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Polymer Nanostructure Approach for Photoelectric Solar Energy Conversions

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ABSTRACT

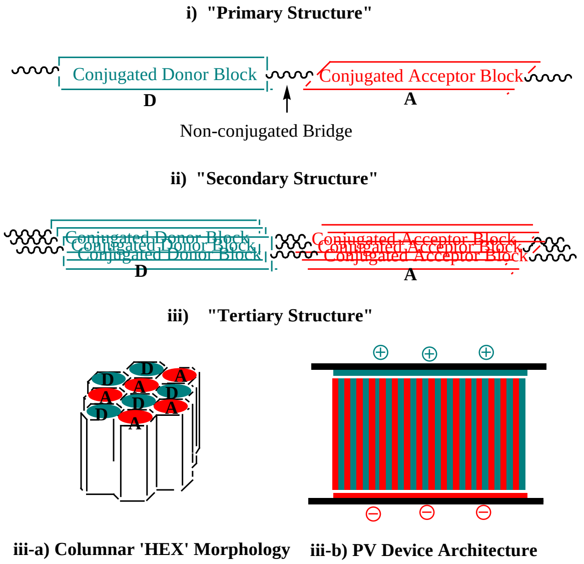
This presentation provides a brief overview on the mechanisms, history, current status, and future prospective of polymer or 'soft materials' based photoelectric conversion materials, with a focus on a block copolymer nanostructure approache to address the loss issues in organic or polymer based solar cells. For instance, a **DBfA** type of block copolymer exhibits a two orders of magnitude enhancement of photoelectric conversion efficiency over its corresponding **D/fA** blend system. Such enhancement is attributed mainly to the **DBfA** self-assembled solid state nanostructure that minimizes the carrier losses.

Keywords: Optoelectronics, solar cells, block copolymer, nanostructure, BONS.

1 INTRODUCTION

At materials molecular level, photoelectric/photovoltaic conversion corresponds to a photo induced electron transfer from a molecular electron rich donor entity to a weakly coupled electron deficient acceptor entity, and the process is also called photo induced exciton dissociation at a donor/acceptor interface [1-3]. In addition to solar energy such as solar cell applications, photoelectric/photovoltaic materials can also be used in photo-detector applications such as in photo-electric signal transducers in optical communication or optical imaging systems. Though certain inorganic semiconductor based solar cells can convert over 30% of sunlight power into electric power [4], in order to economically and eco-friendly utilize Sunlight for future energy needs, particularly in remote areas where large spaces are available, low cost polymer or 'soft materials' based solar sheets become very attractive [1-3]. Polymer based solar cells or photo detectors are particularly attractive for personal or portable/mobile power and sensor needs such as campers where lightweight and flexibility are most desirable. Though power conversion efficiencies for purely organic and polymeric photovoltaic devices have been reported a little over 10% [5], in comparison to inorganic materials, however, semi-conducting conjugated polymers exhibit some inherent advantages such as: (1) lightweight, (2) flexible shape, (3) ultra-fast (up to femtoseconds) opto-electronic response, (4) nearly continuous tunability of materials energy levels and energy gaps via molecular design and synthesis, (5) versatile materials processing and device fabrication schemes, (6) environmentally friendly, (7) biocompatible, and (8) low cost on large scale industrial manufacturing [1-3]. Additionally, as research in organic and polymeric photovoltaic materials rapidly grows, key bottleneck factors, such as the 'photon losses', the 'exciton losses', and the 'carrier losses' that hinder organic/polymeric photoelectric performance become clear [6], high efficiency organic photoelectric systems appear feasible, as all these "losses" can be minimized by systematic optimization in space, energy and/or time domains [6-9].

Due to a need for a finite nano meter scale exciton diffusion domain size and smooth charge carrier transport pathways for both electrons and holes, a bicontinuous ordered nano structure or 'BONS' (shown in Figure 1-iiia) with donor/acceptor separated nano domain phases appears to be very attrative for minimizing both the 'exciton loss' and the 'carrier loss' [6]. Figure 1 exhibits a general scheme of a conjugated block copolymer tertiary nanostructure approach for high efficiency polymer optoelectronic devices.


i) "Primary Structure"

ii) "Secondary Structure"

iii) "Tertiary Structure"

iii-a) Columnar 'HEX' Morphology **iii-b) PV Device Architecture**

Figure 1: Scheme of a desired tertiary nanostructure self-assembly of a DBA type of block copolymer for potential high efficiency polymer photoelectric system.

Specifically, as depicted in Figure 1-i, the primary or chemical sturcture of the block copolymer is composed of a hole conducting conjuated donor block **D** covalently connected to an electron conducting conjugated acceptor block **A** with a non-conjugated bridge unit **B**. The non-conjugated **B** is to provide a convenient molecular pathway for photo induced charge separation between **D** and **A** at the same time it also hinders the charge recombination. Self assembly of **DBA** type block copolymer such as pi-pi stacking in solid state is expected to result in a secondary morphological structure as shown in Figure 1-ii. Finally, a potential and desirable tertiary solid state morphological structure of 1-iiia is expected to simultaneously reduce the exciton and carrier losses [6]. This is because the the domain sizes of the donor or acceptor blocks can be conveniently tailored via chemical synthetic means, and the tertiary solid state morphology can be achived via a variety of polymer procesing protocols and methods [7-9].

As an example, the **$(DBAB)_n$** block copolymer exhibited much better optoelectronic conversion effiicency than the corresponding simple **D/A** blend, and XRD/AFM studies revealed formation of certain crystalline domains in **$(DBAB)_n$** block copolymer thin film after simple thermal annealing [7-8]. However, the size of such crystalline domains are limited due to the dispersive nature of the donor and acceptor blocks in the **$(DBAB)_n$** block copolymers, making the long-range ordering very difficult to realize as shown in Figure 2 (top). To address this issue, a **DBA** type block copolymer (shown in Figure 2 middle) has also been studied recently [9]. **DBA** would allow more flexibility in block copolymer self-assembling and is expected to enable large domain BONS formation even from **DBA** block copolymers with broad polydispersity of **D** and **A** blocks. Furthermore, **DBA** can be blended with **D** and **A** to gain greater flexibility in polymer packing due to the higher mobility of the free donor and acceptor polymer blocks as shown in Figure 2 (bottom).

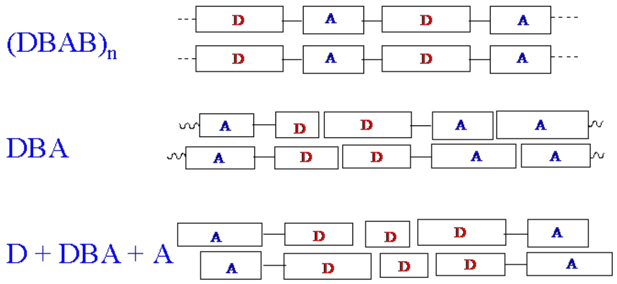


Figure 2: Different stacking possibilities of **$(DBAB)_n$** and **DBA** block copolymers (See text for details).

In order to develop a **DBA** (or a fluorinated **DBfA**) type conjugated block copolymer system, one synthetic approach was to first develop a so called unsymmetrically difunctionalized monomer (*e.g.*, one such example acceptor monomer is shown in Figure 3) having two different functional groups (*e.g.*, one aldehyde and one phosphate), so that a mono-end functional donor or acceptor polymer block with one functional end and one terminating end (like donor block **D** in Figure 3) can be built first [9]. The mono-end functional donor **D** block can then be coupled with large access amount of difunctional bridge unit **B** to form a **DB** unit (Figure 3). The last step is to couple the **DB** with the acceptor block or the acceptor monomer to form the final **DBA** or **DBfA** block copolymers ((**DBfA** synthesis scheme is shown in Figure 3**)**. Compared to a hydrocarbon based **DBA** [9], the fluorinated acceptor block **fA** are expected to enhance the donor and acceptor block phase separations due to chemical differences between the CH and CF groups. In the example synthesis, the size of both donor and acceptor blocks are confined as 10-30 repeat units (corresponding to 6.5-18 nm that is within the PPV average exciton diffusion length), as each PPV repeat unit has a straight distance of about 0.65 nm along the conjugation chain direction (Detailed synthesis of these polymers are being reported separately).

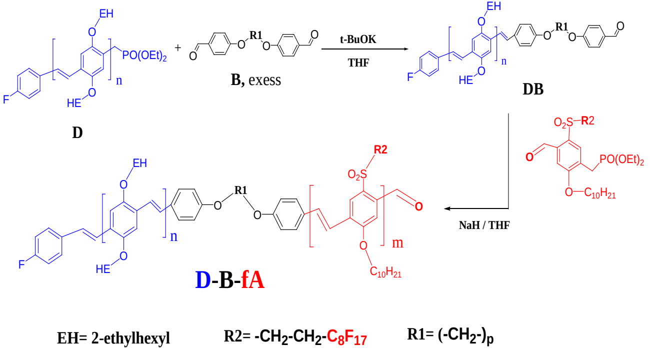


Figure 3: Synthetic scheme of the **DB** and the **DBfA** block copolymer.

2 EXPERIMENTAL

All starting materials, reagents, and solvents were purchased from commercial sources (Sigma-Aldrich or VWR/Fisher) and used without further purification unless noted otherwise. NMR spectra were obtained from a Bruker Advance 300 MHz spectrometer with TMS as the internal reference. Elemental analysis data were obtained from Atlantic Microlab Inc. UV-Vis spectra were collected on a Perkin-Elmer Lambda-1050 Spectrophotometer. Differential scanning calorimetric (DSC) and thermal gravimetric analysis (TGA) were done on a Perkin-Elmer DSC-6/TGA-6 system. Photoluminescence experiments were performed on an HORIBA Jobin-Yvon Flouromax-3 luminescence spectrofluorometer in solution (chloroform) or films. Polymer molecular weights were measured on a Viscotek GPC system using a UV-VIS absorption detector at ambient temperature, tetrahydrafuran (THF) as the solvent eluent, and Polystyrene standards for conventional calibration. Electrochemical studies were performed on a Bioanalytical (BAS) Epsilon-100W tri-electrode cell system. Three electrodes are a Platinum (Pt) working electrode, an ancillary Pt electrode, and a silver reference electrode (in a CH_3CN solution of 0.01 M $AgNO_3$ and 0.10

M tetrabutylammonium hexafluorophosphonate, TBA-HFP). Polymer samples were typically dissolved in hot solvent (typically o-Dichlorobenzene) and then coated onto Pt working electrode. The measurements were performed in 0.10 M TBA-HFP/acetonitrile solution purged with nitrogen gas. Scan rate was 100mV/s. Ferrocene (2 mM in 0.10 M TBA-HFP/CH_3CN solution) was used as internal reference standard, and its HOMO level (-4.8 eV) was used as the reference level. An AM 1.5G solar simulator with one Sun (100 mW/cm^2) intensity was used to study the efficiency of fabricated solar cell devices. A Keithley 237 source-measure unit (SMU) was used to collect the voltage-current data that were processed by computer into J-V curves.

Active polymer solutions were typically prepared by dissolve a mixture of 15mg photovoltaic polymer samples (*e.g.*, 15 mg of **DBfA** for **DBfA** cells, or 7.5mg **D** with 7.5mg **fA** for **D/fA** blend cells) mixed with 15mg acceptor $PC_{71}BM$ (so total active layer materials is 30mg) dissolved in one milliliter *o*-Dichlorobenzene (DCB).

3 RESULTS AND DISCUSSIONS

For the polymer film samples thermally annealed and dried at 150°C, the topography and phase images of atomic force microscopy (AFM) at 500 nm scales of **D/fA** blend films and **DBfA** films are shown in Figure 4. As the images in Figure 4 (b) and (d) reveals, **DBfA** films exhibit phase domain sizes similar to the polymer block sizes, but the **D/fA** blend films in images (a) and (c) did not yield any ordered domain sizes corresponding to the block sizes. X-ray diffraction (XRD) studies also confirmed more cystalline or ordered solid state morphologies of **DBfA** versus **D/fA** blends (reported separately).

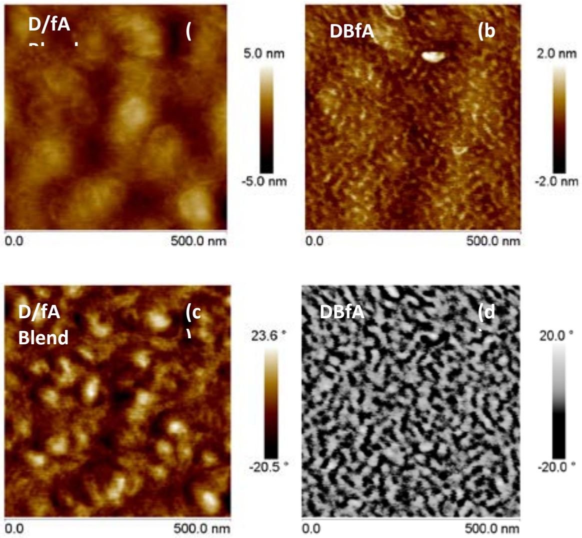


Figure 4. Atomic force microscopy (AFM) thin film topography images of (a) **D/fA** blend and (b) **DBfA** block copolymer, as well as thin film phase images of (c) **D/fA** blend and (d) **DBfA** block copolymer.

Solar cell devices were all composed of multiple stack of layers in a general sequence of ITO/PEDOT:PSS/Polymer:$PC_{70}BM$/Al. Cells made from **D/fA** and **DBfA** as donors were fabricated into solar cell devices and compared. The open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (*FF*), and power conversion efficiencies (η) of fabricated cells are listed in Table 1. A best photo J-V curve (in log scale) among a set of eight cells made of either **D/fA** blend or **DBfA** are shown in Figure 5, where the **D/fA** blend cell exhibits a best photoelectric power efficiency of about 0.002%, but a **DBfA** cell exhibits a best photoelectric power conversion efficiency of about 0.2%, *i.e.*, a two orders of magnitude efficiency improvement was achieved in a **DBfA** cell as compared to a best **D/fA** blend cell. The absolute efficiencies of the cells reported are still relatively low compared to other literature reported best organic cell values (between 5-10%) due to, for instance, the PPVs reported here have much higher energy gaps (more than 2.2 eV) compared to popular donor type polymers (such as regio-regular P3HT) that exhibits lower energy gaps (less than 2.0 eV) and better charge transport, and our cell fabrication protocols as well as polymer solid state morphologies have not yet been systematically optimized. However, higher energy gaps and fluorination of the conjugated polymer may find important applications in certain higher energy radiations, or in applications where hydrophobicity or vacuum lubrication are desired [10]. One important finding of this study is that **DBfA** block copolymer exhibited two orders of magnitude better photoelectric power conversion efficiency than the simple **D/fA** blend under identical or similar conditions. Due to the identical frontier orbital levels of **D** and **fA** in **D/fA** blend cells and in the **DBfA** cell, we therefore attribute such significant improvement of photo electric conversion efficiency mainly to the spatial regime or morphological improvement in the **DBfA** block copolymer cells as compared to the **D/fA** blend cells. Specifically, in **DBfA** cell, more photo generated excitons are able to reach the donor/acceptor interfaces and dissociate into charged carriers due to both donor and acceptor domains sizes in **DBfA** are less than the average exiton diffusion length. The charge transport in **DBfA** are also much better than in **D/fA** blend due to more ordered and bicontinuous nano morphology in **DBfA** as shown in Figure 4.

Polymers used in the cell	J_{sc} (mA/cm^2)	V_{oc} (Volt)	*FF* (%)	*PCE* (%)
D/fA blend	0.052	0.20	19	0.0020
DBfA	1.21	0.65	28	0.22

Table 1. Preliminary data of ITO/PEDOT:PSS/Polymer:PC70BM/Al bulk hetero-junction photovoltaic devices under AM 1.5G/100mW/cm^2.

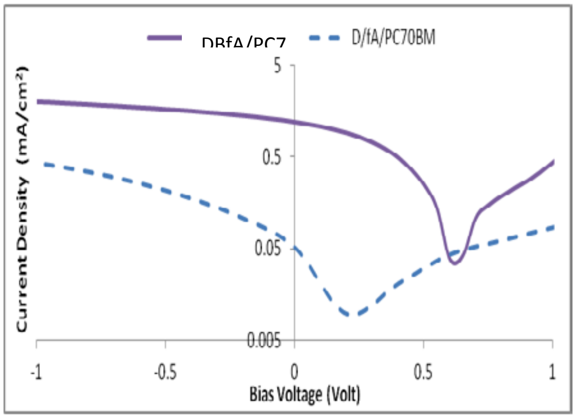


Figure 5: Preliminary photo J-V curves (at AM 1.5G, 100 mW/cm^2) of the solar cell devices made from the **D/fA** blend (dashed curve), and **DBfA** block copolymer (solid line).

4 SUMMARY

In summary, a novel **DBfA** type block copolymer systems composed of an elctron conducting acceptor type conjugated PPV block covalently connected to a hole conducting donor type conjugated PPV block **D** via a non-conjugated bridge unit **B** has been designed, synthesized, characterized, and preliminarily evaluated for optoelectronic such as photovoltaic applications. Specifically, solid state thin film studies revealed more uniform and nano-scale phase separated morphologies in **DBfA** as compared to **D/fA** blend. Preliminary and not yet optimized optoelectronic device studies revealed that, a two orders of magnitude enhancement of photoelectric power conversion efficiency was observed in solar cells made from the **DBfA** block copolymer as compared to cells made from the **D/fA** blend. This study demonstrates that, polymer optoelectronic conversion efficiencies could be significantly affected and/or improved via optimizations in solid state nano morophology alone. With further optimizations in both space and energy regimes, high efficiency and yet cost effective polymer based optoelectronic device are feasible.

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