

Perylene/Polymer Composite Solar Cells

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Abstract

Perylene/Polymer Composite Solar Cells ASHLEY SALOMON (Massachusetts Institute of Technology, Cambridge, MA 02139) ERULF (National Renewable Energy Laboratories, Golden, Colorado)

Due to high cost electricity from power plants and from commercial solar cells, scientists are seeking out alternative materials to inorganic conventional semiconductors such as organic molecules and polymers that are more easily processed and are potentially less expensive to use in large area devices. Liquid processability and atmospheric processing could lead to a new generation of large area low cost devices. In this study, we fabricate novel organic solar cells containing a layer of evaporated perylene molecules (either PPyEI, or PBI) and a layer of spin coated M3EH-PPV semiconducting polymer sandwiched between ITO and gold contacts. In this ITO/perylene/polymer/Au device we demonstrated a power conversion efficiency of up to 1.3% in ITO/PPyEI/M3EH-PPV/Au composite solar cells, and up to 1.25% in ITO/PBI/M3EH-PPVAu composite solar cells with currents as high as 6 mA under the illumination of one sun. By varying thickness of the perylene layers, fabricating control devices with only perylene, and fabricating a “reverse” device of ITO/PEDOT/M3EH-PPV/PBI/Al we determined, to some extent, the nature of the device physics. It is probable that, the exciton dissociation occurs mainly at the polymer/perylene interface and the perylene plays a greater role as a free carrier producer than the polymer. We also determined that the diffusion length of PBI is longer than that of PPyEI in these devices. We expect further increases in the device performance and efficiency when the thickness of the perylenes and polymer layers are both optimized.

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Introduction

Between the years 2020 and 2060, nonrenewable fossil fuels are expected to dwindle appreciably. Fossil fuels also contribute to the greenhouse effect and, hence, global warming which is thought to be caused by excessive carbon monoxide, chlorofluorocarbons (CFC's), and sulfur dioxide emissions. Thus, the search for inexpensive, environmentally sound, and renewable energy sources is an important step toward an alternative to fossil fuels. One option for a renewable energy source is the direct conversion of sunlight. Solar cells, devices that convert light into electricity, are useful as a renewable energy source because, unlike wind, geothermal, and hydroelectric power (which require windy areas, hot water reservoirs, and fast rivers, respectively) solar cells can be used in a larger range of locations. Even in regions where the sky is often cloudy, batteries can store the energy produced from solar cells while the sky is sunny for use at night and on overcast days.

Currently, solar cells are made chiefly from inorganic (non-carbon-based) semiconductor materials such as silicon, amorphous silicon and gallium arsenide. Silicon solar cells have demonstrated efficiencies up to 29%, and gallium arsenide solar cells up to 33%. However, commercial Si solar cells range between 12 and 15%. Solar cell fabrication using these materials is expensive (requiring very clean processes) so savings associated with using solar energy rather than fossil fuel sources for electricity could take more than a decade. Within the first many years of use, solar energy currently costs the equivalent of 20-25 cents per kWh, compared with 8 cents per kWh for conventional electricity. Thus, a key research area is to look for materials that are cheaper to fabricate and that require less energy to produce.

Potential alternatives to silicon are a variety of semiconductor thin films, the Gratzel cell, and organic materials, such as polymers and perylenes (photoconductive organic molecules). Polymer/organic molecule solar cells, are not yet efficient enough to compete with inorganic solar cells; the highest efficiency achieved to date is 2.5% [1], however, organic materials have many desirable aspects, including low-cost fabrication, less toxic manufacturing techniques, the possibility of lightweight, flexible panels, and the possibility of techniques to literally print out the solar cells layer-by-layer in an inexpensive manner.

Originally, polymers were used in electronics as insulating and dielectric layers. The discovery in 1977 of the first intrinsically conducting polymer, doped polyacetylene [2], established new uses for polymers as electronic materials, including light-emitting diodes and photovoltaics.

Like polymers, perylene organic molecules such as perylene bis(phenethylimide), can also be conducting, and they can be used to make inexpensive, flexible devices. Perylenes are derived from a common, inexpensive automobile paint pigment[3] They are the most studied class of organic semiconducting molecules, with possible applications in electroluminescent displays and photovoltaics.

Our research group is studying methods to fabricate organic polymersolar cells layer by layer. The general device geometry is as follows. First, a transparent conducting oxide is deposited as a bottom contact; second, an organic semiconducting molecule layer, such as PPyEI, is evaporated, and then a polymer layer is spun onto the PPyEI; and, finally, a second contact is deposited on the polymer. From our work it appears that the PPyEI/polymer interface serves to disassociate electrons from the excited electron-

hole pair (called an exciton) produced by sunlight in both the PPyEI and the polymer. These disassociated electrons are collected to produce current.

Background: Conducting Polymers and Conducting Perylenes

A polymer is a long chain of repeating subunit molecules. The ones that we are interested in have predominately carbon backbones (the long interconnected main structure of the polymer). Conducting polymers function through the π conjugation of the carbon-carbon double bonds along the polymer backbone (Figure 1). The molecular structure of these conjugated polymers contains carbon-carbon bonds formed from sp^2 hybridized orbitals. The free p_z orbitals are delocalized out of the plane of this carbon chain, forming effectively alternating single and double bonds between the carbon atoms (Figure 2).

These delocalized bonds would act in a similar fashion to metallic periodic lattices with one free electron per site, forming half-filled conduction bands. However, there is a difference in the bond lengths of the single and double bonds between carbon atoms along the polymer that prevents the development of true semiconductor like bandstructure..

Single bonds are longer than the double bonds, producing a perturbation in the electronic states of the polymer and breaking the symmetry of the “lattice,” thus creating a forbidden energy bandgap. This bandgap is similar to the bandgaps of inorganic semiconductors such as silicon and gallium arsenide, leaving a filled conduction band and an empty valence band. In polymers, the valence band is referred to as the highest occupied molecular orbital (HOMO level) and the conduction band is referred to as the

lowest unoccupied molecular orbital (LUMO level). The development of the band structure produces semiconductor behavior at certain temperatures [4].

Polymer semiconductors are different from inorganic semiconductors in that when a photon enters a polymer solar cell device, a number of processes can occur including the formation of excitons and the production of electron hole pairs (as in typical semiconductors). It is the former process that seems to dominate. When a photon enters a polymer solar cell, an exciton -an electrically neutral excited electron-hole pair- is produced. In order to dissociate the exciton into a free electron and free hole (necessary for the creation of external current) an interface is formed with the polymer that has an energy level below the electron's energy level, but above the hole's energy level. In other words, excitons are likely to dissociate from a region of high electron affinity to low electron affinity. This interfacial exciton dissociation appears to be the dominant mechanism for photocurrent production in most organic photovoltaics [5].

The primary polymer used in this study was M3EH-PPV (Figure 3), which is hole transporting when photoexcited. M3EH-PPV absorbs photons primarily in the UV and visible spectrum (Figure 4) which displays a typical absorption curve plotting absorption versus wavelength. In the polymer, the hole, or lack of an electron, can travel across the polymer by the polymer backbone (Figure 2). Conductivity in a polymer is presented by the following formula:

$$\sigma = n e \mu$$

where n is the number of free carriers (electrons or holes), e is the charge in coulombs, and μ is the mobility of the hole or electron.

Perylene bis(phenethylimide) (PPyEI) and Perylene Benzimidazole (PBI) are semiconducting organic molecules [5]. Like the semiconducting polymers, photocurrent generation in devices containing PPyEI, or PBI appears to be controlled dissociation of excitons at an interface[5]. Hence, charge carrier production is dependant on mechanisms to dissociate the exciton created by photon absorption. PPyEI and PBI are n-type semiconductors (ie electron transporters) [6] and interfaces between ITO (Indium Tin Oxide) and PPEI (the precursor of PPyEI) are known to be exciton dissociating [6].

Background: Perylene/Polymer Solar Cells

Both perylences PPyEI and PBI and the polymer M3EH-PPV act as exciton producing photoconductive materials that require some form of interface with a second material so as to dissociate the excitons into electrons and holes. Typically this requires an energy level below the conduction band. In this research, we fabricated and tested a layer-by-layer deposited devices of perylene and M3EH-PPV sandwiched between an ITO and gold (Au) electrodes (Figure 5).

In this device, the polymer/perylene interface itself appears to dissociate the excitons, as opposed to a device that contains just PPyEI, PBI, or just polymer where dissociation occurs at the transparent conducting oxide. Organic photovoltaics often have optimum performance when when the organic films are thin [1]. If the organic layer is too thick, the high electrical resistance of the semiconductors and their low charge carrier mobilities will lower the exciton transport lengths and dissociation rates [1]. If the device is too thin, however, pinholes creating shorts from the Au to the ITO may occur. Using this information, and varying the thickness of PPyEI and PBI in the solar cell device of Figure 5, we created solar cells of various efficiencies and established potential

mechanisms for the photovoltaic effect. We also fabricated some devices with PEDOT layers added to enhance the performance of the contact organic interface. This paper outlines the first recorded fabrication of such a device, and potential physical mechanisms for the device's function.

Materials and Methods

Solar cell devices of the structure shown in Figure 5 (ITO/perylene/M3EH-PPV/Au) were fabricated in a layer-by-layer process. The initial substrate was a patterned ITO film on glass. These slides were cleaned by first rinsing with ethanol and then dipping into a KOH-Isopropanol base bath, with a final rinse in DI water, and then blown dry. For the perylene layer, 3mg of PPyEI was weighed, placed in a quartz boat, and placed in the evaporator. The evaporator was pumped down to 8×10^{-6} mtorr and the PPyEI was evaporated onto the patterned ITO glass slides at ~ 9 amps of current. The M3EH-PPV polymer was dissolved in chlorobenzene in a 0.8% weight-to-volume ratio of polymer to solvent, and then heated at 100°C for 5 minutes. Immediately after dissolution, 50 μl polymer/solvent solution was spin-coated at 2.5 krpm. For the Au contact, the samples were placed once more in the evaporator, which was pumped down to 8×10^{-6} torr. Au was evaporated at 45 amps until the contacts were thick enough to become reflective. The same process was carried out for the solar cells with PBI, although $\sim 4\text{mg}$ of PBI was placed in the quartz boat for evaporation, and evaporated at ~ 11.5 Amps.

PPyEI and PBI thicknesses were varied by changing evaporation times. In order to determine thickness, a non-ITO patterned glass slide was placed in the evaporator at

the same time as the ITO-patterned slide and then measured with a spectrophotometer.

The following thicknesses were used in the devices:

PPyEI : 9.4nm 50nm 80nm
PBI : 10nm 22nm

Two other devices were made, one without M3EH-PPV and one without any perylene to serve as controls for the combined device. A ITO/PEDOT/M3EH-PPV/Al device was also made in a similar manner as that above. The PEDOT was spin coated onto the ITO at 2.5 krpm with the goal of enhancing hole conduction through the ITO contact.. An ITO/PPyEI/Al device was made with aluminum rather than gold as the top positive contact.

In order to determine the degree of polymer activity as a free carrier producer in the device, a reverse device was made such that light would enter the polymer before the perylene (ITO/PEDOT/M3EH-PPV/PBI/Al). For this device, first a layer of PEDOT dissolved in a water base was spin coated at 2.5 krpm on an ITO glass slide. Next, a layer of M3EH-PPV at .8% weight to volume ratio (polymer to chlorobenzene) was spun on at 2.5krpm (30nm layer) and at 4.5 krpm (23nm layer). The PBI was evaporated as before at 8 amps to form a 54.8nm thick layer, and Al was evaporated as before at 45 amps.

All devices were tested for short-circuit current output (I_{SC}) and open-circuit voltage output (V_{OC}) in darkness and in what is the equivalent of one sun illumination. Devices were then measured with a photo-action spectrometer in order to determine their external quantum efficiency vs. wavelength.

Results

The best efficiency for power conversion was on the order of 1.3% for the PPyEI devices, and 1.25% for the PBI devices. These values are relatively high for polymer solar cells (the maximum efficiency reported on the order of 2.5% worldwide).

A general trend of increases in the fill factor as a function of increased PPyEI thickness (where the polymer is held constant at ~40nm) was observed. Although the V_{oc} remains relatively constant from device to device, the I_{sc} decreases with increasing thickness (Figure 6). From 9nm to 49nm, the current falls by a factor of ~30%, while the thickness change of 9nm to 80nm indicated a 48% drop in current (Figure 6). The efficiency of power conversion dropped from 1.3% to 0.7% for thicknesses of 9nm to 80nm, respectively. Fill factors also increase with increasing thickness.

Photoaction spectra of the three devices in Figure 6 were taken. As the thickness of PPyEI increases, the external quantum efficiency (EQE) on these devices decreases (Figure 7). At ~595nm, 20% of the light is absorbed for PPyEI (.2 EQE), however the 10nm device has almost .2 EQE at that wavelength, as well. According to this data, at 595nm the device has almost 100% internal quantum efficiency (Figure 7).

The two PBI devices (thickness ~10nm and ~20nm) revealed an effect the reverse to that of the polymer devices with PPyEI. As the thickness increases, the EQE (Figure 8) and the current intensity increases. According to Figure 8, the PBI has a definite absorbing and photoactive effect at higher wavelengths (the M3EH-PPV absorption ends around 695nm, yet the two devices still continue to absorb past this, in the realm of PBI absorption). Fill factors also decreased with decreasing thickness.

The absorption data of the three PPyEI/polymer devices was used to graph the percent transmission of light through each thickness of perylene. The transmission data represents what percentage of light is making it to the junction between the PPyEI and the polymer. According to Figure 9, for the 9.4nm PPyEI thickness, 75% of the light makes it to the polymer at 495nm. This is significant because highest light absorption of perylene is observed at ~495nm. This information suggests that the polymer is acting as more than a dissociating surface. In this case, as a free carrier producer.

The ITO/PPyEI/Al device exhibited no photovoltaic effect. Open circuit voltages under one sun of light were on the order of -.0002 Volts, and maximum currents were reported to be $8 \mu\text{A}/\text{cm}^2$. The ITO/PEDOT/M3EH-PPV/Al device (Figure 10), under bias with one sun of light produced open circuit voltages as high as .4 Volts, however currents were low ($160 \mu\text{A}/\text{cm}^2$) and conversion efficiencies were only of the order of .018%. These devices revealed very little photovoltaic effect.

Reverse solar cells made with ITO/PDOT/M3EH-PPV/PBI/Al were found to be half as efficient as the ITO/perylene/M3EH-PPV/Au devices, due to the lower short circuit current obtained, despite the high open-circuit voltages on the order of .67 Volts for the 30nm polymer layer, and .71 Volts for the 23nm polymer (Figure 10). Fill factors were found to be relatively high, on the order of 40%.

Discussions and Conclusions

PPyEI/ M3EH-PPV composite solar cells produce conversion efficiencies up to 1.3%, with high short circuit currents produced up to 5 mA and open-circuit voltages up to .7 Volts. PBI/M3EH-PPV composite solar cells produce conversion efficiencies up to 1.1% with short circuit currents as high as 6mA and open-circuit voltages up to .5 Volts.

There remains considerable room for device improvement. Thus it is likely that once the perylene thicknesses are optimized by trial-and-error, and the polymer thickness is optimized as well, these devices will be more efficient and produce higher open-circuit voltages and higher currents. Varying the thickness of the perylene layers in the bi-layer cell has yielded information about possible mechanisms for the device physics. In Figure 8, as the thickness increases, the EQE decreases abruptly in the 450-600nm wavelength of the spectrum. As the PPyEI becomes thicker, less light will transmit to the PPyEI/polymer interface and thus less excitons are produced and dissociate there. The ITO likely does not play an important role as an exciton dissociation surface for the PPyEI because of this effect. If the ITO was a good exciton dissociator, then this drastic dip in the photo-action spectra would likely not be observed.

As the PBI thickness increases in the PBI/M3EH-PPV devices, the EQE, current, and conversion efficiency increase. For the PPyEI devices, however, device performance decreases with increasing thickness. These findings would suggest that PBI has a significantly longer exciton diffusion length than PPyEI.

Transmission of light through the perylene and into the polymer is ~75% at the peak absorption range of 495nm for the polymer. Although it is difficult to determine just how much a role the polymer is playing as an exciton/carrier producer for this device, it is now known that a significant amount of useful light is at least reaching the polymer.

The control device made with just perylene and no polymer revealed no photovoltaic effect. This further supports the assumption that the ITO does not act as a dissociating surface and that the polymer works very well as one.

The reverse device (ITO/PEDOT/M3/PBI/Au) produces efficiencies half that of the perylene/M3 devices, with high open-circuit voltages (on the order of .7 Volts) and lower currents on the order of 1.5 mA. As less light is reaching the perylene in this arrangement, it is not surprising that the devices are not as efficient. As the ITO/PEDOT/M3EH-PPV/Al device was able to produce a minute, yet present photovoltaic effect without any perylenes, it is quite likely that the polymer in this device is generating current (excitons that dissociate), however the degree to which this is occurring is, as of yet, unknown.

The reverse ITO/PEDOT/M3EH-PPV/PBI/Au device with the 23nm polymer layer was more efficient and produced slightly higher open-circuit voltages than the same device with a 30nm polymer layer. This finding suggests that the diffusion length of M3EH-PPV is closer to that of 20nm than 30nm.

These findings provide knowledge of where the excitons produced are dissociating, which material (polymer or perylene) is contributing more to the photovoltaic currents, and a means to optimize thickness layers in order to produce the best device.

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References

B.A. Gregg, "Excitonic Solar Cells: Physics and Chemistry of Organic-Based Photovoltaics," National Renewable Energy Laboratory, Golden, CO

C.K. Chiang, C.R. Finder, Physics Review Letters, **39**, (1977) 108

R.A. Cormier, B.A. Gregg, Journal of Physical Chemistry B, **101**, 1997, 11004-11006

Alison Breeze, Doctoral Thesis, "Polymer Solar Cells."

B. A. Gregg, Chemical Physics Letters, **258**,(1996) 376-380

B.A. Gregg, Applied Physics Letters, **67**, 28 August 1995, 1271

Figures

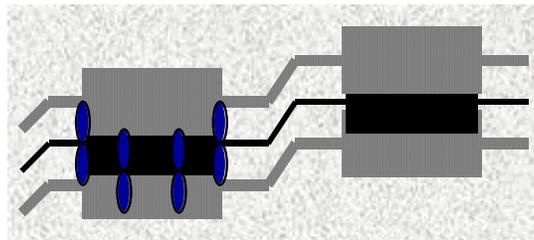


Figure 1: The solid black lines are carbon-carbon bonds. The p_z orbitals are orientated out of the plane of the bonds. Delocalization makes electron transport possible along the pathways shown in grey.

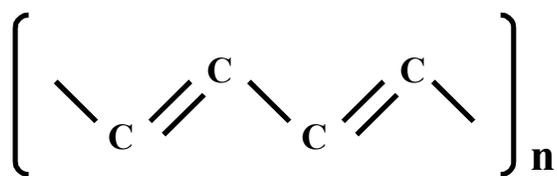


Figure 2: Single and double carbon bonds
 Bond formation and localization

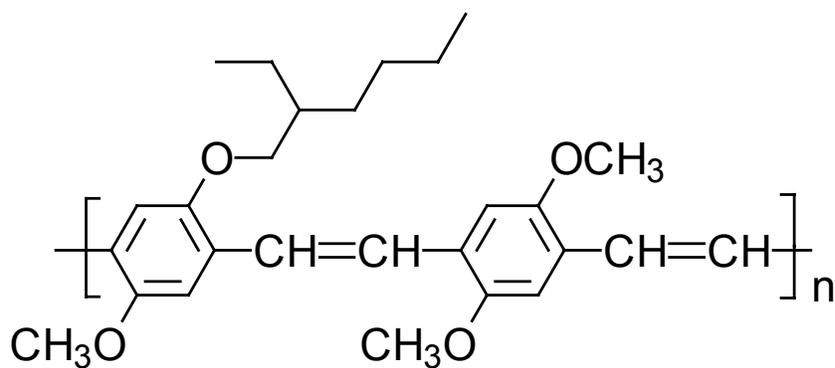


Figure 3: M3EH-PPV is a hole-transporting material once the exciton has been dissociated. The holes move along the p-orbitals in the carbon backbone

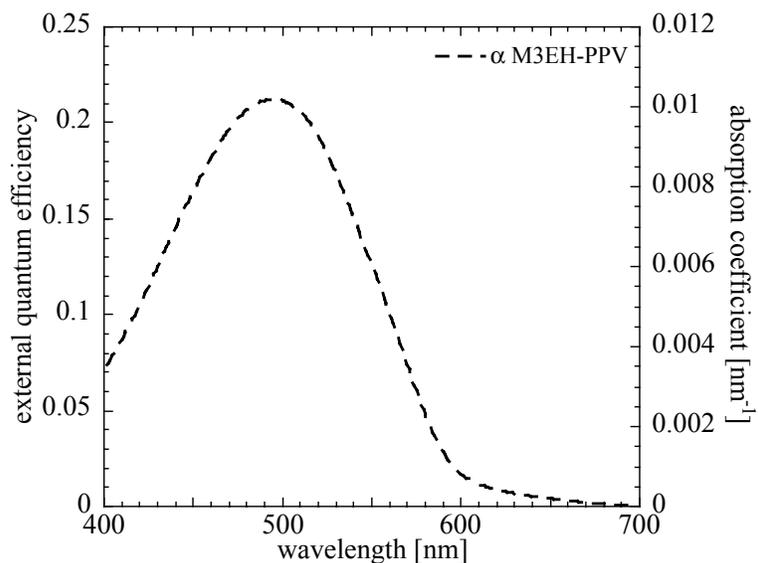


Figure 4: Absorption Spectra of M3EH-PPV

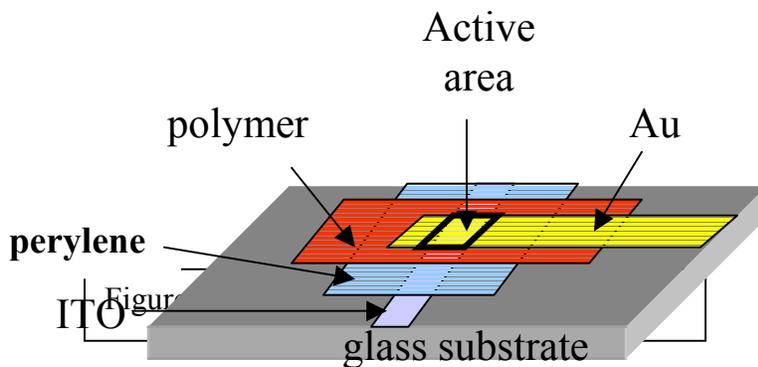
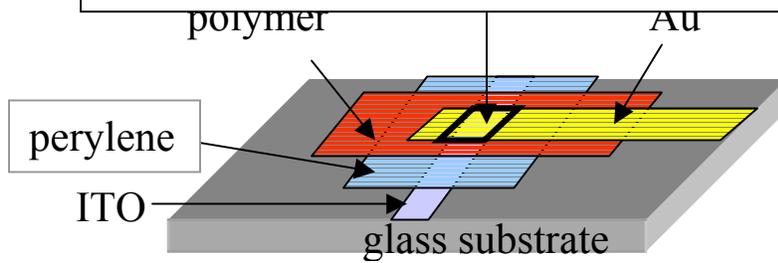


Figure 5: Our glass/ITO/perylene/polymer/Au device. active region occurs where all layers overlap. ITO and Au are contacts.



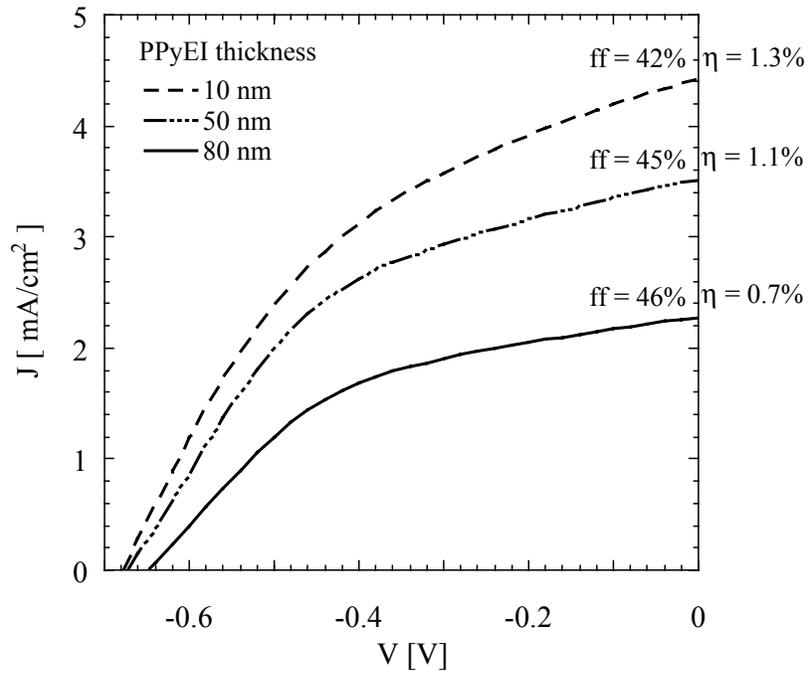


Figure 6: Current vs. Voltage data, efficiency, and fill factor for solar cells with varying PPyEI thicknesses

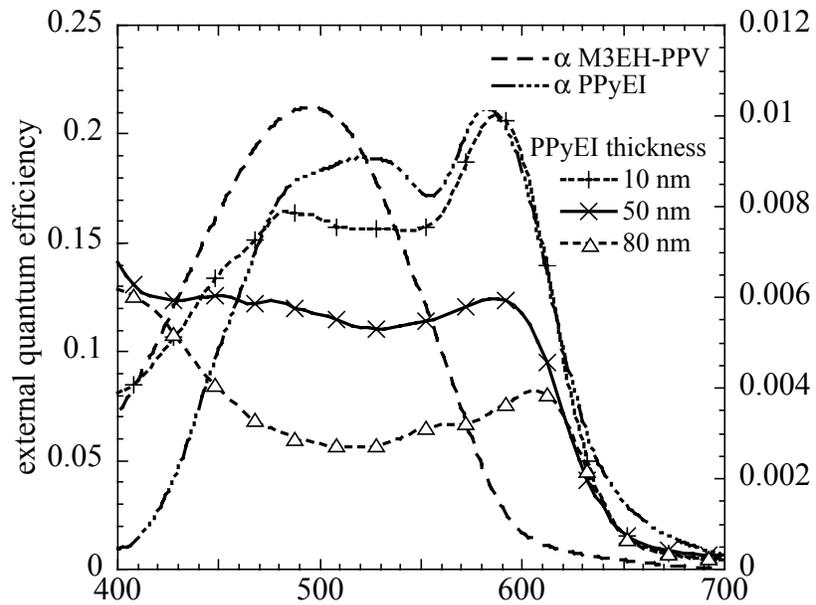


Figure 7: Three different PPyEI/M3EH-PPV devices with different thickness PPyEI layers. PPyEI and M3EH-PPV absorption spectra are incorporated in graph for comparison.

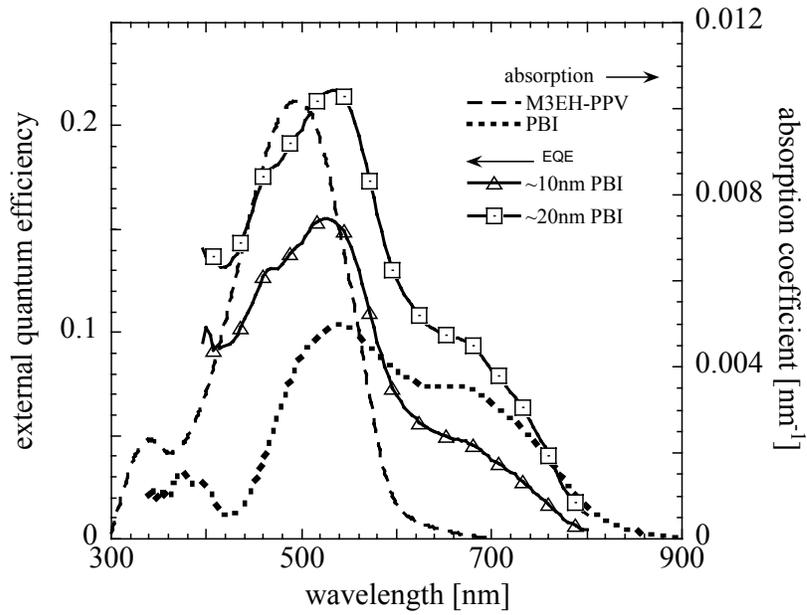


Figure 8: PBI/M3EH-PPV Photo-Action Spectra with M3EH-PPV and PBI absorption curves