

Perylene Diimide (PDI) Based Organic Photovoltaic Cells with Nano-Fabric Composite Structure

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Introduction:

Organic photovoltaic (OPV) cells are considered one of the most important devices for addressing the future energy problems because of the abundance of the solar energy. Perylene diimide (PDI) materials have a long history in OPV, which were used as electron acceptors in the first OPV paper.^[1] Recently, the research groups of Xia and Bao^[2, 3] demonstrated high electron mobility for PDI materials as the active channel in organic transistors. This inspired us to develop PDI-based materials so that we may exploit their excellent electron transporting potential for OPV applications. Family of PDI materials^[4] have been developed with different band gaps to modify absorption and a variety of nanostructures to enhance processibility. Furthermore we have incorporated these materials in a variety of configurations (e.g. nano-fabric composite) to increase the acceptor-donor interactions needed for efficient charge separation. These PDI materials could be one of the best material candidates for electron accepting nanostructures in OPV applications.

Experiments:

For the fabrication of OPV cells, ITO coated glass was used for substrates of the OPV cells. ITO substrates were masked by Scotch tape and etched by 1M hydrogen chloride acid with zinc powder. The substrates were cleaned similarly to the silicon wafer for the field-effect transistors. Al4083 from Bayer was spun on the substrates and transferred into dry boxes. All the following processes were carried out in the dry boxes. The Al4083 layer was baked at 200°C for 10 minutes. Solutions for active layers were spun on the substrates at 600 rpm for 2 minutes. PDI-C₈ powder was thermally deposited on some of the substrates for hole-blocking layers. Then, LiF of 0.7 nm was deposited on all of the substrates by thermal evaporation and an aluminum layer was also deposited with similar way. For the preparation of solutions for active layers, HPLC grade o-dichlorobenzene was used as solvent. Regio-regular P3HT was dissolved at the concentration of 1 wt. %. PDI-C₈ nanofibers were synthesized in methanol, then, vacuum-dried. A blend solution of P3HT and PDI-C₈ nanofibers was prepared by adding the 1 wt. % P3HT solution into the dried PDI-C₈ nanofibers. The weight ratio of P3HT to PDI-C₈ nanofibers was more than 5.

Results and discussion:

PDI materials can be used for collection ionic photo-electrons in organic photovoltaic cells. Its electron

mobility can go up as high as 0.1 cm²/Vs, which is comparable to that of pure fullerene film.^[5] Due to strong π -stacking force and asymmetric molecular shape, PDI derivatives can be formed as fibers with large aspect ratios. The diameters of the fibers can also be controlled by proper selections of functional groups bound to PDI core.^[4] In contrast to poor solubility of the PDI powder, PDI in nanofiber forms enables us to use solution processes to easily build photovoltaic cells, this is one of the key advantages of implementing organic electronics. The PDI absorption peaks range from 470 to 575 nm, which contribute to the creation of photo excited charges by visible light in contrast to optically inactive fullerene based materials (Figure 1). Modification of perylene cores also can tune the electronic levels of the lowest unoccupied molecular orbit (LUMO) and highest occupied molecular orbit (HOMO) for optimal matching of donor-accepter HOMO-LUMO levels.^[5] Bis(octyl)-perylene diimide nanofibers (PDI-C₈, Figure 1b) form through self-assembly in a mixed solvent treatment of Chloroform/methanol.^[2] Fiber diameter is tunable between 10 nm and 1 micron based on solvent treatment.^[4] Various absorption spectra of PDI-C₈ feature multiple vibronic peaks were shown in Figure 1c.

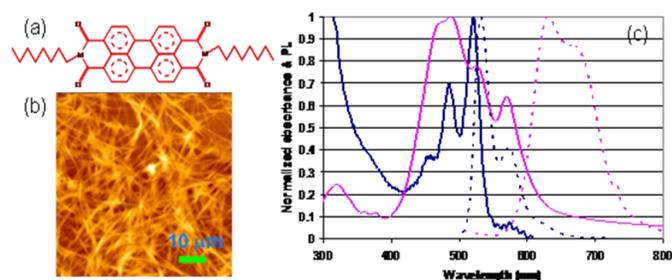


Figure 1. (a) Chemical structure of PDI-C₈ molecule, (b) AFM image of PDI-C₈ nanofibers, and (c) Optical absorbance (solid lines) and photoluminescence (dashed lines) of PDI-C₈ solution in methanol (dark lines) and film (gray lines).

As shown in Figure 2 and 3, four types of OPV cell structures and corresponded energy diagrams were constructed to investigate the role of PDI-C₈ nanofibers, which were classified by adding PDI-C₈ nanofibers or/and PDI-C₈ electron collecting layer (hole blocking layer). Type I and III had active layers of pure P3HT, while Type II and IV had active layers of the mixture. Type III and IV had a bi-layered heterojunction structure with an additional PDI-C₈ electron-collecting layer (hole-blocking layer), while Type I and III were single-layered

photovoltaic cells without any hole-blocking layer. In the comparison of the OPV's without hole blocking layers (Type I and II), the embedded PDI-C₈ nanofibers didn't improve the performance of OPV's. During the mixing of P3HT and PDI-C₈ nanofibers, P3HT surrounded the nanofibers very efficiently, which could be seen by AFM phase-mode images. This makes PDI-C₈ nanofibers in the OPV's had a limited connecting area into LiF/Al electrodes. In fact, the efficiency in Type II OPV was lower than that in Type I due to lower open-circuit voltage, which implied that the work function of the electron collecting electrode (LiF/Al) was pinned to the LUMO of PDI-C₈ rather than that of P3HT. This could also be seen by the open-circuit voltages in Type III and IV OPV's, which was very close to those in Type II OPV's. Thus, PDI-C₈ nanofibers in Type II did accept photo-excited electrons from P3HT absorbing material and fixed its open-circuit voltage. However, the efficiency of electron collection in Type II was low due to the limited connection between PDI-C₈ nanofibers and the LiF/Al electrode.

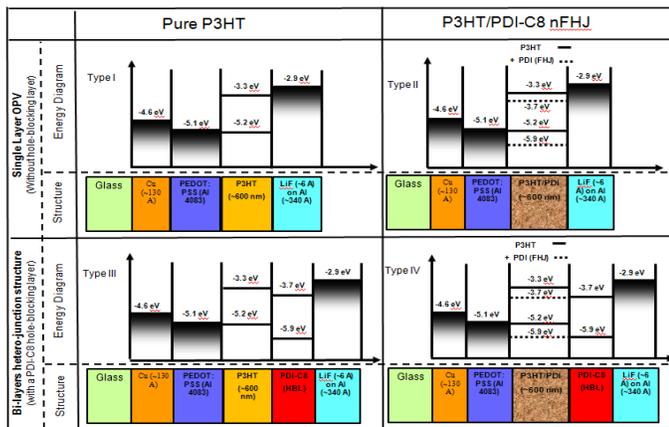


Figure 2: Four types of OPV cell structures and corresponded energy diagrams are constructed to investigate the role of PDI-C₈ nanofibers, where type I and III have active layers of pure P3HT, while Type II and IV have active layers of the mixture of P3HT and PDI-C₈ nanofibers formed FHJ.

The addition of a thin electron-collecting PDI-C₈ layer into Type I OPV significantly improved short circuit currents (I_{SC}). Type III had more contact area between LiF/Al electrode and electron-collecting layer to ensure more photo-excited electron collection than Type II. Moreover, another addition of PDI-C₈ nanofibers into light-absorbing P3HT layer of Type III OPV, i.e. Type IV OPV, significantly improved the efficiency by more than 100%. Thus, PDI-C₈ nanofibers significantly improved OPV performance by extending the heterojunction area to separate the electron-hole pairs, and enhancing the transport of the separated electrons, which also included the electrons generated even in far away from the LiF/Al electrode. The nanofibers also improved the shape of IV

characteristic curves. IV curves of Type III shown high differential resistance near open-circuit voltage (related to series resistance), which implied charge accumulation at the interface of the heterojunction (note that the interfaces at both electrodes were considered to be ohmic).

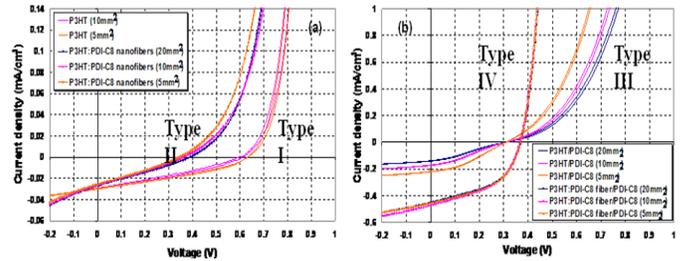


Figure 3. IV characteristic curves of various device structures and areas. Left plot corresponds to Type I and Type II OPV's, right plot to Type III and Type IV OPV's.

Summary:

We have demonstrated the improvement on the power-conversion efficiency of organic photovoltaic cells by implementing organic electron-transporting nanofibers forming nanofibric composite. It turns out that PDI-C₈ is a good electron transporter based on the measurements of field-effect transistors, and it is favorable to form nanofibers due to octyl groups on the PDI core. Sole use of PDI-C₈ nanofibers is not enough to improve the efficiency due to the restricted collection of photo-excited electrons at the aluminum electrode. The use of PDI-C₈ hole blocking layer facilitates electron collection, but the interface between the PDI-C₈ hole blocking layer and the absorbing P3HT layer is questionable because high series resistance is observed in IV characteristic curves near open-circuit voltage. The use of PDI-C₈ nanofibers improves photovoltaic cells in following aspects. One is the facilitation of the photo-excited electron collection in deep sites of absorbing P3HT layer. The second one is improving efficient transport of the electrons into aluminum electrode, which can provide us a solution to overcome the short lengths of exciton diffusion lengths. The third is the removal of accumulated photo-generated charges to raise filled factors of the photovoltaic cells.

References:

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