Comparative Study of M3EH−PPV-Based Bilayer Photovoltaic Devices

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ABSTRACT: We have recently shown that efficient polymer solar cells can be fabricated by using a weakly soluble derivative of poly-*p*-vinylene (M3EH−PPV) as the electron donor. Here we present studies on bilayer devices using organic electron acceptors with varying LUMO levels and M3EH−PPV. It is found that the open-circuit voltage scales linearly with the LUMO level of the acceptor, reaching values as high as 1.5 V when cyano-substituted poly(*p*-phenyleneethynylene)-*alt*-poly(*p*-phenylenevinylene) copolymers are used. Further, we discovered that for an increasing number of triple bonds in the repeat unit of the acceptor polymer the device performance decreases with increasing thickness of the acceptor layer. Also, the quantum efficiency was smaller when using polymers with higher LUMO levels. Thus, further effort is needed to design optimum acceptor polymers for devices exhibiting large open-circuit voltage and high quantum efficiency.

Introduction

Organic photovoltaics is currently an active field of research because of its high potential for use in large area flexible solar cells and the recent progress made in terms of obtained efficiencies.[1−5] Optimized devices based on C_{60} or its derivatives could recently reach white light energy conversions efficiencies (ECE) of around 5%.[3−5] However, the efficiencies of organic solar cells are still below of that of their inorganic counterparts, and more research is needed to understand the fundamental processes limiting their efficiency.

Solar cells based only on conjugated polymers as active layer are of special interest due to their easy processability from solution. It has been well documented that energy conversion efficiencies of solar cells made from only one kind of conjugated polymer are quite low. This is due to the rather high exciton binding energy (200−500 meV) in most organic materials.[6] Higher efficiencies can be achieved if a heterojunction between hole and electron accepting polymers is incorporated e.g. in bilayer[7] or blend structures.[8] The highest efficiencies for pure polymer-based solar cells were reported for bilayer devices produced either by laminating a polythiophene derivative (POPT) with a cyano-substituted poly(*p*-phenylenevinylene) (MEH−CN−PPV) as the electron acceptor (energy efficiency (ECE) = 1.9%)[7] or with PPVs covered by a thin layer of a polybenzimidazobenzophenanthroline ladder polymers (BBL) as the electron acceptor (ECE = 1.5%).[9] However, the laminating technique still has to prove its applicability for large area devices. BBLs are deposited from a strong acid, making them less desirable for mass production.

Since most conjugated polymers exhibit similar solubilities in most organic solvents, direct coating of a second layer on top of the first layer will often partially dissolve the first layer, leading to an undefined interface. A direct preparation of a double-layer is possible if a "perpendicular" solvent for the deposition of the second layer on the first can be found. We present here investigations on double layers where the first layer (the electron donor) is M3EH−PPV (poly[2,5-dimethoxy-1,4-phenylene-1,2-ethenylene-2-methoxy-5-(2-ethylhexyloxy)-(1,4-phenylenevinylene-1,2-ethenylene)])[10] deposited from chlorobenzene. M3EH−PPV can be regarded as a strictly alternating copolymer of the soluble MEH−PPV and the insoluble 2,5-dimethoxy-PPV. Thus, M3EH−PPV is only soluble in polar organic solvents like chlorobenzene, allowing for the preparation of bilayer devices if the second layer (the electron acceptor) is prepared from less polar solvents like xylene.

Furthermore, previous reports on blend and bilayer solar cells based on M3EH−PPV as electron donor proved the excellent suitability of this material for efficient solar cells.[8,11−13] We have previously demonstrated that for blend devices with the cyano-substituted PPV CN−ether−PPV (poly[oxa-1,4-phenylene-1,2-(1-cyano)ethylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)-ethylene-1,4-phenylene])[14] as the electron acceptor high energy efficiency exceeding 1.5% could be achieved.

Here we present further results on the photovoltaic properties of devices comparing three different polymeric acceptors. We show studies of the influence of the LUMO level position on the quantum efficiency and open-circuit voltage of the devices and on the relation between layer thickness and device properties.

Results and Discussion

A CN−ether−PPV[14] and two CN−PPV−PPE[15] copolymers with either one triple bond, poly(2,5-dioctyloxy-1,4-phenyleneethynylene-2,5-dioctyloxy-1,4-phenylene-2-cyanovinylene-2,5-dioctyloxy-1,4-phenylene-1-cyanovinylene) (CN−PPV−PPE1), or two triple bonds, poly(1,4-phenyleneethynylene-2,5-didodecyloxy-1,4-phenyleneethynylene-1,4-phenylene-2-cyanovinylene-2,5-dioctyloxy-1,4-phenylene-1-cyanovinylene) (CN−PPV−PPE2), were used as electron acceptors (see Figure 1 for the chemical structures). The longer dodecyloxy side chains in CN−PPV−PPE2 compared to CN−PPV−PPE1 were necessary for very good solubility of the polymer.

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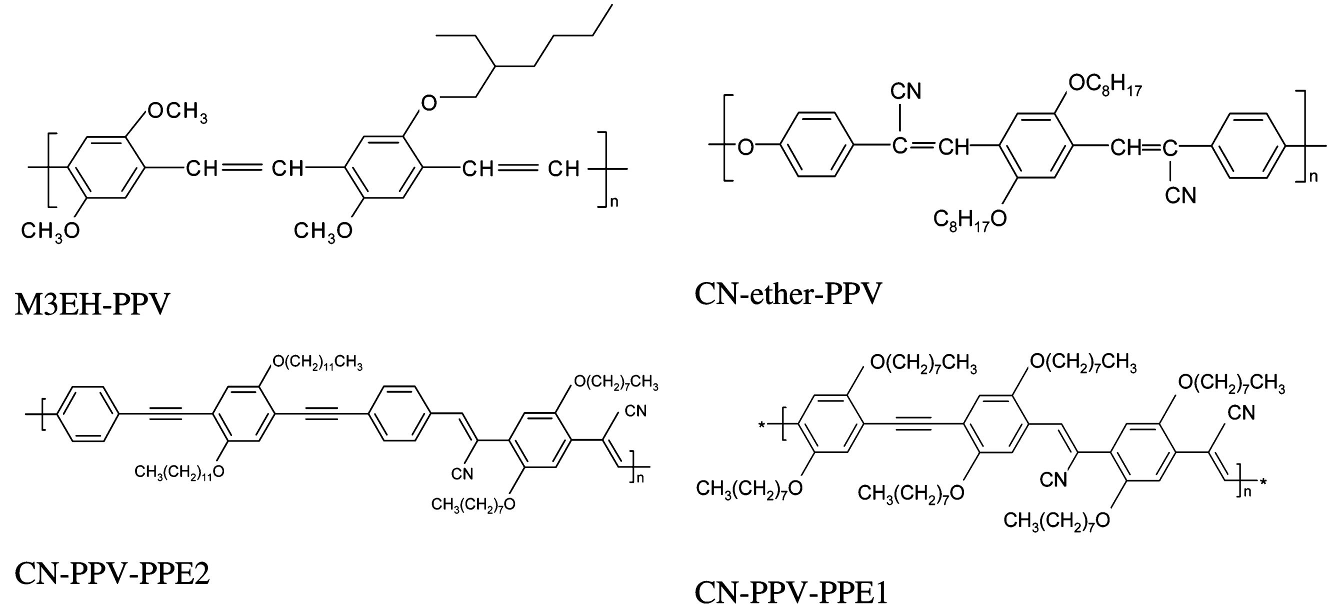

Figure 1. Chemical structures of M3EH−PPV, CN−ether−PPV, CN−PPV−PPE1, and CN−PPV−PPE2.

These acceptors were selected because they show distinct differences in the position of the LUMO levels, which should strongly influence the exciton dissociation probability and the open-circuit voltage. As a reference material, the well-known small molecule fullerene derivative [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) was used. Absorbance spectra and the energies of the corresponding HOMO and LUMO levels of the investigated donor and acceptors are shown in Figure 2.[10,15] Note that combined cyclic voltametry (CV) and electrochemical voltage spectroscopy (EVS) measurements for the CN−PPV−PPE1 give a larger band gap compared to CN−PPV−PPE2, although the optical absorbance spectra indicate otherwise.

Comparing the photoluminescence efficiency of a layer made from the donor polymer and of a bilayer consisting of donor and the acceptor polymer provides information on the exciton dissociation probability for the different donor−acceptor combinations. PL measurements were performed on structures consisting of a 25−30 nm thick layer of M3EH−PPV spin-coated from a chlorobenzene solution on a glass substrate covered with ITO and PEDOT:PSS. After annealing, a 25−30 nm thick acceptor layer was spin-coated on top of the first layer from a xylene solution (M3EH−PPV is nearly insoluble in xylene at RT). These structures were then illuminated at 500 nm (approximately the M3EH−PPV absorption maximum) from the glass side, and the PL spectra were recorded in reflection. Since light passed through the M3EH−PPV layer first, around 50% of the incident photons were absorbed within this layer and only 10−15% in the acceptor layer. Thus, exciton generation took place predominantly in the M3EH−PPV layer. As shown in Figure 3a and summarized in Table 1, bilayers with different acceptors exhibit significantly different emission intensities. The emission spectra consist mainly of M3EH−PPV emission superimposed on the emission of the accepting layer. More detailed analysis shows that there is an additional red-shifted component around 650 nm present, which can be attributed to exciplex emission. Details on the exciplex emission in PPV based blends are the subject of a forthcoming paper.

With PCBM as the electron acceptor, more than 99% of the M3EH−PPV emission is quenched, suggesting efficient dissociation of excitons in M3EH−PPV. Strong quenching is also observed for devices with CN−ether−PPV as electron acceptor, while both PPE−PPV copolymers induce only moderate quenching (ca. 50%) of the M3EH−PPV emission.

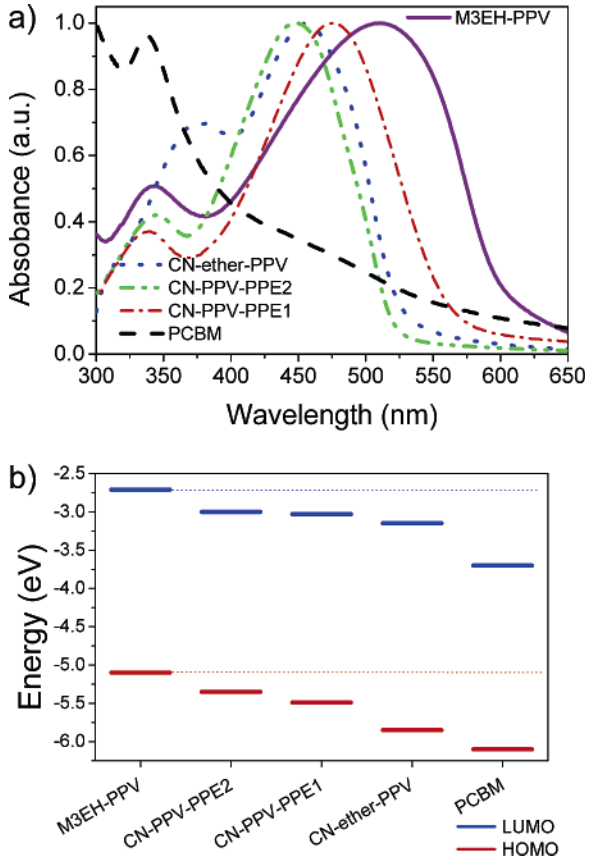

Figure 2. (a) Absorbance spectra and (b) the energetic positions of the HOMO and LUMO levels of M3EH−PPV and the three different electron acceptors investigated here, as determined by CV/EVS measurements using a reference value of −4.4 eV for NHE.[4,10,14,15]

All bilayer solar cells were characterized by spectrally resolved measurements of the incident photon to converted electron efficiency (IPCE) and by recording the current−voltage characteristics under white light illumination at 100 mW/cm^2 (AM1.5) to mimic the solar radiation. The thicknesses of the

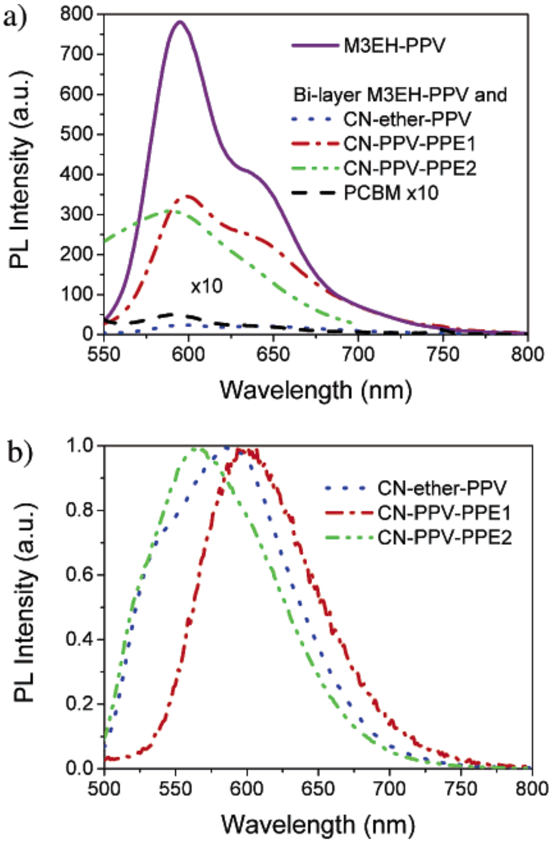

Figure 3. (a) Photoluminescence spectra of a neat M3EH−PPV film on PEDOT:PSS/ITO/glass and of double-layer devices with different types of electron acceptors on M3EH−PPV. The M3EH−PPV layer thickness was 30 nm, and the electron acceptor layer thickness varied between 25 and 30 nm. The bilayer structures were illuminated from the glass side at the absorption maximum of M3EH−PPV (500 nm). (b) Normalized PL spectra the pure electron accepting polymer films.

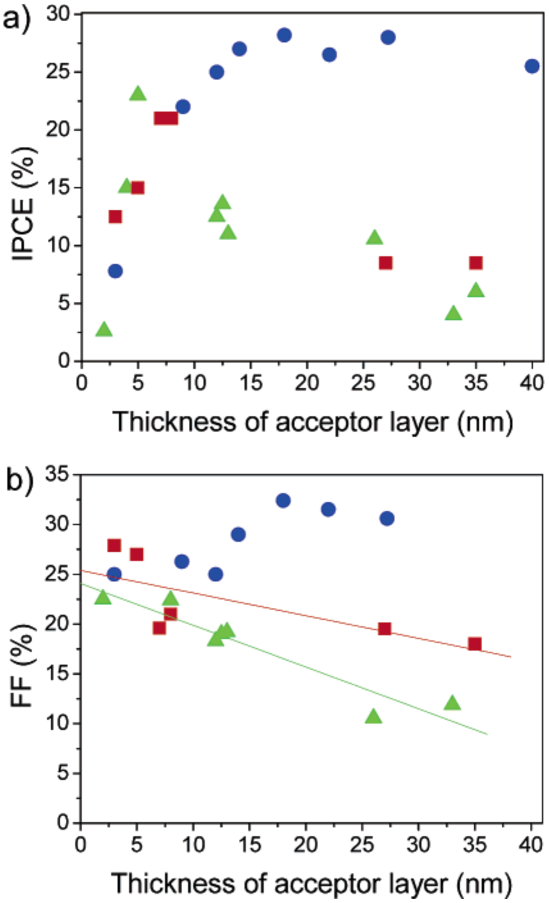

Figure 4. Dependence of (a) the IPCE and (b) the fill factor (FF) on the thickness of the electron acceptor layer for CN−ether−PPV (circles), CN−PPV−PPE1 (squares), and CN−PPV−PPE2 (triangles). A linear fit is included for the copolymers in (b) to show the general trend.

electron accepting layers were varied to study the influence on the solar cell properties.

Interestingly, for M3EH−PPV:CN−ether−PPV devices, the influence of layer thickness on the IPCE was of minor importance in the investigated thickness range (5−40 nm) as shown in Figure 4a. High external quantum efficiencies of up to 29% could be achieved for this material combination. The efficiency is significantly smaller for very thin CN−ether−PPV layers (<5 nm). This observation can be caused by two effects: First, for a very small thickness of the acceptor only isolated islands of CN−ether−PPV on M3EH−PPV might have formed. Second, it is well-known that electrodes will induce rapid decay of excitons.[17,18]

As opposed to these findings, the influence of the layer thickness of PPE−PPV copolymers on the IPCE is dramatic. The highest efficiencies of about 20% were found for very thin acceptor layer thickness around 7−8 nm. Below 7 nm the efficiency drops considerably, for the same reasons described before. When the acceptor layer thickness is increased beyond 10 nm, the efficiency decreases continuously to ca. 5%. At the same time the fill factor (FF) decreases to values less than 13%, as shown in Figure 4. It is notable that the decrease in efficiency and fill factor is more pronounced with increasing number of triple bonds in the acceptor polymer. In the case of CN−PPV−PPE2 (two triple bonds), the FF drops from ca. 23% for the thinnest acceptor layer to less than 13% for the thickest, whereas it drops to ca. 18% for CN−PPV−PPE1 (one triple bond). As shown in Figure 2a, both copolymers have similar HOMO and LUMO positions.[15] Also, the degree of quenching is similar, indicating that the difference in the photovoltaic properties must be due to charge extraction rather than to exciton dissociation. The argument that charge extraction is a major reason for the low efficiency of the CN−PPV−PPE devices is supported by the comparison of the $I(V)$ characteristics under white light illumination of M3EH−PPV:CN−PPV−PPE2 bilayer devices with a 5 nm thick and a 33 nm thick CN−PPV−PPE2 layer, as shown in Figure 5. Most noticeably, the $I(V)$ characteristics for the device with the thicker acceptor layer is even superlinear, which is a strong indication for a transport limited device. On the basis of the present data, we presume that introducing ethynylene units into the backbone of the CN−PPV electron

Table 1. PL Efficiencies of M3EH−PPV/X Bilayer Devices Measured Relative to the PL Emission of a Pure 30 nm M3EH−PPV Single Layer[a]

acceptor X:	M3EH−PPV single layer	CN−PPV−PPE2	CN−PPV−PPE1	CN−ether−PPV	PCBM
relative PL efficiency ($\lambda = 595$ nm)	100%	38%	44%	3%	0.6%
$\mathrm{LUMO_{M3EH}}$−PPV − $\mathrm{LUMO_{acceptor}}$		0.29 eV	0.32 eV	0.44 eV	0.99 eV
$\mathrm{HOMO_{M3EH}}$−PPV − $\mathrm{HOMO_{acceptor}}$		0.24 eV	0.38 eV	0.75 eV	0.1 eV

[a] The PL efficiency depends crucially on the offsets of the HOMO and LUMO levels of the investigated electron accepting polymers with respect to those in M3EH−PPV.[16]

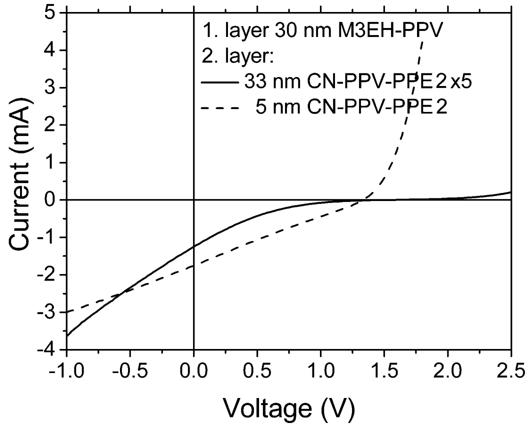

Figure 5. Influence of the thickness of the CN−PPV−PPE2 electron acceptor layer on the shape of the *I*(*V*) characteristics under AM 1.5 illumination.

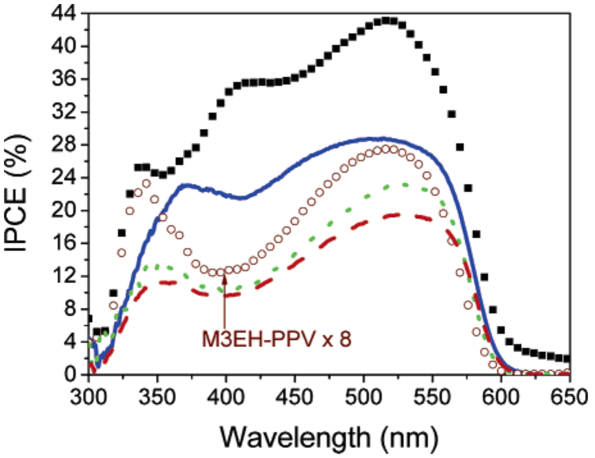

Figure 6. IPCE characteristics for the optimum bilayer devices consisting of a 25−30 nm thick M3EH−PPV layer covered by either a 23 nm thick layer of CN−ether−PPV (solid line), a 5 nm thick layer of CN−PPV−PPE2 (dotted), or CN−PPV−PPE1 (dashed) or of a 20 nm thick layer of PCBM (solid squares). For comparison, the IPCE spectrum of a single-layer M3EH−PPV device (open circles) is also presented.

acceptor reduces the ability to transport electrons. One reason might be the low rotation barrier around the triple bond in the CN−PPE−PPV copolymers. It has been pointed out that such rotational freedom increases the energetic disorder of single polymer chains. More experiments concerning the transport properties of these polymers are needed to support this statement.

The IPCE characteristics obtained for structures with the optimum acceptor layer thickness are shown in Figure 6. Because of the small thickness of the acceptor layer in the case of the PPV−PPE copolymers, the spectra of these devices follow the spectrum of a pure M3EH−PPV solar cell. In the case of the thicker CN−ether−PPV layer there is noticeable contribution from the acceptor in the range of 400−500 nm. For this combination, the IPCE reached about 29%, which is about 2/3 of the efficiency obtained by using the reference material PCBM (IPCE 44%). The M3EH−PPV:CN−ether−PPV bilayer external quantum efficiency is higher than the best previously reported value with a PPV based acceptor.[7] This device exhibited an open-circuit voltage of 1.3 V and a FF of 31%, yielding a white light energy efficiency under AM 1.5 standard conditions of 1.34%. We attribute this high efficiency in part to good electron transporting properties of CN−ether−PPV. More details on M3EH−PPV:CN−ether−PPV devices are contained in an earlier publication.[12] However, an external quantum efficiency of ca. 30% is still well below the degree of exciton quenching observed for the M3EH−PPV:CN−ether−PPV bilayer structure. On the basis of our recent time-resolved experiments, we propose that geminate pairs formed at the heterojunction might recombine via exciplex formation[12] in competition to the dissociation into free carriers.

Table 2. Typical Device Parameters of the Optimized M3EH−PPV:Acceptor Devices Investigated

acceptor	V_{OC} (V)	FF (%)	IPCE (%)	ECE (%)
PCBM	0.73	50	43.1	1.5
CN−ether−PPV	1.30	31	28.9	1.3
CN−PPV−PPE1	1.51	25	19.4	0.6
CN−PPV−PPE2	1.51	23	23.0	0.6

The reference devices with PCBM as acceptor reached an open-circuit voltage of 0.73 V, a fill factor of 49.6%, and an overall energy efficiency of 1.57%. This efficiency is significantly higher than the values obtained for bilayer devices based on PCBM and MEH−PPV or MDMO−PPV as hole acceptors.[19,20]

The open-circuit voltage of CN−PPV−PPE acceptor based devices is ca. 1.5 V, which is ca. 0.2 V higher than the open-circuit voltages found for CN−ether−PPV-based solar cells. However, because of the small fill factor and the lower IPCE, the energy efficiency is only 0.6% in both cases. The larger V_{OC} for the CN−PPV−PPE-based devices can be attributed to the smaller LUMO offset between the CN−PPV−PPE copolymer and M3EH−PPV. In fact, the difference in V_{OC} matches well the difference of the LUMO energy levels of CN−ether−PPV and of the CN−PPV−PPE polymers. When the corresponding values for PCBM are included, a linear decrease of the open-circuit voltage with decreasing LUMO value is found, as is shown in Figure 7. These findings are similar to the linear correlation found when using different fullerenes in combination with MDMO−PPV.[21] On the other hand, increasing the LUMO level of the electron acceptor will reduce the energy available for the electron to dissociate from the hole on M3EH−PPV. For the M3EH−PPV:CN−PPV−PPE copolymer system, the LUMO offset is only 0.3 V, quite comparable to values reported for the exciton binding energy of conjugated polymers. In this case, the only moderate quenching of the M3EH−PPV emission upon coating with CN−PPV−PPE might be due to inefficient exciton dissociation. In contrast, the offset of 0.44 eV for CN−ether−PPV was sufficient to split 95% of the excitons. Apparently, the CN−ether−PPV LUMO level is closer to the optimum in combination of M3EH−PPV. These findings lead to the conclusion that the exciton binding energy is around 0.3−0.4 eV in M3EH−PPV.

Summary

We investigated the influence of different acceptor polymers with different LUMO levels on the PL and photovoltaic efficiencies of M3EH−PPV:acceptor bilayer structures. It was found that with an increasing offset of the LUMO levels of M3EH−PPV and the acceptor the degree of PL quenching increased. While the energy offset of 0.44 eV between M3EH−PPV and CN−ether−PPV was sufficient to split 95% of excitons, the offset of 0.3 eV as for the M3EH−PPV/CN−PPV−PPE pair led to a dissociation of only 50% of the excitons. On the other hand, because of the smaller offset in LUMO levels, higher open-circuit voltages of about 1.5 V could be achieved with the CN−PPV−PPE-type acceptors, but the charge transport in these polymers seems to be far from optimum as shown by the strong decrease in the fill factor for thicker layers.

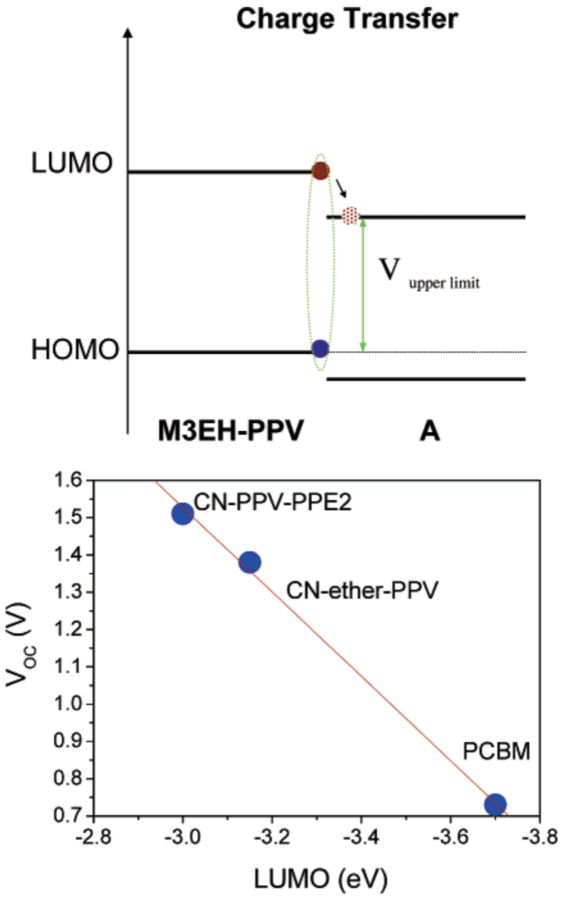

Figure 7. Dependence of open-circuit value on the LUMO energy of the acceptor. The upper limit for it is given by the difference of the HOMO of the donor and the LUMO of the accepting polymer. The V_{OC} is plotted against the energetic position of the LUMO level of the acceptor, and a linear best fit is added.

The bilayer device based on CN−ether−PPV reached an energy efficiency of 1.34% under white light illumination. The small influence of the CN−ether−PPV thickness on device parameters indicates good transport properties in this acceptor material.

Experimental Methods

Preparation. An $\sim$50 nm thick layer of poly(ethylene dioxythiophene) doped with poly(styrenesulfonic acid) (PEDOT:PSS) was spin-coated at 2400 rpm onto commercial glass substrates covered with indium−tin oxide (ITO, 13 ohm/square). The PEDOT:PSS films were dried on a hot plate under a nitrogen atmosphere for 30 min at 170 °C (transmission glass/ITO/PEDOT $>$ 90% from 380 to 650 nm). After coating with M3EH−PPV, the substrates were annealed in a nitrogen atmosphere at 140 °C for 30 min. The second (acceptor) layer was coated from a xylene solution. The devices were completed by evaporating a 25 nm Ca layer protected by 100 nm of Al at a base pressure of 2×10^{-6} mbar. The effective solar cell area as defined by the geometrical overlap between the bottom ITO electrode and the top cathode was 0.25 cm^2. All device preparation and characterization were performed under a nitrogen atmosphere. The thicknesses of the electron acceptor layers were calculated from the absorbance of the bilayer after deconvolution, representing an average thickness.

Device Characterization. The incident photon to electron conversion efficiency (IPCE) as a function of wavelength was measured with an Oriel 150 W Xe lamp in combination with an Oriel Cornerstone 260 monochromator. The number of photons incident on the device was calculated for each wavelength by using a calibrated Si diode as reference.

Spectroscopy. Steady-state fluorescence spectra were measured with Perkin-Elmer LS 55 luminescence spectrometers. The excitation was incident at an angle of 60° on the glass surface, and the emission was recorded in reflection at an angle of 30° with respect to the surface normal.

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