

Dependence of Polymer Hybrid Photovoltaic Performance on Donor-Acceptor Morphology

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In this paper, we present our experimental and numerical studies on polymer-polymer and polymer-inorganic hybrid photovoltaic cells as the donor-acceptor morphology evolves from sharply defined layers, to partial blends and finally homogeneous blends. Results are compared for polyphenylene-vinylene (PPV) polymer donors and a variety of electron accepting materials, including CN-ether PPV, PCBM, and titanium dioxide. We show that optimal device performance is achieved by combining blended and layered structures and by tuning exciton generation rate position by controlling thickness.

Experimental: Devices are fabricated inside an inert glove box atmosphere by spin casting the polymer hybrid solution onto a prepatterned ITO on glass substrate, that has been coated with the appropriate electron and or hole-transporting layer, and then evaporating the top electrode. The ITO is either precoated with a titanium oxide sol-gel layer (sintered at 400 C) or a PEDOT-PSS layer, and the evaporated top electrode is either Au or Al, respectively. Flat band diagrams for the two structures are shown in Fig. 1. J-V curves in the dark and under white-light conditions (100 mW/cm²) were taken inside the glove box. Absorption and steady state PL measurements were taken using Varian and Perkin Elmer spectrometers. Additional steady state and time-resolved PL measurements were taken at NREL.

Device Performance:

In Figure 2a, typical current-voltage (J-V) curves for optimized polymer hybrid blend and layered devices are shown, revealing a more than 3x improvement in J_{sc} over neat M3EH-PPV films on TiO₂ and 13x over M3EH-PPV on PEDOT for polymer-polymer blends. Polymer-PCBM blends results in a further 4x enhancement. Optimized devices had film thickness ~ 30 ± 5 nm, except for polymer layers for which the best device has at thickness of 20 nm M3EH-PPV /50 nm CN-ether-PPV. Blend performance was optimal at 50% and 80% blend wt% for polymer and PCBM blends, respectively. Figure 2b and c show changes in the J_{sc} and fill factor with blend wt%. For polymer blends, the fill factor is limited by poor transport in CN-ether-PPV. Both the fill factor and J_{sc} increase in PCBM as electron transport improves with increase PCBM wt%.

Numerical Simulations:

A quasi-1D model was developed to model the performance of both layered and blended PVs. For blends, a change between phases is allowed at every position throughout the device, and blending at layer interfaces is modeled using mass diffusion into the adjacent layer with 100% being a

homogeneous blend, as described previously [2]. As shown in Fig. 3a, the power efficiency is a strong function of the blend fraction and mobility, and the best performance is achieved for 67% blend fraction. Layered structures (0%) only obtain a power efficiency of <3% due to poor exciton dissociation through the bulk. The decrease in V_{oc} with increasing blend fraction is due to a decrease in the role of the diffusion counter-current in blends. Excellent qualitative agreement between experimental and simulation are obtained for both layers and blends (Fig. 3b shows layer results), with quantitative differences due to uncertainty in mobilities. Fig. 3c reveals that optical reflection /interference effects can result in large differences in exciton generate rate near interfaces and is a determining factor optimizing the performance of layers.

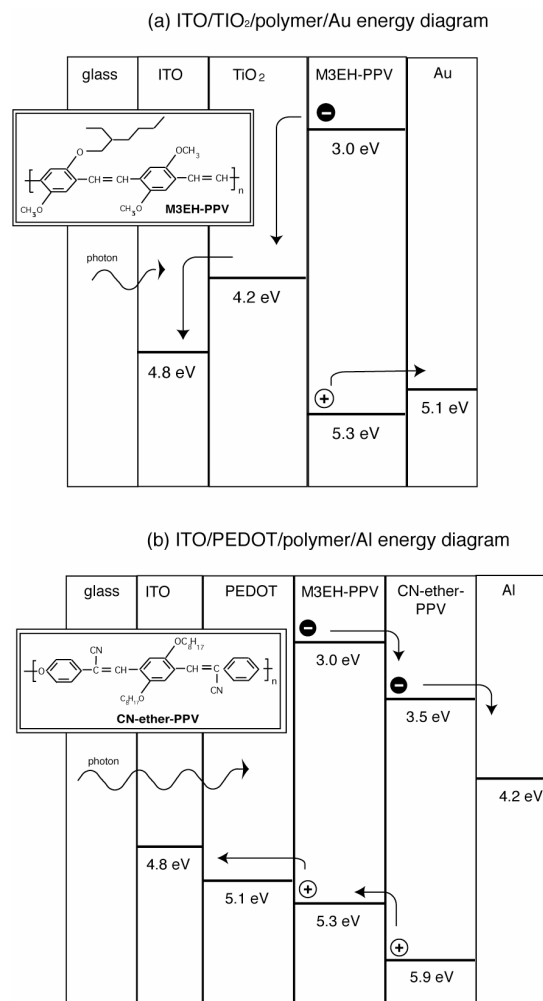


Figure 1: Energy Level diagrams [1].

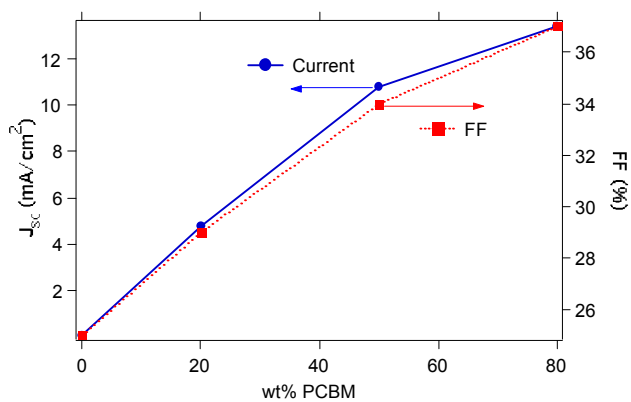
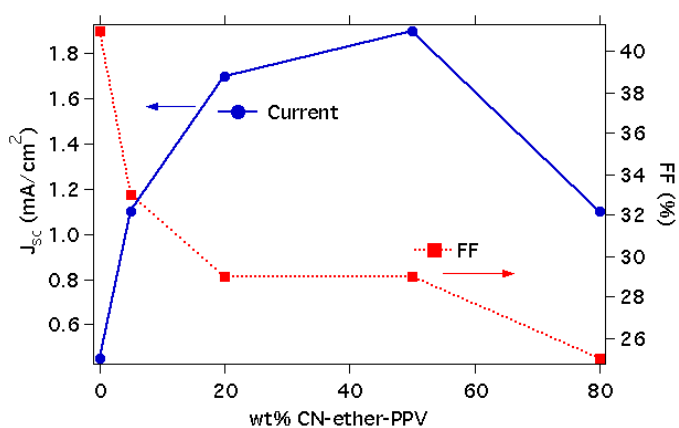
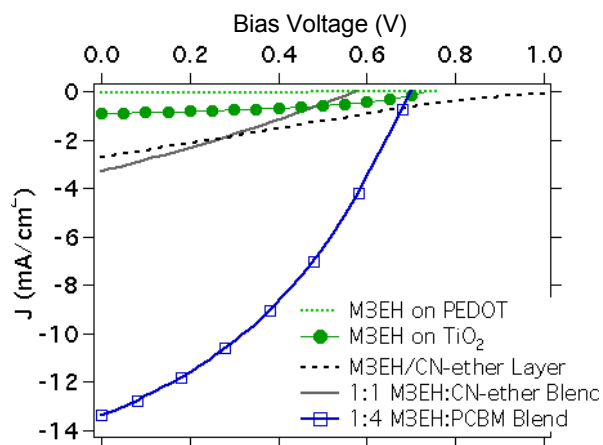


Figure 2: (a) J-V curves for polymer PVs with varying electron acceptor and morphology. (b) J_{sc} and FF as a function of CN-ether-PPV, and (c) PCBM blend wt%. CN-ether-PPV is limited by low electron mobilities which results in low fill factors with increasing wt%.

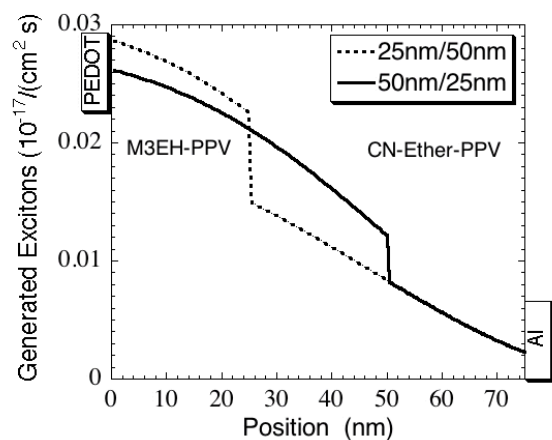
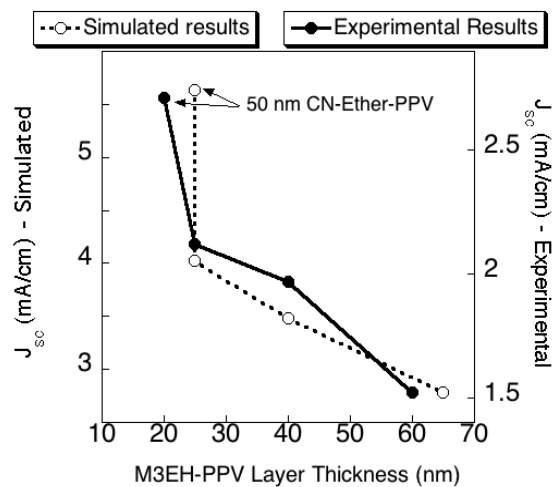
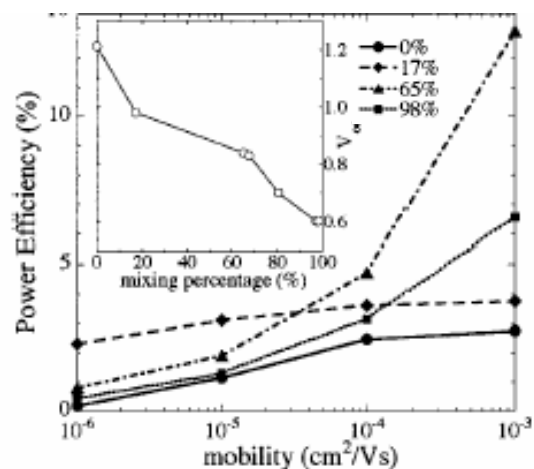


Figure 3: (a) Power efficiency and V_{oc} as a function of blend fraction for polymer/polymer blends [2], (b) comparison of simulations and experiment for layers. (c) exciton generation rate for two different layer thickness with 25 nm/50 nm resulting in significantly more exciton generation at the polymer dissociating interface [3].

Steady State Photoluminescence

The steady state PL is strongly quenched for all layers and blends, with values ranging from 70% for polymer layers to 95% for PCBM/polymer blends. For polymer/polymer systems, the PL and time-resolved data indicate the presence of exciplex formation that can result in exciton scavenging and increased dissociation. For PCBM blends, exciplex formation is not observed; however, a large shift in PL spectrum occurs, due to an effective dilution in the M3EH-PPV at high PCBM wt%.

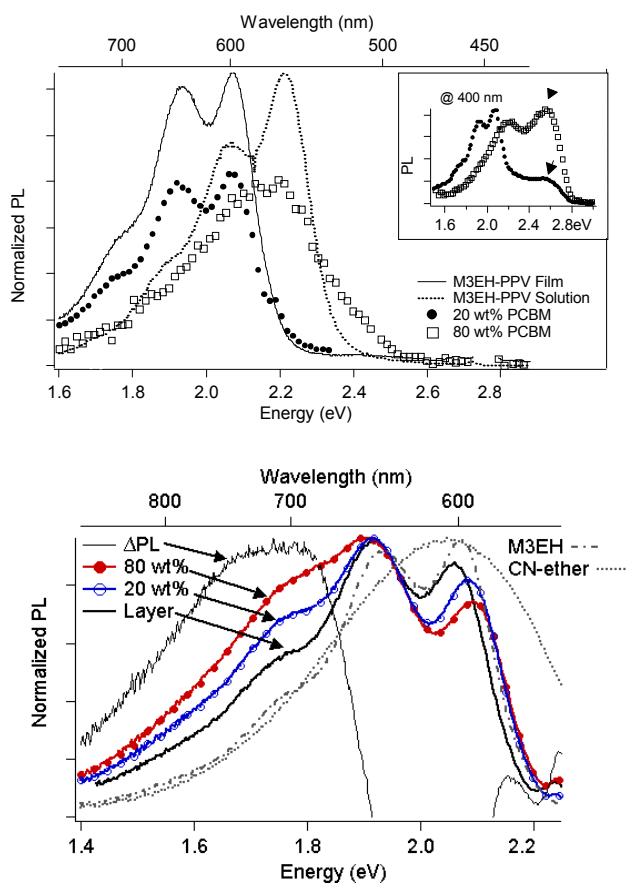


Figure 4: (a) Normalized PL for blend and layered films excited at 540 nm. Δ PL is a subtraction of the M3EH-PPV spectrum from that of the 80% blend, revealing exciplex formation in polymer blends. (b) Normalized PL for PCBM blend

Time Resolved Photoluminescence

In Table 1, the decay times for the pristine polymers as well as the blended and layered structures are summarized. All blends and layers show a very rapid decay time (<0.05 ns). A new decay time of 2.0 ns for polymer/polymer layers and blends is attributed to the formation of an exciplex state. Despite dramatically enhanced device performance in PCBM blends, the quenching percentage for the dominant decay time of M3EH-PPV (0.20 ns) is $\sim 75\%$ for both systems, suggesting that charge transport plays the critical role in improved performance for PCBM blends. This result is further reinforced by the result that 20 wt% PCBM has a shorter decay time (0.02 ns is near instrument response function) even though the power efficiency, η , is much lower.

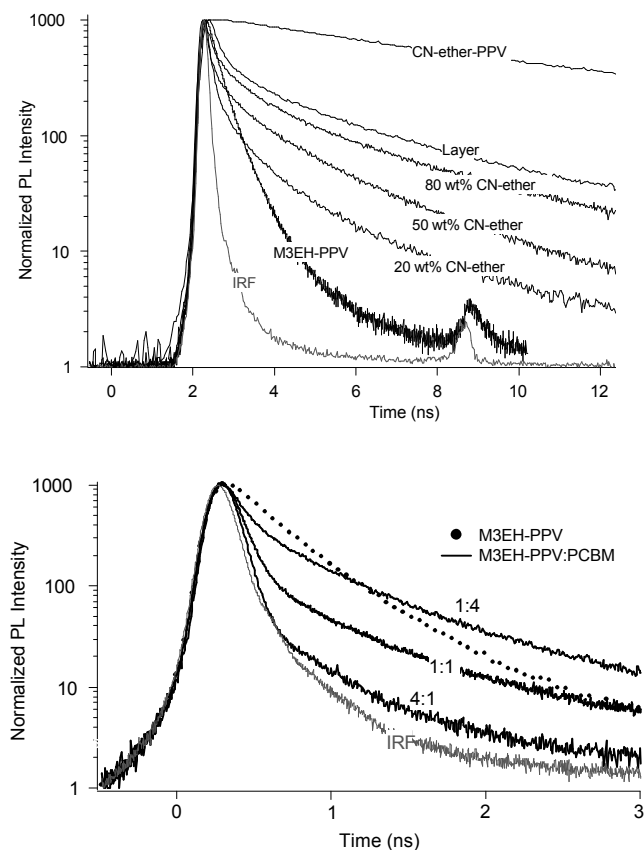


Figure 5: Time-resolved PL data for (a) polymer-polymer layers and blends and for PCBM blends. Note that all the layers and blends exhibit an initial faster decay than the neat M3EH-PPV film although the average decay time is longer (except for 20 wt% PCBM blend). The CN-ether-PPV decay components are readily quenched, but the ~ 0.45 ns M3EH-PPV decay remains.

Table 1: Summary of decay times of CN-ether-PPV and PCBM blends compared to neat film results.

	Film	η	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_{ave} (ns)	Q
<i>Pristine polymers</i>	M3EH-PPV	0.36%	0.20 (43%)	0.45 (53%)	1.7 (3%)	0.38	
	CN-ether-PPV	N/A	0.30 (2%)	4.3 (26%)	12.2 (73%)	10.0	
<i>CN-ether blends</i>	50 wt% CN-ether w/ M3EH-PPV	0.86%	0.05 (51%)	0.46 (20%)	2.0 (22%)	1.0	75%
	M3EH/CN-ether layer	0.89%	0.05 (39%)	0.46 (17%)	2.0 (27%)	1.8	75%
<i>PCBM blends</i>	80 wt% PCBM w/ M3EH- PPV	3%	0.05 (36%)	0.50 (49%)	1.9 (16%)	0.6	75%
	20 wt% PCBM w/ M3EH- PPV	0.9%	0.02 (73%)	0.36 (14%)	1.3 (13%)	0.24	90%

Conclusions:

In summary, the best device performance is observed for PCBM/polymer blends; however, the device with the highest power efficiency also had the longest average decay rate, indicating the importance of charge transport on device performance. Simulations reveal that as the blend mixing percentage increases, the exciton dissociation increases and the diffusion counter-current decreases for all systems, resulting in substantially greater short circuit currents but reduced open circuit voltages. Blended structures are more sensitive to mobility than layers due to bimolecular recombination throughout the bulk, and layer performance is particularly sensitive to relative film thicknesses due to optical reflection effects that result in substantial changes in the exciton generation rate next to dissociating interfaces. Time-resolved PL reveals that decay times were substantially shorter for polymer-polymer blends vs. layers with charge transfer occurring to an intermediate exciplex state for both. Although all systems revealed lack of complete quenching, optimizing the blend morphology for charge transport, rather than exciton dissociation, was more important for achieving high power efficiency. Overall, the experimental power efficiency was limited to ~3% by the low charge (hole) mobilities and control over blend morphology; however, our numerical model indicates that power efficiencies >12% can be achieved with currently available materials for partially blended structures when the zero-field charge mobilities approach $10^{-3} \text{ cm}^2/\text{Vs}$

References:

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