent in order to provide a corrected value of the photocurrent. During exposure, the sensors were mounted in a steel box, in the dark and at room temperature, 10 cm from the X-ray source. Sensor sensitivity was calculated from the slope of a graph of X-ray photocurrent against dose rate and dividing by the active volume under the contact (see Supplementary data, Fig. 1A and B) [5].

3. Results and discussion

Fig. 1A–C show images obtained from polarized optical microscopy of films of PTAA blended with various concentrations of TIPS-pentacene. There is obvious crystallization of the TIPS-pentacene (confirmed separately via X-ray diffraction). The images reveal a needle-like crystal structure in which the crystal size increases with an increasing amount of TIPS-pentacene. The long-axis of the crystals lies in the plane of the film. Analysis of the Si distribution in the blend film using energy dispersive X-ray analysis in a mapping mode (not shown here) has revealed that crystals are uniformly distributed throughout the depth of the film. The average surface roughness of the films increases from 0.28 μm in a pure PTAA film to 5.3 μm for a film of PTAA blended with TIPS-pentacene in a 1:17 molar ratio. This roughening, which is also apparent in optical microscopy, is attributed to faceting from the TIPS-pentacene crystal formation.

Typical room-temperature transient hole TOF photocurrent measurements at two different applied voltages are presented in Fig. 2A for a device whose active layer consists of PTAA blended with TIPS-pentacene in a 1:17 molar ratio. Analysis over a range of applied voltages found an increase in the total collected charge (*i.e.* the area under the