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Parallel-like Bulk Heterojunction Polymer Solar Cells

Liqiang Yang,[†] Huaxing Zhou,[‡] Samuel C. Price,[‡] and Wei You*,[†,‡]

[†]Curriculum in Applied Sciences and Engineering, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3287, United States

[‡]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Here we demonstrate a conceptually new approach, the parallel-like bulk heterojunction (PBHJ), which maintains the simple device configuration and low-cost processing of single-junction BHJ cells while inheriting the major benefit of incorporating multiple polymers in tandem cells. In this PBHJ, free charge carriers travel through their corresponding donor-polymer-linked channels and fullerene-enriched domain to the electrodes, equivalent to a parallel-like connection. The short-circuit current (J_{sc}) of the PBHJ solar cell is nearly identical to the sum of those of the individual "subcells", while the open-circuit voltage (V_{oc}) is between those of the "subcells". Preliminary optimization of the PBHJ devices gives improvements of up to 40% in J_{sc} and 30% in overall efficiency (η) in comparison with single-junction BHJ devices.

The first prerequisite for achieving high efficiency in any type of solar cell is that the solar radiation is absorbed efficiently by the active layer. In a typical bulk-heterojunction (BHJ) polymer solar cell that employs a conjugated polymer as a p-type semiconductor and a fullerene derivative as the n-type semiconductor, the polymer is the major light absorber. However, the intrinsic narrow absorption width of such conjugated polymers, usually with a full width at half-maximum (fwhm) on the order of 200 nm,[1] can overlap with only a small fraction of the solar spectrum. This inefficient light absorption leads to noticeably lower current (usually ~10 mA/cm^2) in comparison with other types of high-efficiency solar cells (e.g., over 40 mA/cm^2 in crystalline Si solar cells), which limits the further improvement on the efficiency of polymer solar cells. Therefore, intensive research efforts have been devoted to the development of new p-type conjugated polymers with better absorption match to the solar spectrum and the pursuit of non-fullerene-based n-type materials that absorb in a complementary region of the solar spectrum.[2] Unfortunately, only incremental progress has been made on either front.

Alternatively, one simple approach to increase the absorption breadth of a polymer solar cell is to blend multiple donor components with different (ideally complementary) absorption features into a BHJ configuration with phenyl-C$_{61}$-butyric acid methyl ester (PCBM) as the electron acceptor. Recently, this simple method has been successfully demonstrated by the addition of a small fraction (1−20%) of dye molecules or a small-band-gap polymer into the archetypical poly(3-hexylthiophene) (P3HT)/PCBM BHJ cells.[3,4] In these ternary- or even quaternary-blend systems, both the dye molecules and the small-band-gap polymer act as "guest" sensitizers to improve the light absorption of the "host" P3HT-based BHJ. It was believed that additional excitons generated by these sensitizers would dissociate at their interface with PCBM and that these extra charge carriers (holes) would be able to transport to the anode via the dominant P3HT phase. This would require these "guest" sensitizers to have their HOMO and LUMO levels in between the corresponding energy levels of the P3HT and those of the PCBM. Such a cascade energy level alignment is crucial to prevent possible energy transfer among the components in the BHJ blend and to ensure efficient exciton splitting and charge transport to the electrodes. However, this imposes stringent requirements on the selection of appropriate materials, thereby limiting the scope and application of this multiblend approach. In contrast, tandem cells offer a more

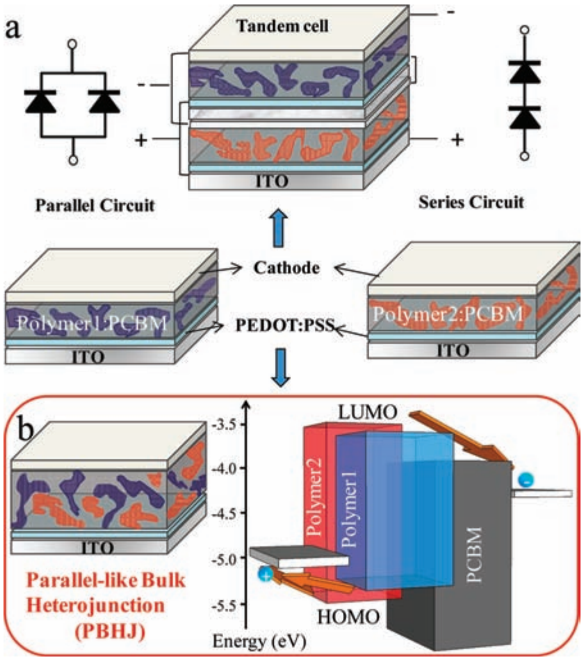

Figure 1. (a) Schematic structure of polymer tandem cells. Intercellular layers are inserted between subcells that act either as recombination centers in series tandem cells or as optical spacers in parallel ones. (b) Schematic structure and energy diagram of PBHJ devices.

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effective approach to broaden the light absorption and enhance its utilization.[5] This is because tandem cells stack multiple subcells in either series or parallel connections, so each subcell incorporating a particular polymer only needs to absorb a specific range of the solar spectrum (Figure 1a).[6−9] The subcells work individually without any energy or charge transfer between them, significantly reducing the thermalization losses in the multiblend system.[4] Furthermore, this important feature of tandem cells—independent working subcells—essentially lifts the restrictions on the design and selection of materials in the multiblend system, allowing versatile selections of materials and device designs. However, tandem cells are technically challenging. Instead of dealing a sandwiched electrode/active layer/electrode structure with two interfaces as in a typical BHJ solar cell, one must carefully design and optimize additional intercellular layers between the subcells. These intercellular layers not only create more interfaces that must be optimized to reach the designed efficiency but also reduce the amount of transmitted light, let alone the added cost of fabrication.[10−12]

Our new design, the parallel-like bulk heterojunction (PBHJ) solar cell, overcomes the aforementioned technical challenges and increased cost associated with tandem cells, since it maintains the fundamental structure of a single-junction BHJ cell having two electrodes sandwiching the active layer (Figure 1b). Meanwhile, the PBHJ bears the advantage of conventional multiblend systems, namely, an increased absorption width. Importantly, in comparison with a conventional multiblend system, which can incorporate only a small quantity of additional donor molecules/polymers as sensitizers, PBHJ solar cells can employ two or more polymers with different band gaps at any composition, regardless of their HOMO or LUMO levels. In our PBHJ device incorporating two donor polymers and PCBM as the acceptor (see below), excitons generated in an individual donor polymer would migrate to the respective polymer/PCBM interface and then dissociate into free electrons and holes, as would occur in a conventional BHJ cell. Electrons would be transported through the PCBM-enriched domain prior to their collection by the cathode. Meanwhile, besides a possible charge transfer at the polymer/polymer interface, holes generated from different donor polymers would mainly travel through their corresponding polymer-linked channels to the anode. Thus, all free charge carriers generated from two donor polymers and PCBM (i.e., two polymer/PCBM blends) can be collected by the same cathode and anode, which indicates that this structure is equivalent to a parallel connection of two single BHJ cells. The PBHJ cell essentially merges two (or more) single-junction cells into one integrated design that combines the simple device structure (and low fabrication cost) of single-junction BHJ cells *and* the much improved light harvesting of tandem cells.

As a proof-of-concept, we chose two groups of polymers for use in constructing PBHJ devices: (1) poly(benzodithiophene−dithienylbenzotriazole) (TAZ)[13] and poly(benzodithiophene−dithienylbenzothiadiazole) (DTBT),[14] and (2) poly(benzodithiophene−dithienyldifluorobenzothiadiazole) (DTffBT)[14] and poly(benzodithiophene−dithienylthiadiazolopyridine) (DTPyT).[15] Each group contains two polymers having different band gaps and HOMO levels (Figure 2). Two PBHJ devices with ~100 nm thick active layers were then fabricated, consisting of TAZ/DTBT/PCBM (0.5:0.5:1 weight ratio) and DTffBT/DTPyT/PCBM (0.5:0.5:1 weight ratio), respectively. For the purpose of comparison, we also fabricated four conventional single-junction BHJ cells based on binary 1:1 polymer/PCBM blends with ~50 nm thick active layers. These four single-junction BHJ cells contain approximately same quantity of individual components as in the corresponding PBHJ cells with 100 nm thick active layers, conceptually similar to the subcells in tandem cells. To avoid confusion, quotation marks have been used for "subcells" when this term refers to these 50 nm thick single-junction BHJ cells. The first notable feature is that the absorption spectra of these PBHJ cells are essentially linear combinations of the spectra of their two "subcells" (Figure 3a,b), since PBHJ cells have no interfacial layers that could undesirably reflect or absorb the incident light and thereby reduce the total amount of light absorbed by the active layer. Because two polymers having different band gaps

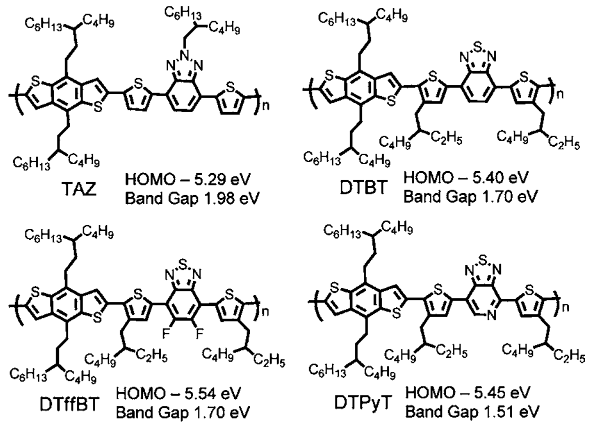

Figure 2. Chemical structures, HOMO energy levels, and band gaps of TAZ, DTBT, DTffBT, and DTPyT.

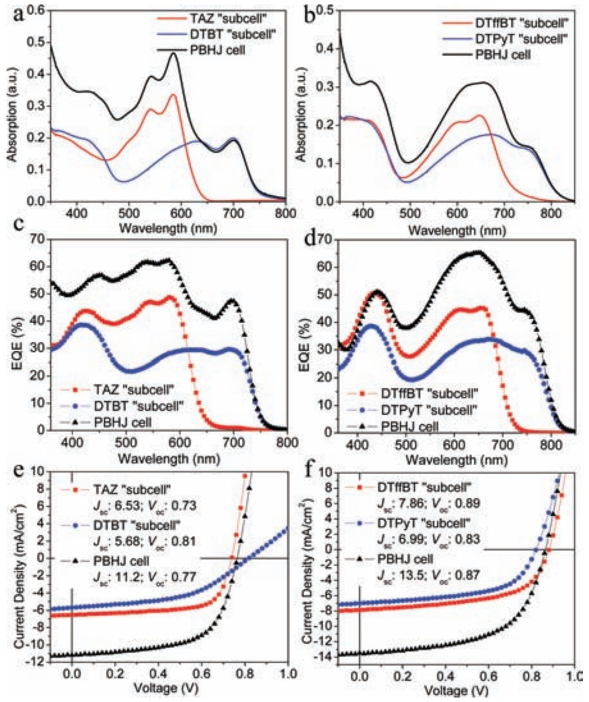

Figure 3. (a,b) Absorption spectra of the PBHJ devices and their "subcells" based on (a) TAZ/DTBT and (b) DTffBT/DTPyT. (c,d) EQEs of the PBHJ devices and their "subcells" based on (c) TAZ/DTBT and (d) DTffBT/DTPyT. (e,f) Characteristic *J*−*V* curves of the PBHJ devices and their "subcells" based on (e) TAZ/DTBT and (f) DTffBT/DTPyT.

and absorption behavior are employed, these PBHJ cells exhibit much broader absorption width in comparison with the large-band-gap polymer-based “subcells” and significantly increased absorption strength in the low-wavelength regions relative to the small-band-gap polymer-based “subcells”.

The most interesting feature of these PBHJ devices is their external quantum efficiency (EQE) spectra. As shown in Figure 3 c,d, the EQE spectra of the PBHJ devices are approximately the sum of those of the individual “subcells” in the short-wavelength range, where both donor polymers contribute to the formation of electron/hole pairs (and thereby the photocurrent). This indicates that most of the free charge carriers generated in each “subcell” of the PBHJ device are successfully collected by the respective electrodes. Interestingly, in the long-wavelength range, where the larger-band-gap polymer no longer absorbs photons and thereby contributes zero current, the EQE of the PBHJ device is higher than that of the smaller-band-gap “subcell”. For example, the EQEs of the DTBT and DTPyT “subcells” are ~30% at wavelengths of 700 and 750 nm, respectively, whereas the EQEs of the TAZ/DTBT- and DTffBT/DTPyT-based PBHJ cells are over 40% at the corresponding wavelengths. It is highly possible that the large-band-gap polymer with high mobility can serve as an additional charge transport channel in the PBHJ device, thereby facilitating the charge transport and consequently enhancing the internal quantum efficiency (IQE) in the lower-band-gap absorption range. Collectively, much-enhanced EQE spectra (over 40% across a width of over 400 nm) were observed in both of our PBHJ devices. As a result, the J_{sc} values of the PBHJ devices are significantly increased and almost identical to the sum of those for the two single “subcells” (Figure 3e,f). On the other hand, the V_{oc} values of the PBHJ devices are between those measured for the individual “subcells”, which establishes that PBHJ solar cells are different from conventional multiblend systems, where the observed V_{oc} is pinned to the smallest V_{oc} of the corresponding binary blend.[4,16] This is the case because in conventional multiblend systems, the dominant hole transport and collection occurs through the donor component with the highest HOMO level. This highest HOMO level therefore determines the observed V_{oc} of the multiblend system, independent of the origin of photocurrent generation.[4] However, in our PBHJ devices, neither the energy transfer nor the charge transfer between different donor materials is dominant. Holes generated from individual donor polymers mainly travel through their corresponding polymer-connected channel to the anode, similar to the parallel connection of two single-junction BHJ cells. Thus, the observed J_{sc} combines those from each “subcell”, whereas the V_{oc} is between those of the single “subcells”, both of which clearly indicate a parallel connection.[17−20]

To investigate further the individual contributions from each donor polymer in the PBHJ device and to identify the optimal device conditions (e.g., blending ratio and film thickness), we varied the composition of the two related donors for each PBHJ device and also optimized the film thicknesses. Figure 4a,b summarizes the EQE spectra of the PBHJ devices whose donor compositions were systematically varied, together with those of the single-junction binary BHJ devices with the optimal thickness for reference. In the PBHJ device based on TAZ/DTBT, as the proportion of TAZ decreases, the EQE in the region between 450 and 600 nm is attenuated (Figure 4a). However, this does not lead to a decreased J_{sc} (Figure 4c), since the correspondingly increased proportion of DTBT results in an increased EQE response from 600 to 750 nm that compensates for the decrease in EQE in the low-wavelength region. As a result, the J_{sc} values for the PBHJ devices with all compositions (Table 1, entries 2−4) are significantly improved relative to the binary BHJ devices (Table 1, entries 1 and 5). Similar composition-dependent behavior is also observed in the EQE spectra of the PBHJ devices consisting of the donor polymers DTffBT and DTPyT (Figure 4b), resulting in enhanced J_{sc} for all PBHJ cells (Table 1, entries 7−9). Unlike conventional multiblend systems, which can employ only small amounts of additional donor materials as sensitizers to improve the J_{sc},[3,4] our PBHJ devices with any composition of the two donor polymers exhibit enhanced J_{sc} (Figure 4c,d), regardless of the various HOMO levels of the donor polymers. This is additional evidence for a parallel-like junction in these PBHJ devices.

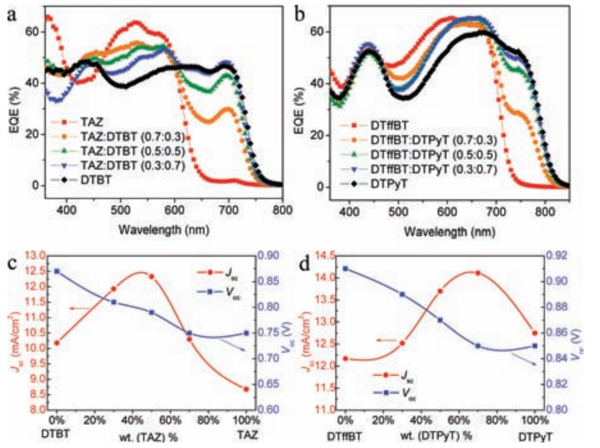

Figure 4. (a,b) EQEs of the PBHJ devices with different compositions of (a) TAZ/DTBT and (b) DTffBT/DTPyT. (c,d) J_{sc} and V_{oc} for the PBHJ devices as functions of the amounts of (c) TAZ in DTBT and (d) DTPyT in DTffBT.

Table 1. Photovoltaic Performances of Devices with Optimized Thicknesses[a]

Entry	*Cells*	*Thickness* (nm)	J_{sc} (mA/cm^2)	V_{oc} (V)	*FF* (%)	η (%)
1	TAZ:DTBT 1:0	96	8.68	0.75	62.4	4.06
2	TAZ:DTBT 0.7:0.3	102	10.3	0.75	62.0	4.79
3	TAZ:DTBT 0.5:0.5	111	12.3	0.79	59.8	5.80
4	TAZ:DTBT 0.3:0.7	79	11.9	0.81	60.8	5.88
5	TAZ:DTBT 0:1	88	10.2	0.87	49.6	4.39
6	DTffBT:DTPyT 1:0	138	12.2	0.91	56.5	6.26
7	DTffBT:DTPyT 0.7:0.3	84	12.5	0.89	59.3	6.60
8	DTffBT:DTPyT 0.5:0.5	94	13.7	0.87	58.9	7.02
9	DTffBT:DTPyT 0.3:0.7	81	14.1	0.85	56.5	6.78
10	DTffBT:DTPyT 0:1	89	12.8	0.85	58.1	6.30

[a] All polymers were blended with PCBM at a weight ratio of 1:1 in dichlorobenzene.

In particular, the PBHJ device consisting of a 50:50 weight ratio of TAZ and DTBT showed the highest J_{sc} of 12.3 mA/cm^2, which is about 40% and 20% higher than those of TAZ-based (8.68 mA/cm^2) and DTBT-based (10.2 mA/cm^2) binary BHJ devices, respectively. Meanwhile, the highest J_{sc} of the DTffBT/DTPyT-based PBHJ solar cell is 14.1 mA/cm^2, which is about 16% and 10% higher than those of binary BHJ devices based on DTffBT (12.2 mA/cm^2) and DTPyT (12.8 mA/cm^2), respectively. Interestingly, unlike the TAZ/DTBT-based PBHJ cells, where the highest J_{sc} appears at the 50:50 ratio, the highest J_{sc} in the DTffBT/DTPyT-based PBHJ devices was achieved with the device consisting of 30% DTffBT and 70% DTPyT (Figure 4d and Table 1, entry 9), which indicates that the optimum composition of a PBHJ device depends on the optical and electronic properties of the constituent polymers, such as the overlap of the EQE spectra of the individual polymer-based binary BHJ cells. On the other hand, as the proportion of the donor polymer exhibiting the higher V_{oc} in its single-junction BHJ cell increases, the observed V_{oc} of the related PBHJ solar cell shows a continuous improvement from 0.75 to 0.87 V in the TAZ/DTBT system and 0.85 to 0.91 V in the DTffBT/DTPyT system(Figure 4c,d and Table 1). This further confirms that the PBHJ device belongs to the parallel connection of two single-junction BHJ cells, since the voltage of a parallel circuit is the weighted average of the individual voltages of these subcells. Because of the much-improved J_{sc}, all of the PBHJ devices (though with different compositions) exhibit increased overall efficiencies in comparison with their corresponding binary BHJ devices (Table 1). However, we note that the highest efficiency observed in these two exemplary PBHJ systems is not from the PBHJ device with highest J_{sc}, since the overall efficiency of solar cells is also affected by the V_{oc} and the fill factor (FF). In these two specific PBHJ systems, the TAZ/DTBT PBHJ system exhibits the highest efficiency of 5.88% at a composition of 30% TAZ and 70% DTBT, whereas the DTffBT/DTPyT PBHJ system with an equivalent proportion of DTffBT and DTPyT offers the best efficiency of over 7%. The results from our PBHJ devices were alluded to in an earlier work,[21] where Thompson et al. demonstrated tunable V_{oc} in their ternary blend BHJ cells with P3HT as the donor but various fullerene derivatives as the acceptors. It is likely that their discovery also belongs to the PBHJ concept.

In summary, a conceptually new device configuration, the parallel-like bulk heterojunction (PBHJ), has been proposed and successfully demonstrated with two prototypical systems. PBHJ eliminates the need for careful design and precise control of the interfacial layers in tandem cells, thereby significantly reducing the complexity of the device fabrication. More importantly, unlike conventional multiblend systems, which can incorporate only small amounts of additional donor materials as sensitizers, PBHJ enables the effective use of multiple donors with much improved light absorption and conversion. Thus, PBHJ combines the advantages of both tandem cells and conventional multiblends. In the two prototypical systems, the J_{sc} of the PBHJ device was up to 40% larger than that of the optimum single-junction binary BHJ devices, resulting in noticeably enhanced overall efficiency of the PBHJ device. Though the detailed working mechanism and specific rationale in pairing multiple polymers in PBHJs remain to be further investigated, we believe that PBHJs open a new avenue to accelerate improvement in the efficiency of polymer solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, UV−vis absorption spectra of all polymers, and *J*−*V* curves for all of the devices. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

wyou@unc.edu

Notes

The authors declare no competing financial interest.

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