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Efficient Solar Cells from Layered Nanostructures of Donor and Acceptor Conjugated Polymers

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Efficient photoinduced charge transfer and separation accompanied by large photovoltaic power conversion efficiencies were observed in layered nanostructures of acceptor poly(benzimidazobenzophenanthroline ladder) (BBL) and donor poly(*p*-phenylenevinylene) (PPV) or poly(2-methoxy-5(2′-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH−PPV) at practical sunlight intensities. Nearly complete quenching of photoluminescence and large shortening of fluorescence decay lifetimes of donors PPV and MEH−PPV evidenced fast efficient photoinduced charge transfer and separation in PPV/BBL and MEH−PPV/BBL bilayers. ITO/PPV(60 nm)/BBL(60 nm)/Al photovoltaic cells had an external power conversion efficiency of 1.5% and 4.6% under AM1.5 white light illumination intensities of 80 and 1 mW/cm^2, respectively, in ambient air. Under single-wavelength (460 nm) 0.5 mW/cm^2 illumination, the same PPV/BBL diodes had a power conversion efficiency of 5.4% and incident photon-to-current conversion efficiency of 62%. ITO/MEH−PPV(60 nm)/BBL(60 nm)/Al cells had slightly reduced photovoltaic properties, for example 1.1% power conversion efficiency at 80 mW/cm^2 AM1.5 white light illumination, due primarily to the red shift of MEH−PPV absorption band as revealed by the photoaction spectra of the diodes. Studies of donor(PPV)/acceptor polymer diodes with a series of 5 acceptor polymer semiconductors having electron affinities (LUMO levels) of 2.7−4.0 eV showed that high electron affinity was essential to efficient photoinduced charge transfer and large photovoltaic power conversion efficiencies. These results demonstrate that efficient photovoltaic cells can be realized in layered donor/acceptor conjugated polymer semiconductors having complementary electronic and optical properties.

Introduction

Organic- and polymer-based solar cells are currently of much research interest as potential low cost approaches to efficient solar energy conversion.[1−10] Because the absorption of light by a molecular semiconductor produces excitons or strongly bound electron−hole pairs,[1d,11] rather than free charge carriers, a single-layer conventional Schottky-barrier photovoltaic cell of the type metal1/molecular semiconductor/metal2 usually has very poor charge collection and power conversion efficiencies.[1,8] Photoinduced electron transfer between donor (D) and acceptor (A) molecules with significantly different HOMO/LUMO levels can efficiently dissociate excitons generated in either, providing a general strategy to more efficient organic photovoltaic cells.[1−10]

Extensive studies of polymer-based photovoltaic cells have focused largely on blends or nanocomposites of donor polymer with acceptor materials including fullerenes,[3] CdSe nanocrystals,[4] TiO$_2$ nanoparticles,[5] carbon nanotubes, acceptor polymers,[6] and acceptor small molecules.[7] Photovoltaic cells made from polymer−fullerene blends were recently shown to have power conversion efficiency as high as 2−3% under AM1.5 white light illumination (80−100 mW/cm^2).[3] Composites of poly(3-hexylthiophene) and CdSe nanorods were also

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recently used to demonstrate photovoltaic power conversion efficiency as high as 1.7% under AM1.5 white light illumination at 100 mW/cm^2.[4] A potential problem with this strategy is that charge carrier mobilities of polymer blends are usually significantly reduced compared to the component materials.[12] Controlling the polymer blend morphology to achieve the ideal bicontinuous interpenetrating network of acceptor and donor phases on the 10−50 nm length scale is also currently difficult.[3,13] Block conjugated copolymer assemblies with covalently tethered[14a] or physically sequestered[14b] fullerenes, and homopolymers with tethered fullerenes, and alternating donor−acceptor copolymers[15] are being explored as alternative approaches to address some of these problems.

The layered donor/acceptor heterojunction is an attractive architecture for achieving efficient polymer solar cells if suitable donor and acceptor polymer semiconductors having complementary electronic and optical properties can be developed.[1e,9,11b] Photogenerated electrons and holes are largely confined to the acceptor and donor sides of the interface, respectively, facilitating facile transport to collecting electrodes and minimizing charge recombination. Crystallinity or structural order, and hence high charge carrier mobilities, can be maintained in the bilayer thin films as in single layers of the component polymers. Essential Ohmic contact at the polymer/metal interfaces requires that the HOMO level of the donor polymer match the anode electrode work function such as indium tin oxide (ITO, $\Phi = 4.8$ eV) and that the LUMO level of the acceptor polymer match the cathode electrode work function such as aluminum (Al, $\Phi = 4.3$ eV). However, very few studies of the photovoltaic properties of polymer/polymer donor/acceptor heterojunctions have been reported due largely to the current lack of acceptor conjugated polymers with high electron affinities.[9,16]

In this paper, we report studies of photoinduced electron transfer and photovoltaic properties of a series of layered donor/acceptor (D/A) thin films of conjugated polymer semiconductors. Bilayer D/A polymer/polymer heterojunctions were prepared from donor poly(*p*-phenylenevinylene) (PPV) and poly(2-methoxy-5(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH−PPV) and a series of 5 acceptor conjugated polymers having electron affinities (LUMO levels) in the 2.7−4.0 eV range. The molecular structures of these polymers and a schematic of the photovoltaic cells are shown in Figure 1. It was found that nanoscale bilayers of high electron affinity acceptor poly(benzimidazobenzophenanthroline ladder) (BBL, EA = 4.0 eV) with donor PPV or MEH−PPV exhibited fast and efficient photoinduced charge transfer and large photovoltaic power conversion efficiencies under AM1.5 white light illumination. We thus show that efficient photovoltaic cells can be developed from layered donor/acceptor nanoscale thin films of suitable conjugated polymer semiconductors.

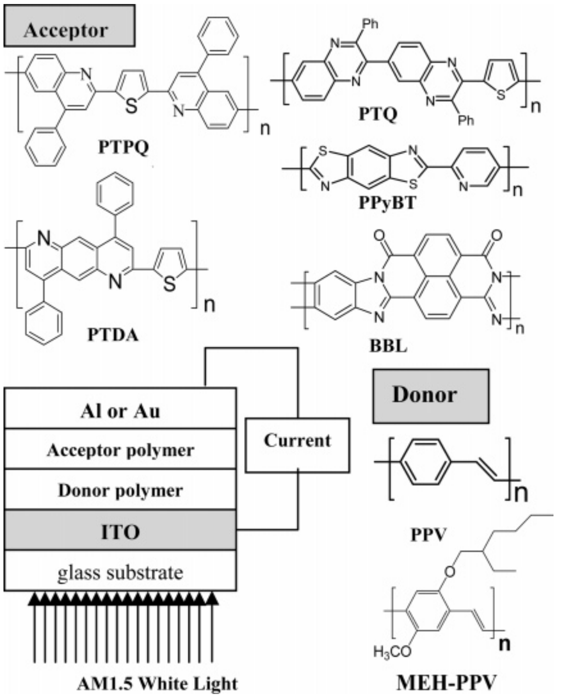

Figure 1. Molecular structures of the conjugated polymers investigated and the schematic cross section of the layered donor/acceptor polymer photovoltaic cells.

The acceptor conjugated polymers (Figure 1) we investigated combine high-temperature stability (glass transition temperature $T_g > 300-500$ °C) with known photochemical and electrochemical stability,[17] good photoconductive properties,[18] n-type dopability,[19] and solution processibility.[20] In the case of BBL, its electrochemically estimated electron affinity (LUMO level) of 4.0−4.4 eV (depending on whether the saturated calomel electrode [SCE] energy level relative to vacuum is taken to be −4.4 or −4.8 eV)[19] compares favorably with that of fullerene C_{60} (EA = 3.9−4.1 eV)[2b] which has been extensively studied as the acceptor in polymer blend photovoltaic cells.[3] In a preliminary communication we found that PPV/BBL bilayers in which BBL thin films were prepared from BBL−$GaCl_3$ complexes in nitromethane solutions[20] showed promising photovoltaic

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properties.[9] Our group recently discovered that highly crystalline BBL thin films with high field-effect mobility of electrons can be processed from methanesulfonic acid solutions.[12] Here, we have exploited these recent advances in acceptor (n-type) conjugated polymers to fabricate and investigate layered donor/acceptor polymer photovoltaic cells.

Experimental Section

Materials. Poly(2,2′-(2,5-thiopheneyl)-6,6′-bis(4-phenylquinoline)) (PTPQ), poly(2,7-(2,5-thiopheneyl)-4,9-diphenyl-1,6-anthrazoline) (PTDA), poly(2,2′-(thiophene-2,5-diyl)-6,6′-bis(3-phenylenequinoxaline)) (PTQx), and poly(2,5-pyridine-ylbenzobisthiazole) (PPyBT) used in this study were synthesized in our laboratory. Their synthesis, characterization, electrochemical, optical, and electroluminescent properties were previously reported.[19,21,22] BBL was also synthesized in our laboratory and had an intrinsic viscosity of 32 dL/g in methanesulfonic acid (MSA) at 30 °C.[23] The sulfonium precursor of PPV in $\sim$1 wt % methanol solution and poly(2-methoxy-5(2′-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH−PPV, M_w $\sim$85 000) were purchased from Lark Enterprise (Webster, MA) and American Dye Sources, Inc. (Quebec, Canada), respectively. All solvents were of spectroscopic grade and were used as received.

Photophysics. Optical absorption spectra were obtained on a Lambda-900 UV/vis/near-IR spectrophotometer (Perkin-Elmer). Photoluminescence (PL) studies were carried out on a PTI QM-2001-4 spectrofluorometer (PTI Inc., Ontario, Canada). The PL spectra were recorded by using both front and inverted faces geometry.[24a] The film thicknesses were measured by an Alpha Step profilometer (model 500, KLA Tencor, San Jose, CA) with an accuracy of ±1 nm and confirmed by an optical absorption coefficient technique.

Time-resolved PL decay measurements were performed by using the time-correlated single-photon counting technique.[24] The excitation system consisted of a cavity pumped dye laser (Coherent model 703D) circulating rhodamine 6G, synchronously pumped by a mode-locked frequency-doubled Nd:YAG laser (Quantronics model 416). The dye laser pulses were typically 10 ps duration at a repetition rate of 38 MHz, and the samples were excited at 425 nm in both PPV and MEH−PPV systems. The PL decay was detected at the PL emission peak of PPV at 516 nm and MEH−PPV at 590 nm.

Fabrication and Characterization of Photovoltaic Cells. The layered photovoltaic devices were fabricated by sequential spin coating of the polymer layers onto cleaned indium−tin-oxide (ITO) coated glass substrates (Delta Technologies, Ltd., Stillwater, MN; sheet resistance = 8−12 Ω/□). PPV thin films were spin coated onto cleaned ITO from a sulfonium precursor solution in methanol, followed by thermal conversion in a vacuum at 250 °C for 1.5 h.[9,22] MEH−PPV thin films were spin coated from a 0.6 wt % solution in chloroform onto ITO and dried at 60 °C in a vacuum for 8 h. On top of the resulting PPV (or MEH−PPV) thin film a layer of BBL was spin coated from its 0.5 wt % solution in MSA and immersed in deionized water for 12−14 h to remove the MSA solvent. Thin films of PTPQ, PTDA, PTQx, and PPyBT were each spin-coated from their 0.5 wt % solution in formic acid and dried at 60 °C in a vacuum for 8 h. The bilayered thin films were dried in a vacuum at 60 °C for 10 h before thermal deposition of the metal electrode. It is noteworthy to mention that the donors PPV and MEH−PPV neither dissolve nor swell in formic acid or MSA. Similarly, BBL and other acceptor polymers neither dissolve nor swell in CHCl$_3$ or methanol. Thus, good layered thin films were obtained from these D/A polymers. Finally, a 100−120 nm thick metal electrode (aluminum or gold) layer was thermally deposited under high vacuum ($\sim 3 \times 10^{-6}$ Torr) onto the resulting polymer layers to form an active device area of 0.2 cm^2 (5 mm diameter). Some photovoltaic devices of the type ITO/PPV/BBL/Al and ITO/MEH−PPV/BBL/Al were annealed for 30 min in a vacuum furnace prior to aluminum deposition.

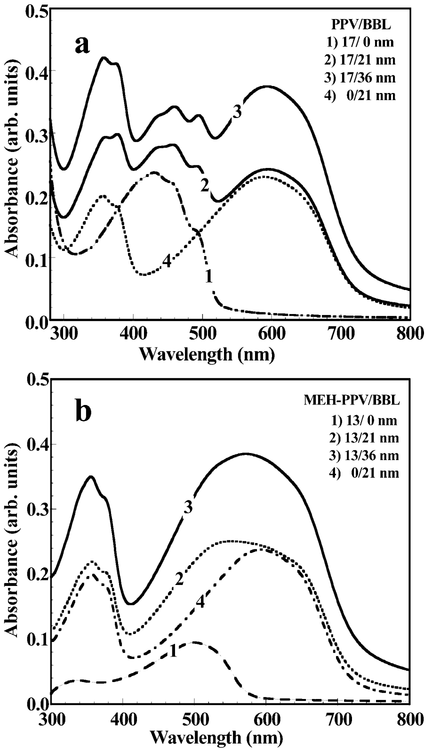

Figure 2. Optical absorption spectra of PPV/BBL bilayers and single-layers (a) and MEH−PPV/BBL bilayers and single-layers (b).

The current−voltage characteristics of photovoltaic cells in the dark and under simulated AM1.5 sunlight illumination were measured by using a Hewlett-Packard 4155A semiconductor parameter analyzer (Yokogawa Hewlett-Packard, Tokyo).[9,22] The AM1.5 sunlight was produced from a Solar Light Co. (Philadelphia, PA) model 165-300 W/PS light source and the light intensity was measured with a calibrated Solar Light PM2141 pyranometer.[9] The photocurrent response spectrum was determined from the measured short-circuit current of a device under illumination from the PTI spectrofluorometer (monochromatic) light source of 0.5 mW/cm^2 intensity. All the photovoltaic properties were evaluated in ambient air conditions at room temperature (20−22 °C). No corrections were made for losses due to absorption/reflection of incident light illumination of devices at the glass/ITO/polymer interfaces.

Results and Discussion

Photoinduced Charge Transfer in Layered Donor/Acceptor Conjugated Polymers. Optical absorption spectra of thin films of PPV, BBL, and PPV/BBL bilayer are shown in Figure 2a. The absorption band of PPV covers 300−540 nm with a peak at 430 nm, and that of BBL extends to the near-infrared ($\sim$720 nm) with

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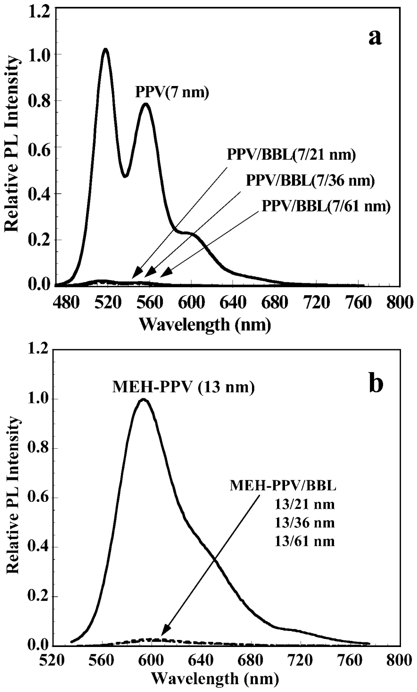


Figure 3. Relative PL emission spectra of single-layer and D/A bilayer thin films: (a) PPV/BBL system (λ_{ex} = 425 nm) and (b) MEH−PPV/BBL system (λ_{ex} = 490 nm).

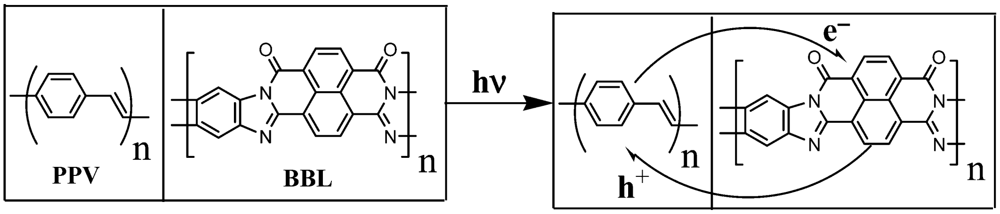
a peak at 590 nm,[9,23] suggesting good prospects for complementary solar light harvesting in the layered PPV/BBL heterojunctions. The absorption spectra of PPV/BBL heterojunctions were essentially simple superpositions of those of the component polymer layers. The PPV/BBL bilayers have a broad absorption spectrum covering the 300−720 nm range. Similar features of spectral superpositions were observed in the optical absorption spectra of MEH−PPV/BBL heterojunctions as shown in Figure 2b. However, an important difference is that unlike PPV/BBL bilayers, the MEH−PPV/BBL system lacks absorption in the 350−460 nm range due to the significant redshift of the MEH−PPV absorption band compared to that of PPV.

The results of photoluminescence (PL) quenching experiments are shown in Figure 3a for the PPV/BBL bilayer system. The characteristic PL emission spectrum of PPV with vibronic progression (peaks at 516 and 554 nm)[9,22] was observed upon excitation (425 nm) of a single-layer PPV thin film (~7 nm). Addition of a 21- or 36-nm BBL layer to create a PPV/BBL (D/A) heterojunction resulted in 96−99% quenching of the PPV emission (Figure 3a) by illuminating the layered films and monitoring the PL emission from the PPV side. Energy transfer is excluded from the mechanism of the PPV luminescence quenching in the PPV/BBL heterojunction because the characteristic emission of BBL was not observed when the heterojunction was excited in the 300−540 nm range. Furthermore, excitation of the PPV/BBL heterojunction at 600 nm, where PPV does not absorb, resulted in substantial quenching of the BBL emission at 745 nm. Very similar PL quenching results were observed for the MEH−PPV/BBL heterojunctions as shown in Figure 3b.

We propose that the observed quenching of photoluminescence that occurs in both PPV/BBL and MEH−PPV/BBL heterojunctions is due to photoinduced electron transfer from donor PPV or MEH−PPV to acceptor BBL (Scheme 1). Extensive prior studies of donor PPV (or MEH−PPV) and acceptor C_{60} and other fullerene derivatives (for C_{60}, EA = 3.9−4.1 eV)[2b,25] in multilayered thin films or blends have clearly established that ultrafast photoinduced electron transfer from photoexcited PPV (or MEH−PPV) to fullerene molecule accounts for PL emission quenching in the combined materials.[3a,c,25] In the present PPV/BBL and MEH−PPV/BBL systems, photoinduced electron transfer from excited PPV (or MEH−PPV) to BBL is highly favored energetically, based on the known electron affinities (EA) and ionization potentials (IP) of PPV (EA = 2.7 eV and IP = 5.1 eV),[22] MEH−PPV (EA = 2.9 eV and IP = 5.1 eV),[5b,22c] and BBL (EA = 4.0 eV and IP = 5.9 eV).[9,19,22b]

Additional evidence that the observed quenching of the PL emission in PPV/BBL and MEH−PPV/BBL heterojunctions (Figure 3) is due to photoinduced electron-transfer comes from the film thickness dependence of the quenching. The quenching of PL emission of PPV by BBL was monitored as a function of the PPV layer thickness while holding constant the film thickness of BBL (36 nm) in the PPV/BBL bilayer (Figure 4a). The PL emission of PPV was quenched 99% by BBL when the PPV layer was 8 nm or less. Quenching of the PPV emission decreased with increasing thickness of the PPV layer in the bilayers. Similar results of the quenching of PPV PL emission were observed when a 21-nm BBL film thickness was used. The reason for this film thickness dependence of the PL emission quenching in the PPV/BBL bilayers is that excitons produced in PPV are dissociated at the PPV/BBL heterojunction interface by electron transfer.[3a,6,9] As the PPV film thickness increases the fraction of excitons reaching the PPV/BBL interface decreases due to limitations of the exciton diffusion length (L_d). In fact, from the measurements in Figure 4a the exciton diffusion length (L_d) in PPV can be estimated to be 8 ± 1 nm, which agrees with prior reported estimates of $L_d = 7$ nm for PPV.[5a,26] From similar PL quenching data for MEH−PPV/BBL heterojunctions (see Supporting Information, Figure S2a), an exciton diffusion length L_d of 13 ± 2 nm was obtained for MEH−PPV, which is reasonable and lies between prior reported values of 10−20 nm.[5a,6a,26]

Scheme 1



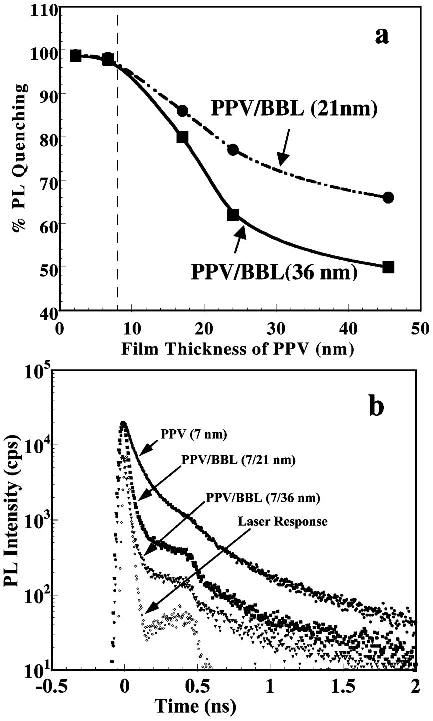


Figure 4. (a) Film thickness dependence of PL quenching in PPV/BBL bilayers, the lines are to guide eyes only. (b) PL decay curves of PPV(7 nm)/BBL bilayers (λ_{ex} = 425 nm, PL decay monitored at 516 nm).

The photoinduced electron transfer from donor PPV (or MEH−PPV) to acceptor BBL is further supported by time-resolved PL decay dynamics. Picosecond time-resolved PL decay curves of PPV/BBL bilayers are shown in Figure 4b along with that of single-layer PPV. The PL decay kinetics of the single-layer PPV can best be described by three exponential fits with one dominant lifetime after deconvoluting the instrument response from the decay curve.[22a,24] The observed dominant PL lifetime of PPV was 220 ps, which agrees well with the reported value of 240 ps in the literature.[26] From the estimated exciton diffusion length (L_d = 8 nm) and measured lifetime τ = 220 ps, the exciton diffusion coefficient (D) was calculated to be 2.9×10^{-3} cm^2 s^{-1} for PPV using the relation $L_d = \sqrt{(D\tau)}$.[24a,27] The PL lifetime of PPV was significantly shortened with increasing thickness of BBL in the PPV/BBL bilayers, reaching 11 ps (same as the resolution of the instrument) at a BBL layer thickness of 36 nm. The reason for the dependence of the PPV lifetime on the BBL layer thickness is not fully clear yet, it may be due to pinholes in the thinner PPV layer. From the known PL quantum efficiency (ϕ_{PL}) of 0.27[26] and measured PL lifetime (τ) of 220 ps, the values of the radiative rate constant (k_r) and nonradiative rate constant (k_{nr}) were estimated to be $\sim 1.24 \times 10^9$ s^{-1} and 3.3×10^9 s^{-1}, respectively, for the single-layer PPV (7 nm) film by using the relations (i) $\tau = 1/(k_r + k_{nr})$ and (ii) $\phi_{PL} = k_r/(k_r + k_{nr})$.[22a,26a] For the PPV(7 nm)/BBL(36 nm) bilayer with measured τ = 11 ps, the value of k_r was estimated to be $\sim 2.5 \times 10^{10}$ s^{-1}.

The dominant PL lifetime of MEH−PPV was similarly measured to be 250 ps, which is similar to the prior reported value of 200−300 ps,[26] in single-layer MEH−PPV (13 nm) film. A dominant lifetime of 12 ps was also measured in the MEH−PPV(13 nm)/BBL(36 nm) bilayer. Using these PL lifetime values along with the reported PL quantum efficiency of MEH−PPV (ϕ_{PL} = 0.15),[26] the radiative rate constants (k_r) were estimated to be $\sim 6.0 \times 10^8$ s^{-1} for the single-layer MEH−PPV (13 nm) film and $\sim 1.3 \times 10^{10}$ s^{-1} for the MEH−PPV(13 nm)/BBL(36 nm) bilayer.

The huge shortening of PL decay lifetime or the much faster nonradiative rate constant (k_{nr}) of the donors PPV and MEH−PPV within the PPV/BBL and MEH−PPV/BBL bilayers, compared to that of single-layer PPV (or MEH−PPV) thin film, is due to photoinduced electron transfer from donor PPV (or MEH−PPV) to acceptor BBL at the heterojunction interfaces,[18,24a,27] and is consistent with the observed steady-state PL quenching results. These results also suggest that the time scale of the photoinduced electron transfer is of order 10 ps or less; determination of the exact time scale was limited by the pulse width of the picosecond laser we used. Ultrafast laser spectroscopy of MEH−PPV/fullerene systems has established that the photoinduced electron-transfer process is faster than 100 fs.[25]

Studies of PL quenching and hence photoinduced electron transfer were also done for bilayers of PPV with the other acceptor polymers. When PTPQ, PTDA, PTQx, or PPyBT was used as an acceptor layer in the PPV/acceptor polymer bilayer heterojunction, only small quenching (<15%) of the PPV emission was observed. The observed small PL quenching is due to the low electron affinities (2.7 −3.0 eV)[19a,b,22a,b] of these acceptor polymers. We can conclude that photoinduced electron transfer is not efficient in these later donor/acceptor bilayers. In addition, the absorption bands of these acceptor polymers covered the 320−570 nm spectral range with peaks at 470 nm for PTPQ, 540 nm for PTDA, 440 nm for PTQx, and 400 nm for PPyBT. The PPV/acceptor polymer (PTPQ, PTDA, PTQx, or PPyBT) bilayers thus lack ability to harvest light of wavelength over 570 nm (see Supporting Information, Figure S1).

Effects of Electron Affinity on Photovoltaic Properties. To understand the role of the electron affinity (EA) of the acceptor conjugated polymer in layered donor/acceptor photovoltaic cells, we fabricated and investigated a series of donor/acceptor bilayer devices of the type ITO/PPV(50 nm)/acceptor polymer-(50−60 nm)/Al in which the EA of the acceptor polymer varied from 2.7 to 4.0 eV while the donor polymer PPV was fixed. When PTPQ (EA = 2.7 EV),[19,22b] PPyBT (EA = 2.8 eV),[19,22b] PTDA (EA = 2.9 eV),[19a,b,22b] or PTQx (EA = 3.0 eV)[21c] were each used as an acceptor layer in the photovoltaic (PV) cells, relatively high open circuit voltages (V_{oc}) in the 0.9−1.6 V range were obtained with 10 mW/cm^2 AM1.5 white light illumination (Figure 5). These photovoltages are more than 2-fold higher that

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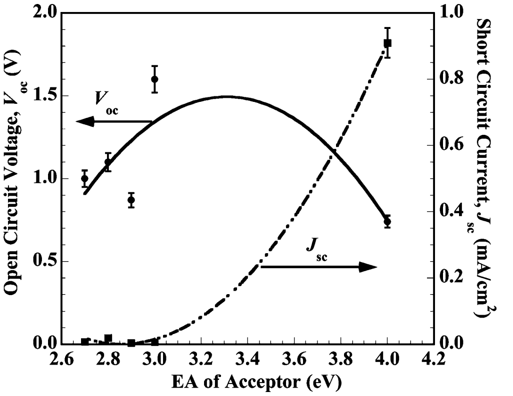

Figure 5. Effect of electron affinity of acceptor polymers on the open-circuit voltage and short-circuit current density of ITO/PPV/acceptor polymer/Al photovoltaic cells under 10 mW/cm^2 AM1.5 white light illumination.

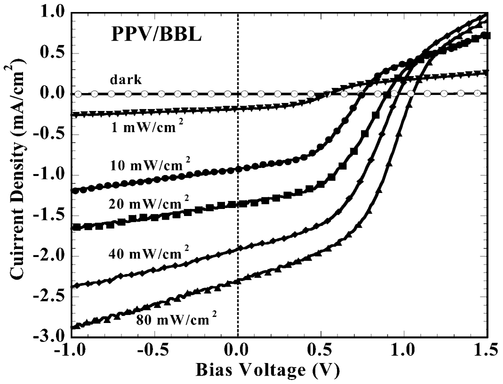

Figure 6. Current density−voltage characteristics of ITO/PPV(60 nm)/BBL(60 nm)/Al photovoltaic cells in the dark and under AM1.5 white light illumination in air. The PPV/BBL bilayer was annealed at 60 °C prior to deposition of Al electrode and was tested in ambient air and room temperature.

the work function difference between the two electrodes ($\Delta\Phi = 0.5$ eV). We did not find any linear trend between the observed photovoltages and the electron affinity of the acceptor polymer (Figure 5). However, the corresponding short-circuit current densities (J_{sc}) were small (<0.03 mA/cm^2) as shown in Figure 5. The power conversion efficiency (η_p) for all these devices was also low, about 0.07% or less, which is only slightly better than that of the single-layer PPV Schottky-barrier device ITO/PPV/Al which had a power conversion efficiency of 0.03% at 10 mW/cm^2 illumination. The poor photovoltaic properties of these D/A heterojunctions containing acceptor polymers with low EAs is consistent with the observed small PL quenching ($<15\%$). In fact, similar ITO/PPV/acceptor polymer/Al diodes were observed earlier to exhibit efficient electroluminescence.[22b] These results can thus be interpreted as evidence of inefficient photoinduced charge transfer/separation at the acceptor polymer/PPV interfaces.

Layered donor/acceptor photovoltaic cells containing BBL (EA = 4.0 eV), ITO/PPV(60 nm)/BBL(60 nm)/Al, were observed to have an open-circuit voltage of 0.74 V and very high short-circuit current density (0.91 mA/cm^2) at the 10 mW/cm^2 AM1.5 white light illumination (Figure 5). Although the open-circuit voltage is about the same as in the devices made from the other acceptor polymers, the factor of >30 better photocurrent suggests that BBL is a more promising acceptor polymer for constructing D/A photovoltaic cells. This is in accord with the PL quenching and PL decay lifetime shortening results which showed that photoinduced electron transfer and exciton dissociation at the PPV/BBL heterojunction interface was substantially more efficient than that at the other PPV/acceptor polymer heterojunctions. The photovoltaic properties of PPV/acceptor polymer heterojunctions with the series of 5 acceptor polymers including BBL demonstrate that a high electron affinity of the acceptor polymer is essential to efficient charge photogeneration in donor/acceptor polymer heterojunctions. Therefore, we focused all subsequent studies on BBL-containing nanostructured D/A heterojunction photovoltaic cells.

BBL-Based Photovoltaic Cells. To simplify the present studies we did not attempt to optimize the photovoltaic properties as a function of the bilayer film thicknesses. We selected the donor PPV and MEH−PPV and acceptor BBL layer thicknesses to each be 60 nm based on the need to get significant absorption by each layer in a bilayer and our preliminary results which suggested that suitable film thicknesses would fall in the 20−60 nm range.[9] The current density−voltage ($J-V$) characteristics of an ITO/PPV(60 nm)/BBL(60 nm)/Al device measured under different intensities of simulated AM1.5 white light illumination are shown in Figure 6. The dark current follows an excellent semiconductor diode behavior with a rectification ratio of $\sim 1 \times 10^3$ at ± 1.5 V. The photocurrent is seen to increase with incident light power intensity P (mW/cm^2) in Figure 6. Relatively high short-circuit current density J_{sc} in the range 0.185 to 2.30 mA/cm^2 and open-circuit voltages of 0.55 to 1.06 V are obtained. The photovoltaic (PV) device parameters including the fill factor (FF) and power conversion efficiency (η_p) were obtained from Figure 6 by using the following usual definitions. The fill factor is given by $FF = (JV)_{max}/J_{sc}V_{oc}$, where $(JV)_{max}$ is the maximum rectangle under the $J-V$ curve.[1−3,9] The power conversion efficiency is given by $\eta_p = (FF \cdot J_{sc} \cdot V_{oc})/P$, where P is the incident light intensity.[1−3,9] The ITO/PPV(60 nm)/BBL(60 nm)/Al device of Figure 6 achieves a power conversion efficiency of 1.4% at 80 mW/cm^2 light illumination with $J_{sc} = 2.3$ mA/cm^2, $V_{oc} = 1.06$ V, and $FF = 47\%$. The power conversion efficiency increases to 4.5% at 1 mW/cm^2 with $J_{sc} = 0.185$ mA/cm^2, $V_{oc} = 0.55$ V, and $FF = 44\%$ (Table 1). Under the same experimental conditions, the photovoltaic effect was not observed in the ITO/BBL/Al diode, which indicates that neither electrode forms a Schottky-barrier junction with BBL. These results confirm the effectiveness of the layered donor/acceptor heterojunction PV architecture for improving the photovoltaic properties of polymer semiconductors. Compared to the single-layer PPV diode, the short-circuit photocurrent and power conversion efficiency of the PPV/BBL diode are enhanced by factors of 45 and 93, respectively, at 10 mW/cm^2 light intensity.

Figure 7 shows the current density−voltage ($J-V$) curves of an ITO/MEH−PPV(60 nm)/BBL(60 nm)/Al PV diode taken under different intensities of AM1.5 white light illumination. The dark current of the diode also showed an excellent rectification ratio of 1.3×10^3 at ± 1.5 V. The MEH−PPV(60 nm)/BBL(60 nm) PV cell of Figure 7 achieves a power conversion efficiency of 0.8%

Table 1. Photovoltaic Properties of ITO/PPV/BBL/Al Cells at Different Annealing Temperatures Prior to the Deposition of Al Electrode[a]

annealing temperature (°C)	P (AM 1.5) (mW/cm^2)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η_p (%)
60	1	0.185	0.55	44.0	4.5
60	10	0.91	0.74	48.0	3.2
60	80	2.30	1.06	47.0	1.4
100	1	0.182	0.54	47.0	4.6
100	10	0.86	0.76	52.2	3.4
100	80	2.15	1.10	50.0	1.5
125	1	0.18	0.53	46.0	4.4
125	10	0.90	0.74	47.0	3.1
125	80	1.91	1.08	51.0	1.3
140	1	0.178	0.51	45.0	4.0
140	10	0.88	0.73	47.3	3.0
140	80	1.89	1.08	49.7	1.3

[a] All devices were characterized at ambient room temperature in air.

Table 2. Photovoltaic Properties of ITO/MEH−PPV/BBL/Al Cells at Different Annealing Temperatures Prior to the Deposition of Al Electrode[a]

annealing temperature (°C)	P (AM 1.5) (mW/cm^2)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	η_p (%)
60	1	0.142	0.65	39.0	3.6
60	10	0.90	0.80	39.0	2.8
60	80	1.95	0.94	35.0	0.8
100	1	0.144	0.62	41.0	3.7
100	10	0.88	0.77	43.0	2.9
100	80	2.00	0.98	42.0	1.0
125	1	0.140	0.64	41.0	3.7
125	10	0.96	0.80	36.0	2.8
125	80	1.98	0.93	47.0	1.1
140	1	0.138	0.62	37.0	3.2
140	10	0.86	0.78	37.4	2.5
140	80	1.88	0.96	39.5	0.9

[a] All devices were characterized at ambient room temperature in air.

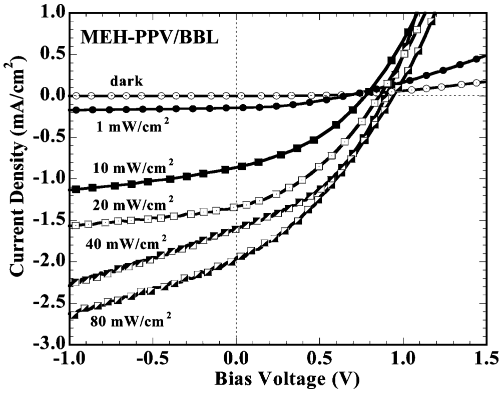

Figure 7. Current density−voltage characteristics of ITO/MEH−PPV(60 nm)/BBL(60 nm)/Al photovoltaic cells in the dark and under AM1.5 white light illumination in air. The MEH−PPV/BBL bilayer was annealed at 60 °C prior to deposition of Al electrode and was tested in ambient air and room temperature.

at 80 mW/cm^2 light illumination with J_{sc} = 1.95 mA/cm^2, V_{oc} = 0.94 V, and FF = 35%. The power conversion efficiency increases to 2.8% at 10 mW/cm^2 and 3.6% at 1 mW/cm^2 light illumination for the same diode (Table 2). Under the same experimental conditions, the single-layer ITO/MEH−PPV/Al diode had a power conversion efficiency (η_p) of 0.004% at 10 mW/cm^2 with J_{sc} = 0.003 mA/cm^2, V_{oc} = 0.68 V, and a fill factor of 20%. The layered donor/acceptor MEH−PPV/BBL PV cells thus have a factor of 2 improvement in the fill factor and over a 700-fold enhancement in power conversion efficiency compared to the single-layer MEH−PPV Schottky-barrier cells.

A comparison between the photovoltaic properties of PPV/BBL and those of MEH−PPV/BBL shows that there is a significant difference in favor of PPV/BBL heterojunctions. For example, the fill factor and power conversion efficiency of the ITO/PPV/BBL/Al diodes are superior by 35% and 75%, respectively, compared to the ITO/MEH−PPV/BBL/Al diodes under identical AM1.5 80 mW/cm^2 white light illumination. Since the HOMO energy levels or ionization potentials of both donor polymers are identical at 5.1 eV,[5b,22] contact to ITO electrode can be ruled out as the potential source of the difference. Two main factors that can account for the observed difference in photovoltaic properties of PPV and MEH−PPV heterojunctions with BBL are the following: (i) the complementary optical absorption of PPV/BBL which covers the 300−720 nm spectral range, whereas MEH−PPV/BBL lacks absorption in the 350−460 nm range (Figure 2); and (ii) the greater crystallinity and structural order of PPV compared to MEH−PPV. The first factor implies that more excitons will be produced and dissociated in the PPV/BBL heterojunctions, resulting in an increased photocurrent as indeed observed. A greater structural order can be expected to improve both the photocurrent and fill factor.

Annealing Effects on Photovoltaic Properties. We thought that annealing at a higher temperature (>60 °C) might influence the morphology of the individual nanoscale polymer thin films within the layered heterojunctions as well as the interfacial adhesion between the layers. Any resulting changes in the crystallinity of the polymers or in the contacts at the D/A interface could in turn influence the PV properties. Therefore, we investigated PPV/BBL and MEH−PPV/BBL PV diodes annealed at 100, 125, or 140 °C prior to the deposition of Al electrode. Representative PV properties, including the short-circuit current J_{sc}, open-circuit voltage V_{oc}, fill factor FF, and power conversion efficiency η_p, are summarized in Tables 1 and 2 at the different annealing temperatures and illumination intensities. There is some improvement in the PV properties in going from 60 °C to 100−125 °C annealing, most notably in the fill factor and power conversion efficiency η_p, followed by a decrease at the highest temperature (Figure 8).

In the case of PPV/BBL diodes, maximum power conversion efficiencies of 1.5% at 80 mW/cm^2 and 4.6% at 1 mW/cm^2 were obtained by annealing the bilayer thin films at 100 °C. The best performance of MEH−PPV/BBL diodes was achieved by annealing the bilayer thin films at 125 °C, resulting in power conversion efficiencies of 1.1% at 80 mW/cm^2 and 3.7% at 1 mW/cm^2. The MEH−PPV/BBL devices are the most improved (~40% increase in η_p) by the higher temperature annealing compared to devices annealed at 60 °C. This annealing induced improvement in photovoltaic properties of MEH−PPV/BBL bilayer thin films must be a result of increase in crystallinity or structural order of MEH−PPV since the annealing temperature 125 °C is

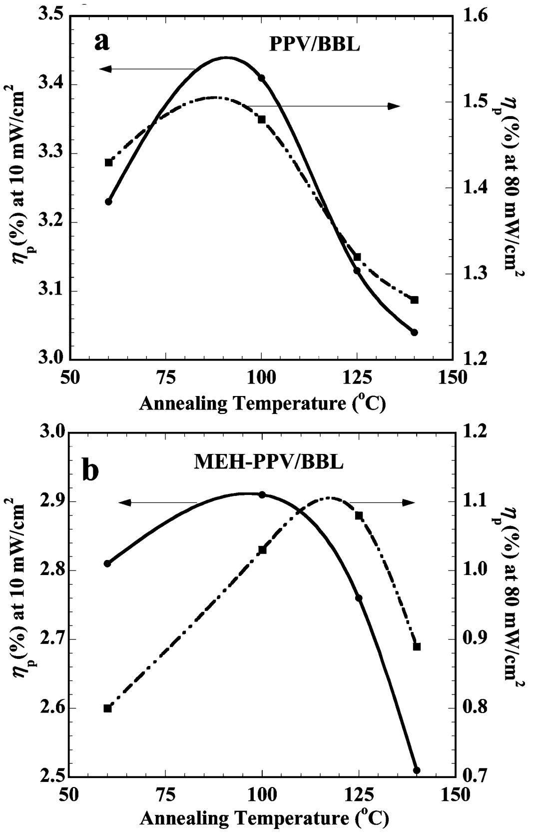

Figure 8. Power conversion efficiency of (a) ITO/PPV(60 nm)/BBL(60 nm)/Al and (b) ITO/MEH−PPV(60 nm)/BBL(60 nm)/Al diodes as a function of annealing temperature prior to the deposition of Al electrode.

far above the known T_g (65 °C) of this polymer. Such an increased crystallinity or structural order can improve the mobility of charge carriers and thus photovoltaic properties.

Light Intensity Dependence of PV Properties. The dependence of the short-circuit current density (J_{sc}) on the incident AM1.5 white light intensity (P) in the 1−100 mW/cm^2 range was found to be $J_{sc} = 0.21\ P^{0.56}$ for the PPV/BBL cells and $J_{sc} = 0.18P^{0.57}$ for the MEH−PPV/BBL cells. The V_{oc} also increased with illumination light intensity according to the relation $V_{oc} = 0.55P^{0.15}$ for the PPV/BBL cells and $V_{oc} = 0.65P^{0.087}$ for the MEH−PPV/BBL cells. The observed maximum open-circuit voltages, 1.1 V for PPV/BBL cells and 1.0 V for MEH−PPV/BBL cells at 100 mW/cm^2, are approximately equal to the difference between the highest occupied molecular orbital (HOMO level) or IP$_D$ of donor PPV (or MEH−PPV) and the lowest unoccupied molecular orbital (LUMO level) or EA$_A$ of acceptor BBL. For both PPV/BBL and MEH−PPV/BBL the $\mathrm{IP_D} - \mathrm{EA_A} = 1.1$ eV, since both donors have an identical IP of 5.1 eV and the EA of BBL is 4.0 eV. Since the work function difference between ITO and Al electrodes ($\Delta\Phi = 0.5$ eV) is only about half the observed V_{oc}, we conclude that the photovoltage of these polymer/polymer heterojunction photovoltaic cells does not originate from the electrode work function difference. We propose that the internal potential for charge separation arises from the donor/acceptor polymer/polymer interfaces.[9,16b]

The dependence of the external power conversion efficiency η_p of both PPV/BBL and MEH−PPV/BBL bilayer PV cells on illumination intensity is shown in Figure 9. A significant decrease of η_p with intensity is observed; $\eta_p = 4.5P^{-0.15}$ for PPV/BBL and $\eta_p = 3.65P^{-0.16}$ for MEH−PPV/BBL up to about 25 mW/cm^2, above which there is a more rapid decrease. We note that prior studies of D/A heterojunction PV cells based on copper phthalocyanine (CuPc) and C$_{60}$ have shown that η_p *increased* with illumination intensity in the 1−100 mW/cm^2 range.[2b] The layer thicknesses in the CuPc/C$_{60}$ bilayers were in the range of 10−30 nm and comparable to the exciton diffusion lengths of the materials. The unexpected large decrease of η_p with illumination intensity in our PPV/BBL and MEH−PPV/BBL devices suggests that the bilayer thicknesses (60 nm for all polymers) are not optimum. To ensure that all excitons generated can reach the D/A interface, the thickness should ideally be equal to the excition diffusion length L_d, which as previously discussed is 8 nm for PPV, 13 nm for MEH−PPV, and unknown for BBL. It is unlikely that L_d for BBL is as large as 60 nm. Therefore, the film thicknesses of all the polymers in the D/A bilayer PV cells far exceed the exciton diffusion lengths of the polymers. A major consequence of this is increased series resistance due to the occurrence of space charge buildup and charge carrier recombination at high illumination intensities. However, this does not fully explain the observed rather large drop in power conversion efficiency in the 50−100 mW/cm^2 illumination intensity range (Figure 9). An additional factor that could account for these results is photooxidative degradation of the arylene vinylene donor polymers PPV and MEH−PPV at the high illumination intensities

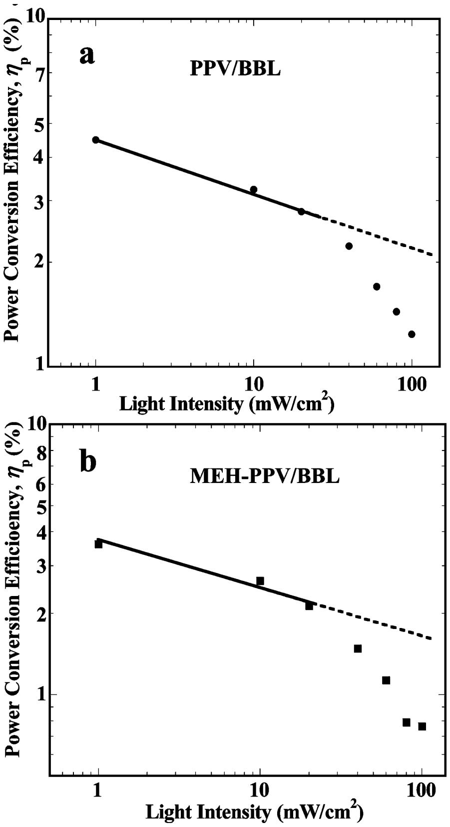

Figure 9. Power conversion efficiency dependence on AM1.5 white light intensity in air for the same (a) ITO/PPV/BBL/Al and (b) ITO/MEH−PPV/BBL/Al diodes in Figures 6 and 7.

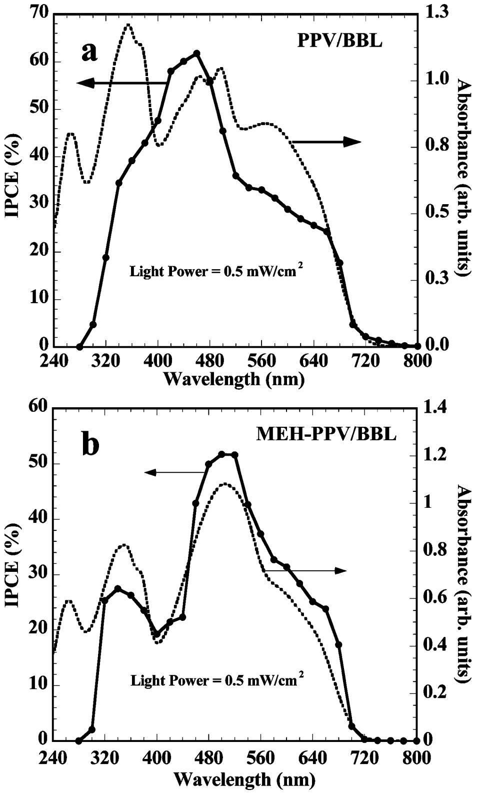

Figure 10. Spectral responses of (a) ITO/PPV(60 nm)/BBL(60 nm)/Al and (b) ITO/MEH−PPV(60 nm)/BBL(60 nm)/Al devices under zero bias at 0.5 mW/cm^2 light illumination. The absorption spectra shown are for the PPV(60 nm)/BBL(60 nm) and MEH−PPV(60 nm)/BBL(60 nm) bilayer thin films without the Al metal electrodes.

since all the devices were tested under ambient air conditions.[28]

Photoaction Spectra. The photoaction spectra along with the absorption spectra of the PPV(60 nm)/BBL(60 nm) and MEH−PPV(60 nm)/BBL(60 nm) bilayers are shown in Figure 10. The charge collection (η_c) or incident photon-to-current conversion efficiency (IPCE = 1240 $J_{sc}/\lambda P$, where λ is the wavelength in nm)[1,9] show that the photoresponse of both PPV/BBL and MEH−PPV/BBL diodes turns on at ~720 nm and then follows the absorption spectra of the bilayers. A comparison of the photoaction spectrum to the absorption spectrum shows that both polymer layers in the bilayer contribute to solar light harvesting and charge-carrier photogeneration. A maximum charge collection efficiency η_c of 62% electrons/photon at 460 nm for the PPV/BBL cell (Figure 10a) and 52% at 500 nm for the MEH−PPV/BBL cell (Figure 10b) were observed. These efficiencies for the conversion of absorbed photons to electrons in the bilayer cells are the highest ever reported for polymer/polymer photovoltaic cells.[6,16] The corresponding monochromatic power conversion efficiency η_p of the PPV/BBL diode was 5.4% (J_{sc} = 0.115 mA/cm^2, V_{oc} = 0.53 V, and *FF* = 44%) at 460 nm with an illumination intensity of 0.5 mW/cm^2. For the MEH−PPV/BBL cell, a power conversion efficiency of 4.4% (J_{sc} = 99 μA/cm^2, V_{oc} = 0.57 V, and *FF* = 39%) at 500 nm with an illumination intensity of 0.5 mW/cm^2 was achieved.

The observed differences in the photoaction spectra of the PPV/BBL and MEH−PPV/BBL PV cells correctly reflect the absorption spectra of the bilayer thin films. The previously noted more complementary absorption bands of PPV/BBL bilayer components compared to those of MEH−PPV/BBL are seen to actually translate to better light harvesting and overall better photovoltaic properties.

PV Cells with Gold Cathode Electrodes. All the PV cells investigated so far had aluminum top electrodes which formed Ohmic contacts to the BBL layer. To investigate the role of a high work function metal contact to the present D/A heterojunction cells and to further shed light on the origin of the photovoltage we fabricated and studied ITO/PPV(60 nm)/BBL(60 nm)/Au PV cells. This cell had a power conversion efficiency of η_p = 1.0% at 80 mW/cm^2 with J_{sc} = 1.92 mA/cm^2, V_{oc} = 0.90 V, and *FF* = 46%, and η_p of 2.4% at 10 mW/cm^2 with J_{sc} = 0.75 mA/cm^2, V_{oc} = 0.69 V, and *FF* = 48%. The fill factors of this diode are essentially identical with those of the Al-cathode devices. However, there are decreases in the short-circuit current density as well the open-circuit voltage, leading to about 30% decrease in power conversion efficiency of the Au-cathode devices compared to those of the Al-cathode devices. The decrease in photocurrent and power conversion efficiency of the Au-cathode devices can be explained by a contact resistance at the Au/BBL interface because of the large mismatch of the energy level of BBL with the work function of Au (5.1 eV).[5b−d,16] However, the open-circuit voltage of the ITO/PPV/BBL/Au cells is much greater than the work function difference between ITO and Au ($\Delta\Phi$ = 0.3 eV),[5b−d,16] again indicating that the photovoltage originates primarily from the difference in energy levels (HOMO/LUMO) of the D/A polymer semiconductors. Similar photovoltaic properties were observed for ITO/MEH−PPV/BBL/Au cells.

Conclusions

Our systematic study of photoinduced electron transfer and photovoltaic properties of donor/acceptor bilayers containing donor PPV or MEH−PPV and a series of acceptor polymers with electron affinities in the range 2.7−4.0 eV shows that both the charge-transfer efficiency at the polymer/polymer interface and the power conversion efficiency of the devices were maximized when the highest electron affinity acceptor polymer BBL (EA = 4.0 eV) was used. The observed power conversion efficiencies of 1.5−4.6% for ITO/PPV/BBL/Al cells under white light illumination of 1−80 mW/cm^2 are among the largest achieved to date in organic and polymer solar cells. Optimization of the bilayer film thicknesses and improvements in the hole mobility and photooxidative stability of the donor polymers can be expected to substantially increase the power conversion efficiency of donor/acceptor polymer solar cells at high illumination intensities (80−100 mW/cm^2). The observed photovoltages in the donor/acceptor bilayer cells were approximately equal to $IP_D - EA_A$ and were about 2−3

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times larger than the difference in the work function of the electrodes. The results of this study demonstrate that the layered donor/acceptor heterojunction is a promising architecture for developing efficient polymer solar cells.

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Supporting Information Available: Optical absorption and photoluminescence spectra, film thickness dependence and PL decay curves, current density−voltage characteristics, and short-circuit current density and open-circuit voltage dependence curves of the subject layered nanostructures. This material is available free of charge via the Internet at http://pubs.acs.org.

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