

Photovoltaic enhancement of organic solar cells by a bridged donor-acceptor block copolymer approach

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The authors show that a photovoltaic device composed of a -donor-bridge-acceptor-bridge- type block copolymer thin film exhibits a significant performance improvement over its corresponding donor/acceptor blend (V_{oc} increased from 0.14 to 1.10 V and J_{sc} increased from 0.017 to 0.058 mA/cm²) under identical conditions, where donor is an alkyl derivatized poly-*p*-phenylenevinylene (PPV) conjugated block, acceptor is a sulfone-alkyl derivatized PPV conjugated block, and bridge is a nonconjugated and flexible unit. The authors attribute such improvement to the block copolymer intrinsic nanophase separation and molecular self-assembly that results in the reduction of the exciton and carrier losses. © 2007 American Institute of Physics. [DOI: 10.1063/1.2437100]

It has been observed that photoinduced electron-hole charge separation at the interface of an organic donor and acceptor can be orders of magnitude faster than the decay of the photogenerated exciton and the charge recombination.¹⁻⁴ These imply that high efficiency photovoltaic devices using organic donor/acceptor binary material systems are feasible. Organic solar cells have already been demonstrated using donor/acceptor bilayers² and donor/acceptor blends (also called “bulk heterojunction”).³⁻⁷ The relatively low photoelectric power conversion efficiencies of organic photovoltaics (typically less than 6%)^{6,7} can be attributed mainly to the “photon loss,” the “exciton loss,” and the “carrier loss.”^{1,8-10} As an example, the relatively small or limited donor/acceptor interface and long range exciton diffusion path in donor/acceptor (D/A) bilayer system would result in only a very small fraction of the photogenerated excitons being captured and dissociated into charged carriers. The discontinuous or isolated morphology in D/A blend could result in poor carrier transport that lead to severe carrier loss. The inappropriate frontier orbital energy levels, gaps, and offsets of the donor and acceptor pair could result in severe photon and carrier losses.⁹ All these losses must be minimized or eliminated in order to achieve high photoelectric conversion.¹⁰

One approach that can simultaneously minimize the exciton loss and carrier loss would be to develop a donor/acceptor nanophase separated and “bicontinuous” morphology, and that block copolymer systems appear ideal for this purpose.^{1,8-13} Block copolymers are known to phase separate on a size scale determined by the block length forming a variety of bicontinuous morphologies via molecular self-assembly, which can be controlled via synthesis and processing.¹¹⁻¹³ It is expected that when the phase separation is on the order of the average exciton diffusion length [e.g., about 10 nm for polyphenylene vinylene (PPV)], the exciton capture and charge dissociation can be maximized. Addition-

ally, the bicontinuous phases may lead to quasiballistic carrier transport. Recently, we designed and synthesized a processable -donor-bridge-acceptor-bridge- (DBAB) type of block copolymer as shown on top of Fig. 1.¹³ In this system, the flexible and wide band gap bridge unit (B) not only retard electron-hole recombination between the donor and acceptor blocks but also help the rigid donor and acceptor segments to self-assemble to form potential “secondary” and “tertiary” structures that are very desirable for photovoltaic functions.⁸

For comparison, the D/A blend samples were also prepared with same mole ratio as in the block. 1,2-dichlorobenzene was used as the solvent for all polymer processing. The concentrations of the blend and block solutions prepared for device fabrication were (by w/v) 0.56% acceptor/1.4% donor for the blend and 0.54% for the block. Indium tin oxide ITO coated glass slides of 1.5 × 1.5 cm² were used as the transparent conducting positive electrode. As shown as inset in Fig. 1, the ITO layer was partially etched and its surface cleaned in an ultrasonic bath with acetone and isopropanol as cleaning solvents. On top of the ITO substrate, poly(ethylene-dioxythiophene) doped with polystyrenesulphonic acid (PEDOT:PSS) (purchased from the Bayer AG) was spin coated from an aqueous solution (0.5 w/v %, PEDOT: PSS 2:3), giving an average thickness of 80 nm. The PEDOT:PSS layer (which has been known to facilitate hole collection at ITO electrode)¹ was then dried in vacuum for at least 3 h at 60 °C. The active PV polymer layer was then spin coated to about 100 nm thick. During spin coating, the block copolymer (DBAB) solution was heated roughly between 90 and 100 °C and the blend (D/A) was heated between 120 and 130 °C to get good film quality. The dried film slides were brought into the metal electrode evaporation chamber (BOC-306), where the metal was evaporated onto the substrate in high vacuum (<10⁻⁶ Torr). A metal mask was used to define the electrode size of the deposited cell. A total of three photovoltaic cells were simultaneously fabricated and tested at the same time on one ITO slide, and each cell is patterned to be 0.3 × 0.4 cm² size. All cells shared the same ITO layer as their common positive

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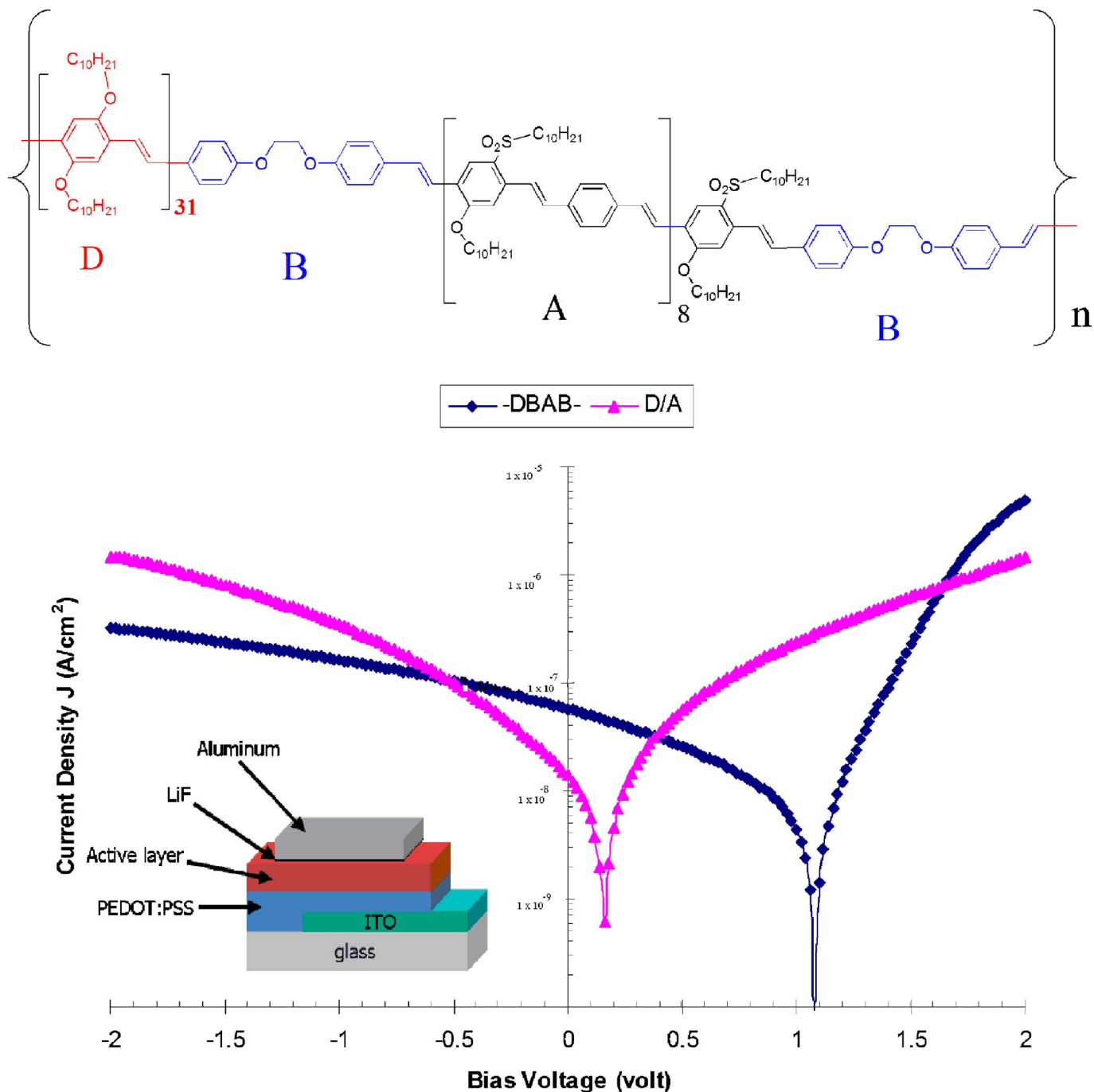


FIG. 1. (Color online) Chemical structure of the $(DBA_2B)_n$ block copolymer (top); a general scheme of the cell (inset) and J - V curves (in absolute log scales) of a best D/A blend (triangle) and DBAB-block copolymer (diamond) thin film photovoltaic devices under 1.5 AM one sun irradiation.

electrode. Before the metal electrode evaporation, LiF (which has been known to facilitate the electron collection at organic/metal electrode)¹ was first evaporated to 0.6 nm, followed by Al to a thickness of 100 nm.

Figure 1 shows the best J - V curves of a D/A blend (triangles) and a $(DBA_2B)_n$ block copolymer (diamonds) PV devices. The J - V data exhibited a much improved photovoltaic performance in the block copolymer versus the corresponding polymer blends (1.10 vs 0.14 V, and 0.058 vs 0.017 mA/cm²). Figure 2 is our recent x-ray diffraction (XRD) data that revealed some interesting molecular self-assembled domains of the block copolymer which were absent in the D/A₂ blend. The data also revealed that such molecular self-assembly domain would grow even with

simple thermal annealing. Figure 3 shows a molecular packing pattern together with the crystalline "unit cell" parameters: $d_1=24.4$ Å (with second order of $d_1=11.1$ Å), $d_2=7.4$ Å, and $d_3=4.4$ Å. The parameters are obtained from XRD, in-plane and out-of-plane grazing incidence x-ray diffraction, and atomic force microscopy images (the measured d parameters are also confirmed well with molecular parameter calculations) to be reported separately.¹⁴ Since the frontier orbital energy levels [lowest unoccupied molecular orbital (LUMO)/highest occupied molecular orbital (HOMO): $-2.91/-5.15$ V for the donor and $-3.07/-5.52$ V for the acceptor]¹³ and offsets are the same in both cases, we therefore attributed the significant optoelectronic improvement of the block copolymers over the blends to the follow-

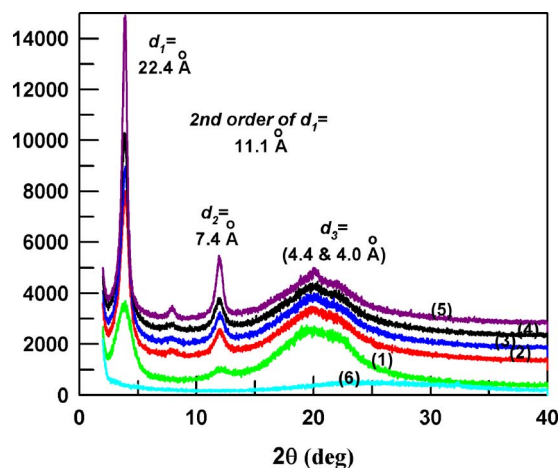


FIG. 2. (Color online) XRD data of (DBA₂B)_n block copolymer film (1) before annealing and after annealing at 110 °C for (2) 1 h, (3) 3 h, and (4) 5 h and (5) after annealing at 140 °C for 5 h. Substrate XRD (6) is also shown.

ing: In the blend, the D/A₂ phase separation was on the order of several hundred nanometers,¹³ while in the block copolymer, the D/A₂ phase separation are on the order of around 20 nm (D phase) and 10 nm (A₂ phase).¹³ This means a significant reduction of exciton loss in the block copolymers as typical organic exciton diffusion lengths are on the order of 5–50 nm.¹ Additionally, the more ordered D/A crystalline domains in the block copolymer also improved charge carrier transport. It is known that charge transport can be dramatically improved in a self-assembled or crystalline polymer domain.¹⁵ The 1.10 V open circuit voltage is, in fact, very impressive among organic/polymeric solar cells. However, the measured V_{oc} (reflecting the donor/acceptor quasi-Fermi level difference) was still less than the maximum achievable V_{oc} , which is expected to be the difference of the donor HOMO and acceptor LUMO (5.15 – 3.07 = 2.08 V).¹⁶ Additionally, the short circuit current

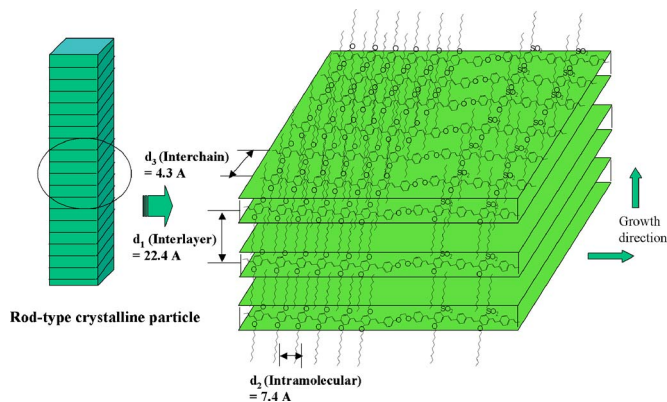


FIG. 3. (Color online) (DBA₂B)_n block copolymer self-assembly domains after annealing at 140 °C for 5 h.

density (0.017 mA/cm² for blend and 0.058 mA/cm² for the block) and fill factors (about 0.20 in both cases) are very low, and these cause an overall power conversion efficiency well below 1%. Both the lower than expected currents and voltages may be attributed to a number of factors, such as severe photon loss due to poor materials energy gap match to sunlight (E_g of 2.24 and 2.45 eV for D and A₂ blocks, respectively,¹³ far away from most intense sunlight at 1.3–1.6 eV). It is also known that the open circuit voltages and short circuit currents in organic cells are very sensitive to a number of factors including materials morphology, photo-oxidation, organic-metal interface treatment (e.g., over 0.2 V drop in an organic/metal interface is quite common), room temperature thermal leakage currents, disorder and defects, etc.^{1–10}

In summary, this study shows that the photovoltaic performance of a -DBAB- type block copolymer was much improved than in a corresponding D/A simple blend. This may be attributed to the intrinsic nanoscale phase separation and molecular self-assembly in the block copolymer that minimizes the exciton and carrier losses.

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