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Single conjugated polymer nanoparticle capacitors

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ABSTRACT

The hole injection from a carbazole derivative hole transport layer into nanoparticles ($r = 25 \pm 15$ nm) of the conjugated polymer MEH-PPV was investigated by an indirect single-particle fluorescence-quenching technique. The results suggest that there is a kinetic barrier for hole injection that prevents polymer particles from being charged in the dark. This barrier can be overcome with the assistance of optical excitation of the MEH-PPV nanoparticles, achieving a thermodynamic population of injected holes at positive bias. The amount of injected holes at equilibrium is observed to depend upon the bias in a manner highly consistent with device simulations based on a continuum model. Overall, the results demonstrate that the hole injection into nano domains of conjugated polymers is a complex process depending upon molecular interfacial effects determined by device geometry and electrostatic interactions.

1. Introduction

The transfer of positive charge (holes) between organic semiconductors across heterojunctions is a central process in organic light emitting displays (OLEDs) [1–5] and other organic electronic devices [6–9]. The energetic barrier for hole injection into a conjugated polymer (CP) layer from an adjacent hole-transport layer (HTL) is generally believed to be controlled by two major factors: the offset of the energy of the highest occupied molecular orbital of the two materials ($E_{\mathrm{HOMO,CP}} - E_{\mathrm{HOMO,HTL}}$) and modifications to this energy due to surface dipoles and other effects which can shift the vacuum level energy.

A closely related issue to charge injection across heterojunctions is the nature of positive charge carriers (holes) in organic conjugated polymers. There are apparently two main types of holes, i.e. shallowly trapped (mobile) holes and the much less well understood and investigated deeply trapped holes (DTH). The extreme hysteresis that is commonly observed in the current (I) vs. voltage (V) curves for various types of organic electronics (also known as the bias stress effect) may be due to the creation and interfacial build-up of DTH [10–15]. This implies that a build-up of DTH can significantly alter the energetics necessary to inject holes, but the physical and chemical origin of DTH remains obscure despite decades of research [2,12,15–23]. One proposal is that DTH are due to the chemical rearrangement/modification of the specific materials [10–12,16,18,21–23].

We recently have been investigating hole injection from various types of HTL into single polymer chains of the conjugated polymer poly(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as a means of exploring the barriers and rates of hole injection in semiconductor nano domains [24]. Conjugated polymers have potential practical applications in organic electronic devices such as light emitting diodes [2,25], solar cells [26,27], field effect transistors [28–30], etc. The experiments employed a device geometry (analogous to the one shown in Fig. 1a) in which holes are injected into single molecule capacitors from a carbazole derivative (CBP). The experimental amount and rate of hole injection from the CBP HTL into individual, isolated polymer chains was monitored by single-molecule fluorescence spectroscopy using fluorescence quenching as a measure of the charge density in each polymer chain. Direct electrical measurements of charge would be difficult due to the small number of charges injected per single molecule.

Despite the use of HTL/CP combinations, such as CBP/MEH-PPV, that would be expected to exhibit energetically favorable thermal hole injection (see Fig. 1b), no injection was observed in the dark under positive bias (see Fig. 1a for the sign convention). This result suggests that the effective E_{HOMO} of single conjugated polymer chains is actually lower than the bulk material, due perhaps to environmental or conformational effects. Interestingly, while no charge injection was observed in the dark, optical excitation of MEH-PPV (producing MEH-PPV excitons) was observed to induce

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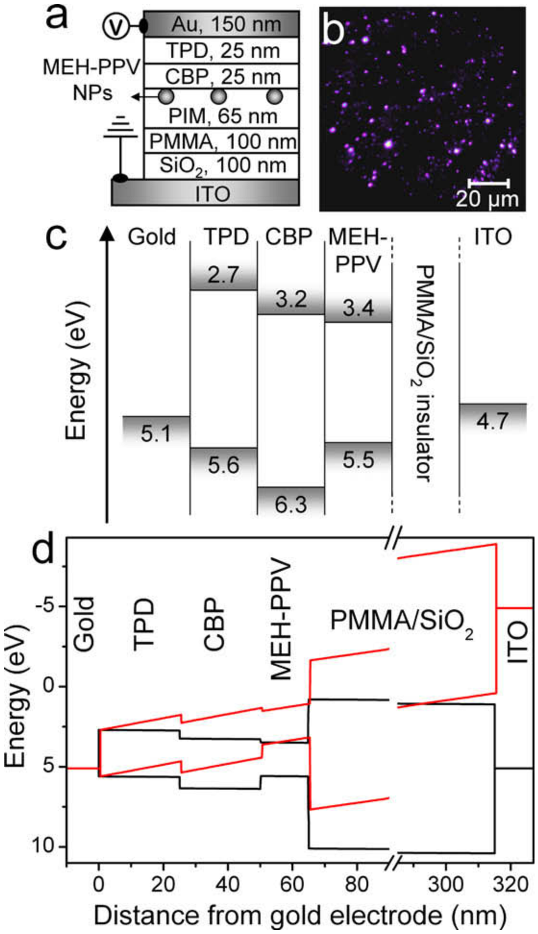

Fig. 1. (a) TPD-CBP hole-injection device containing MEH-PPV NPs. (b) Wide-field fluorescence image of a hole injection device. (c) Energy diagram of the device shown in (a). (d) Simulation results for the energy levels of the device shown in (a). The black and red lines represent the LUMO (top) and HOMO (bottom) energy levels at 0 V (equilibrium) and 10 V (before significant charging has occurred), respectively.

hole injection from the CBP layer. The light-assisted injection of positive charge carriers (holes) was assigned to a light-induced hole-transfer mechanism (denoted by LIHT). The hole injection process involves charge transfer from a CBP hole to a MEH-PPV singlet exciton at the CBP/MEH-PPV interface, perhaps additionally involving the formation of a DTH in MEH-PPV. The molecular level description of the process however has not been established.

This paper describes a continuation of our investigation of hole injection across heterojunction into conjugated polymer nano domains. In this work, we study injection of holes into single self-assembled MEH-PPV nanoparticles (NPs) comprised of ~10–100 polymer chains per particle and which have a radius in the range of ~10–40 nm. These particles are significantly larger than the single polymer chains that were described above ($r < 7$ nm). Previous spectroscopic studies that compared single polymer chains, conjugated polymer NPs, and bulk thin-films indicate that the morphological state of the conjugated polymer in the NPs and bulk, thin-film forms are similar [31]. In contrast, the single-polymer chains possess a morphology (conformation) with less chain-chain interactions [32–36]. Thus, the investigation of holes into MEH-PPV NPs is a means of determining whether the LIHT process is specific to single polymer chains or more general. In addition, self-assembled conjugated polymer NPs are interesting in their own right, e.g. as alternatives to quantum dots as biological labels [37,38], and as model systems in electrochemistry [39,40] and electrogenerated luminescence [41]. This paper explores hole injection into MEH-PPV NPs in devices containing a CBP HTL. As in the study of single polymer chains, injected holes are measured by fluorescence quenching using single particle spectroscopy.

2. Experimental

The electrical charging and discharging processes of MEH-PPV NPs were studied in large-area multilayer hole-injection capacitor devices.

2.1. Device structure and assembly

The general structure of the single-molecule hole-injection device is shown in Fig. 1a. The device was assembled bottom up on commercial ITO electrodes (Evaporated Coatings, Inc., sheet resistance 50 Ω/□) that were cleaned by successive sonication in trichloroethylene (Sigma-Aldrich, HPLC), acetone (Fisher, HPLC) and methanol (Fisher, HPLC). The SiO_2 insulating layer was deposited by inductively-coupled plasma chemical vapor deposition (ICP-CVD) at 200 °C (Oxford instruments, Plasmalab 80plus). The poly(methyl methacrylate) (PMMA, Sigma Aldrich, average MW = 101 kg/mol) layer was deposited by spincoating from toluene (Sigma Aldrich, anhydrous 99.8%). The function of this layer was to isolate single nanoparticles of MEH-PPV (Uniax, average MW = 1000 kg/mol) from the SiO_2 layer.

Nanoparticles were prepared by a re-precipitation technique [38,40,41]. Briefly, a small aliquot of a concentrated solution of MEH-PPV (~1 mg/ml) in tetrahydrofuran is 'flash'-injected into a solution of poly(isobutyl methachrylate) (PIM, Acros, average MW = 300 kg/mol) in cyclohexane. The size of the resulting NPs ($r = 25 \pm 15$ nm) was estimated by comparing the single NP fluorescence intensity distribution to that of a reference NP sample with a known size distribution (measured by Scanning Electron Microscopy). The resulting colloidal suspension is spin-cast to form the PIM/NP layer (10 nm), the NP concentration was adjusted to obtain an areal density of ~0.1 particles/μm^2 in the sample.

The device contains two HTLs in series as shown in Fig. 1a, a layer of 4,4′-*N*,*N*′-dicarbazole-biphenyl (CBP) and a layer of *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidene (TPD). Thermal evaporation was used to deposit the TPD and CBP hole transport layers and the gold electrode (Cerac, 99.99%). Thermal depositions were carried out at $\sim 10^{-4}$ Pa and typical rates were 1–2 Å/s as measured by a quartz crystal microbalance. Layer thicknesses were measured by atomic force microscopy (Digital Instruments, Dimension 3100) and/or ellipsometry (J A Woollam Co. Inc., M-2000) and are as shown in Fig 1a unless otherwise noted. All device fabrication was performed in a glove box (O_2 and H_2O concentration are <10 ppm and <1 ppm, respectively) except for the SiO_2 deposition.

2.2. Single particle fluorescence–voltage (F–V) technique and experimental setup

The hole charging/discharging processes in individual NP of conjugated polymers in capacitor devices were studied using the previously described fluorescence voltage single molecule spectroscopy, *F–V* SMS technique [42,43]. This technique determines indirectly the density of holes in individual fluorescent molecules or nanoparticles by measuring single-particle fluorescence quenching. The principle of the technique is based on the well know quenching effect of singlet excitons by hole polarons in organic semiconductors [44].

Two instruments were used to measure the fluorescence intensity of individual NPs in this work: a fluorescence confocal micro-