

Photovoltaic Properties of Dye Functionalized Single-Wall Carbon Nanotube/Conjugated Polymer Devices

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Photovoltaic properties of dye, *N*-(1-pyrenyl)maleimide (PM), functionalized single-walled carbon nanotubes (SWNT)–conjugated polymer, poly(3-octylthiophene) (P3OT), blend composites are reported. Devices were fabricated by drop or spin cast from the solution of composite onto ITO-coated glass. Improved performance was achieved by functionalizing the SWNT with dye molecules. Photovoltaic behavior with an open circuit voltage of 0.6–0.7 V was measured in diodes (Al/SWNT+PM–polymer/ITO). The short circuit current was found to increase by more than an order of magnitude compared to the SWNT–polymer diode without dye. Optical absorption spectra showed considerable ground-state interaction between SWNT+dye and the polymer. It is proposed that the main reason for the increase in short circuit current is due to efficient transfer of holes by dye molecules to P3OT at the dye/polymer interface and the rapid transfer of the generated electrons to the SWNTs at the dye/nanotube interface. It is shown that the dye functionalized SWNT–conjugated polymer composites represent an alternative class of organic semiconducting materials for dye-based organic photovoltaic cells.

1. Introduction

The development of semiconducting polymers as a novel class of optoelectronic materials has raised interest regarding their use in the field of photodetectors^{1,2} and photovoltaic cells,^{3–5} due to the promise of low cost, tunable optical properties, and large area coverage on flexible surfaces. However, efficiencies of such devices are currently much lower than those of their inorganic counterparts,⁶ requiring a further search for more efficient materials and better understanding of the device physics.

The photovoltaic effect involves the generation of electron hole pairs under optical excitation and their collection at opposite electrodes. In inorganic materials illumination creates free charge directly, while in organic materials illumination causes a delocalization of photoexcited states, which leads to the generation of bound electron–hole pairs, excitons.⁷ These excitons have to dissociate into free holes and electrons to obtain

a donor/acceptor-type of photovoltaic system which is suitable for delivering an appreciable photocurrent, a key requirement for photovoltaic power generation. Dissociation often occurs at the interface between materials of high electron affinity and low ionization potential.⁸ In this respect a percolated system of donor and acceptor phases, that is, a network of heterojunctions through the entire film, is advantageous. In this work we show that by including a properly matched organic dye at the junction interface it is possible to very significantly enhance the performance of polymer photovoltaic cells.

After the discovery of photoinduced charge transfer between conjugated polymers (as donor) and buckminsterfullerene C₆₀ (as acceptor), several improved photovoltaic systems have been demonstrated.^{9,10} Photoconductive polymers such as P3OT are good hole conductors but significantly worse electron conductors. This places a limitation on the photocurrent, and hence power, available from a polymer photovoltaic cell. The possibility of enhancing exciton dissociation and electron transport through the percolating single-walled nanotubes to the negative electrode has been shown by Kymakis et al.^{11,12} However the photocurrent of such devices mainly relies on the optical absorption of the polymer in the solar spectrum as the C₆₀ molecules and nano-

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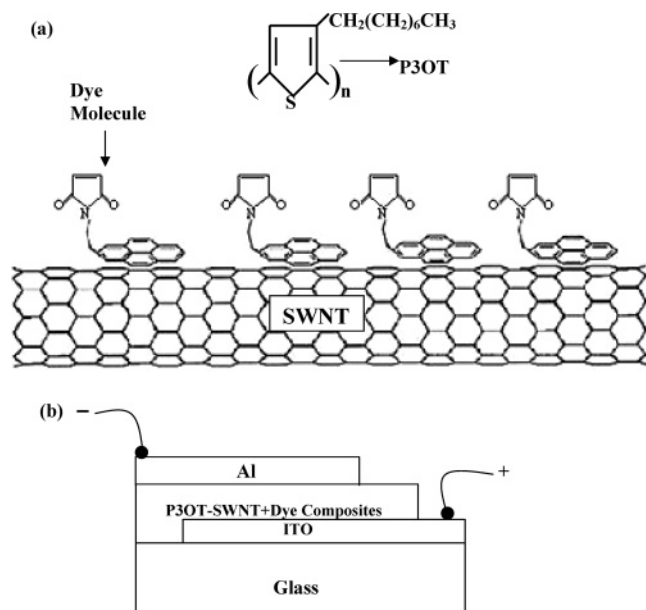


Figure 1. Chemical structure of poly(3-octylthiophene) (P3OT), single walled nanotube (SWNT), *N*-(1-pyrenyl)maleimide (PM), detailed scheme of the dye molecule (PM) attachment to the SWNT surface via π -stacking, and device architecture of the photovoltaic cell.

tubes do not contribute to photogeneration process. This problem can be overcome by the incorporation of an organic dye at the polymer/acceptor junctions, a process known as sensitization.¹³ In this work we use poly(3-octylthiophene) (P3OT) as the photoexcited electron donor which is blended with pure single-walled nanotubes (SWNTs) as well as with *N*-(1-pyrenyl)maleimide (PM) functionalized SWNTs to fabricate two types of photovoltaic cells: ITO/P3OT-SWNTs/Al and ITO/P3OT-SWNTs+PM/Al, respectively. The choice of dye was based on the possibility of its attachment to the SWNT surface and its photoabsorption spectrum which is well matched to the peak power region in the solar spectrum.

2. Experimental Details

Noncovalent functionalization of SWNTs with PM molecules is shown schematically in Figure 1(a). PM molecules irreversibly adsorb onto the inherently hydrophobic surfaces of SWNTs in the organic solvent chloroform. The highly aromatic pyrenyl group is known to interact strongly with the basal plane of graphite via π -stacking,^{14,15} and also strongly interacts with the sidewalls of SWNTs in a similar manner.¹⁶ SWNTs obtained from Carboxex, Inc., USA were used in this study. The powder purity was estimated to be about 60% from transmission electron microscopy. As-prepared SWNTs were purified by the hydrothermal method.¹⁷ P3OT and PM having 99% purity (Sigma-Aldrich) were used. SWNTs in powder form were added to chloroform solution (0.2 mg/ml) and dispersed with the aid of a high-power ultrasonic probe. The nanotubes were then blended with P3OT solution in chloroform (10 mg/ml) to make the composites without dye. For the dye functionalization of nanotubes, PM solution in chloroform was

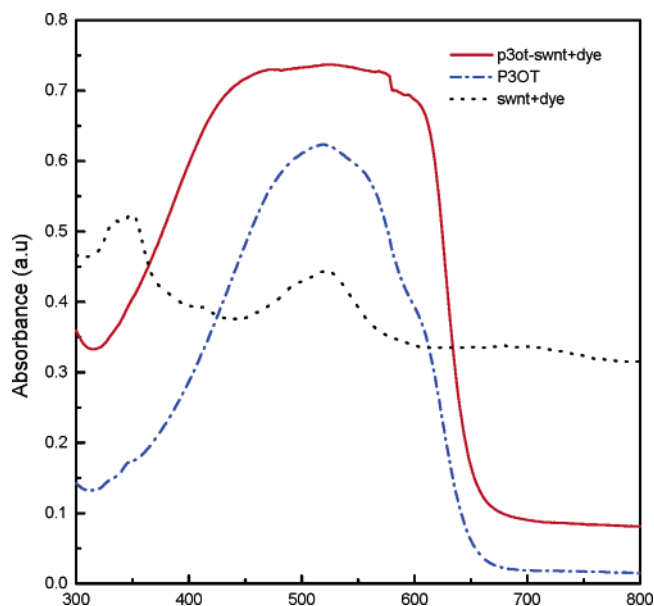


Figure 2. Unnormalized UV-vis absorption spectra of P3OT (---), SWNT+PM (···), and SWNT+PM-P3OT (red solid line) thin films on quartz substrates taken in transmission mode. Broadening of the absorption peak in SWNT+PM-P3OT composites indicates the ground-state interaction between SWNT+PM and P3OT.

added to the chloroform solution of the nanotube dispersion having a mass ratio 10:1 and kept for 3 h, following which it was blended with P3OT solution (10 mg/mL). TEM results show that this process is successful in achieving good dispersion of the SWNTs in P3OT.^{11,12} The nominal thickness of all the films deposited was 100 nm.

The photocells were fabricated in the sandwich configuration as shown in Figure 1b. Composite films were deposited by drop and spin coating at 2000 rpm for 1 min from a chloroform solution having a concentration of 10 mg/mL onto an indium tin oxide (ITO)-coated glass substrate. Aluminum electrodes were thermally evaporated under vacuum. After processing, the devices were stored in a nitrogen-filled glovebox before measurement. Electrical characterization under dark and illuminated (AM 1.5 through the glass/ITO side) conditions were carried out using an HP 4140B impedance analyzer. The samples for the optical characterization were spin coated onto the quartz substrate. A UniCam UV2 UV/VIS spectrophotometer was used to take the optical absorption data.

3. Results

Figure 2 shows the unnormalized absorption spectra of P3OT, SWNT+PM, and P3OT-SWNT+PM blend composite films. P3OT-SWNT+PM blend materials show broad spectral response over the wavelengths 420 to 610 nm, which indicates that there is a significant ground-state interaction between P3OT and SWNTs+PM. The high absorption band between 420 and 610 nm also matches the peak power region in the solar spectrum. The optical characteristics of the P3OT-SWNT composite reveal refractive index values of n (real) = 1.4 and k (imaginary) = 0.6 at the absorption peak around 520 nm.¹⁸ At this concentration of SWNTs in P3OT (2 wt %) the macroscopic optical characteristics of the composite are almost identical to that of the P3OT alone. There is no evidence of ground-state interaction between the P3OT and the SWNT from the macroscopic optical absorption spectra.¹⁸ Indeed, it would be difficult

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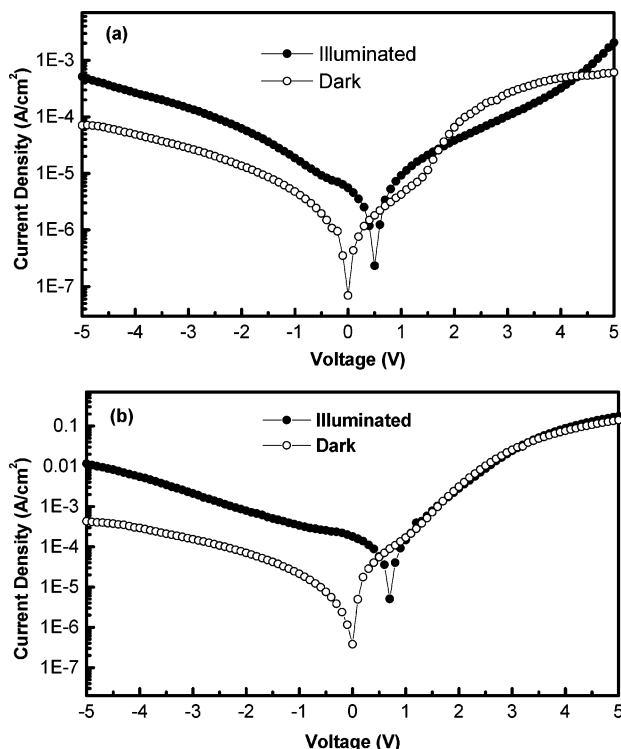


Figure 3. (a) Logarithmic plot of current–voltage characteristics of an ITO/P3OT-SWNTs/Al device in dark and under white light illumination. (b) The same data for an ITO/P3OT-SWNTs+PM/Al device shows the photovoltaic behavior.

to see any such interaction given the small fraction of SWNTs included within the polymer. With the PM added, there is a broadening and increase of the absorption in the 400–600 nm band, Figure 2. This is expected given the much higher proportion of dye, by weight compared to SWNTs, blended with the polymer.

Figure 3a and b show the current–voltage (I – V) characteristics of the devices ITO/P3OT-SWNT/Al and ITO/P3OT-SWNT+PM/Al cells under dark and white light illumination (AM 1.5, 100 mW/cm²) from the ITO side. The ITO side was connected to the positive terminal during forward biasing. The distinct diode behavior is indicated by the fact that the forward bias current is higher than that in reverse bias for voltages in excess of 1 V under dark conditions. The short circuit photocurrent density (I_{sc}) and open circuit voltage (V_{oc}) for the cell with dye under illumination are 0.18 mA/cm² and 0.6 V, respectively (Figure 4a), while the cell without dye shows $I_{sc} = 5.5 \mu\text{A}/\text{cm}^2$ and $V_{oc} = 0.5$ V (Figure 4b). Characteristics of the P3OT only cell in comparison to the SWNT-P3OT cell can be found in the literature^{11,12} for comparison.

According to metal–insulator–metal (MIM) diode model the upper limit of V_{oc} is determined by the work function difference of the two electrodes. The work function of Al is 4.3 eV and the work function of ITO is 4.6 eV.¹⁹ Then according to the MIM model V_{oc} should be in the range of 0.3 V. However, the V_{oc} measured for both types of devices (0.5 V and 0.6 V) is significantly higher. A possible explanation for this higher V_{oc} is due to the cell structure. An ultrathin layer of P3OT is placed between the ITO and polymer/SWCNT composite

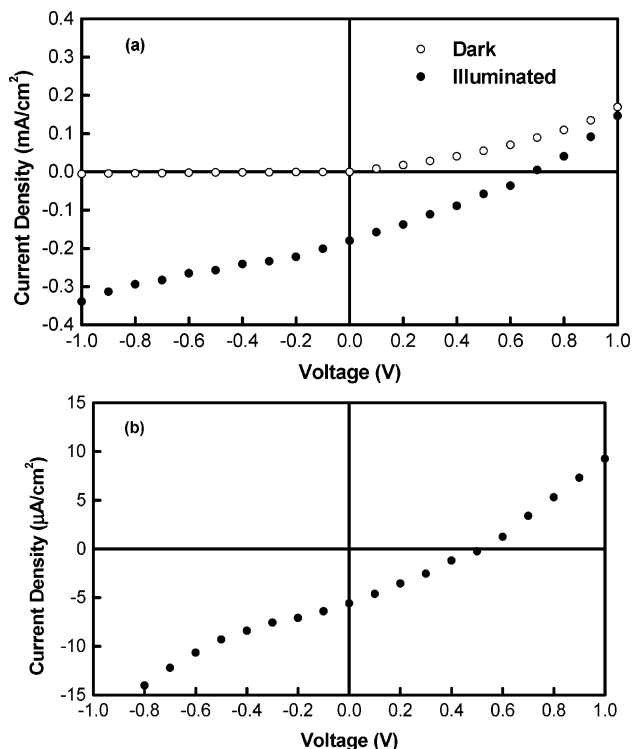


Figure 4. (a) I – V Characteristics of an ITO/P3OT-SWNTs+PM/Al device in dark and under white light illumination. (b) The same data for an ITO/P3OT-SWNTs/Al device under white light illumination.

film to prevent nanotube percolation paths forming short circuits between the ITO and Al contacts. The upper limit of V_{oc} would then be determined by the difference of SWNT work function (assuming that the SWNTs are metallic) and highest occupied molecular orbital (HOMO) energy of P3OT, and not by the difference of the electrode work functions. The SWNTs can be ascribed a work function of 4.6 eV,²⁰ with the HOMO level of the P3OT being 5.25 eV²¹ below the vacuum level. Therefore the maximum expected V_{oc} would be around 0.65 V, which is consistent with the experimentally observed value of 0.6 V at nominal room temperature (300 K) operation. There is, however, some doubt as to which value of work function should be used for SWNTs, as there are indications that it will change with chirality and hence on whether they are semiconducting or metallic²² for tubes with fixed diameters (1.4 nm) used. The value of 4.6 eV assumed for the work function remains valid for metallic SWNTs of diameter 1.4 nm from the data reported in ref 22.

The fill factor (FF), one of the characteristics which gives the power delivery capability of a photovoltaic cell is calculated by $FF = (V_m I_m) / (I_{sc} V_{oc})$, where V_m and I_m are the voltage and the current in the maximum power point of the I – V curve in the fourth quadrant. The FF values for the cells with dye and without dye are 0.35 and 0.28, respectively. The low value of the fill factor in both cases is likely to be due to the thin CNT-free P3OT layer which in effect introduces a significant

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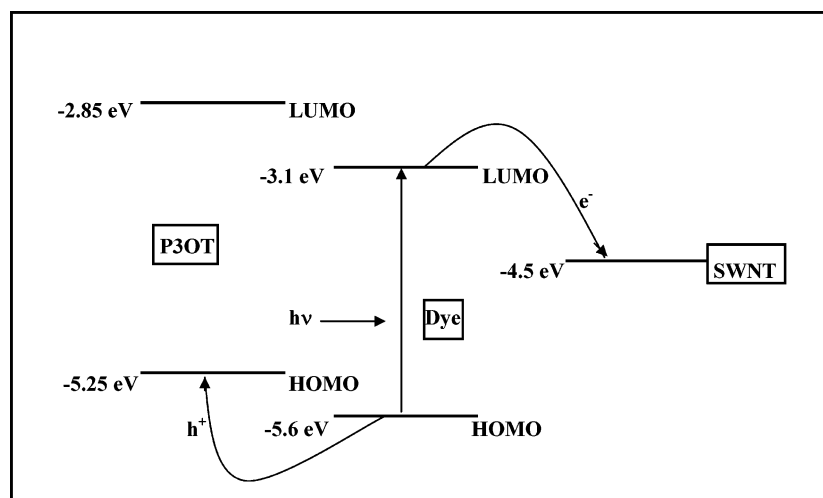


Figure 5. Schematic diagram of energy levels for P3OT, dye, and SWNT relative to vacuum shows the proposed energetically possible charge-transfer process from photoexcited dye molecule to SWNT and P3OT.

series resistance component to all the distributed heterojunctions within the photo current generation region. The nominal power conversion efficiency was calculated from the expression

$$\eta = \frac{FF \times I_{sc}(A/cm^2) \times V_{oc}(V)}{P_{in}(W/cm^2)} \quad (1)$$

where V_{oc} , I_{sc} , FF , and P_{in} are the open circuit voltage, the short circuit current, the fill factor, and the incident light power, respectively. The power conversion efficiency for the device with dye has increased from $7.5 \times 10^{-4} \%$ to 0.036% with respect to the device without dye. The important comparison here is the relative performance. The active cell efficiency values can be higher if the input power coupled into the cell is lower than the incident optical power P_{in} in eq 1. This is an important consideration in calculating power conversion efficiency as in this work assumes an incident optical power of 1 kW per square meter across the solar spectrum. There are reports on higher power conversion efficiencies on internal heterojunction polymer solar cells (e.g., >2% using CdSe nanorods in P3HT²³) where the light intensity used is monochromatic with much lower incident power, ~5 W per square meter in ref 23. Scaling of the photocurrent with light intensity can be sublinear due to the dynamics of recombination.²⁴ Thus the important factor to note is the dramatic improvement in *relative* photovoltaic power conversion achieved by insertion of dye into the P3OT/SWNT blend structure. The I_{sc} in the device with dye is more than an order of magnitude (~30×) larger than that in the device without dye. V_{oc} and FF in the device with dye are also improved.

4. Discussion

It is proposed that the enhancement in the photovoltaic properties is due to the insertion of dye molecules between the nanotubes and polymer junction. Sensitiza-

tion at the polymer/nanotube interface is expected to take place via charge transfer. The photoexcited dye transfers an electron to the nanotube, resulting in a positively charged dye and a negatively charged nanotube. Subsequently, a hole is transferred to the higher lying HOMO of the P3OT. The possible energy levels diagram for the charge-transfer process is shown in Figure 5. The energy of the lowest unoccupied molecular orbital (E_{LUMO}) of the dye is calculated from the semiempirical formula $E_{LUMO} = -(EA + 1.9)$ eV,²⁵ assuming an electron affinity (EA) value 1.2 eV for the dye, which is equal to that of a similar molecule Pyrene.²⁶ Energies of the LUMO and HOMO levels for P3OT are -2.85 eV and -5.25 eV, respectively,²¹ and the Fermi level of the metallic SWNT is -4.6 eV relative to the vacuum level. In this model we have taken the photo-generated carriers in the dye to be the dominant source of photocurrent. This is reasonable given that the photocurrent is enhanced by more than an order of magnitude due to the presence of the dye; i.e., the photocurrent component from the photogenerated exciton dissociation in the polymer is considered insignificant in comparison. This in effect turns the SWNT+dye-polymer cell into a device in which active photogeneration occurs in the dye layer. The SWNTs and the P3OT act as electron and hole transport channels to the negative and positive electrodes, respectively. The results achieved by using PM as the dye are in stark contrast to our earlier work where we used naphthocyanine (NaPC) with an absorption peak in the 650–850 nm band with SWNTs and P3OT in a similar cell structure. There it was found that the short circuit current under AM 1.5 light was in fact reduced by a factor of 5 due to a change in the recombination dynamics introduced by the NaPC dye molecule.²⁷

Conclusion

The improvement in efficiency of the polymer(P3OT)/SWNTs blend cell by insertion of dye molecules (PM)

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between the nanotubes/polymer junctions is very significant. The working principle of this device is that the interaction of dye molecules with the nanotubes and polymer allows the efficient electron transfer to nanotubes and hole transfer to polymers. The introduction of dye molecules was found to dramatically improve the photovoltaic performance of P3OT/ SWNTs blend de-

vices revealing a photocurrent larger than 2 orders of magnitude compared to that of P3OT/SWNTs blend devices. The combination of SWNTs, polymers, and dyes points to an effective route for obtaining low cost "all organic" solar cells for power conversion.

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