P3HT:PCPDTBT:PCBM Multi-polymer single layer solar cells

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Author’s Abstract— OPV efficiencies are limited by their narrow absorption; rather than using tandem architecture to overcome this obstacle, our group combined P3HT and PCPDTBT into a single layer BHJ solar cell that achieved 2.0% PCE. This is 33% higher than the pure P3HT control from this group, proving that multi-polymer solar cells have the potential to outperform their single-polymer components.

Index Terms— bulk heterojunction, integrated circuit, organic photovoltaics, semiconductor device, thin-film solar

I. INTRODUCTION

Solar cells harvest energy by absorbing photons and converting them to electricity. The maximum energy that can be produced by one solar cell depends on its ability to efficiently absorb photons and transfer this energy to mobile electrons. Traditional silicon based solar cells have active layers up to 1mm thick because of their low absorptivity [1]. However, thin film polymer based solar cells absorb much better in the visible spectrum, and use active layers on the order of one thousand times thinner than silicon based cells, greatly reducing material and manufacturing costs [2]. Thin film devices may also be printed inkjet style onto flexible rolls of plastic, whereas working the brittle silicon wafers is a more labor-intensive, costly procedure [2].

Most polymers used in organic photovoltaics (OPVs) have narrow absorption, with full with half maximaums (FWHM) on the order of 200nm [3]. This limits current density and efficiency based solely on the lack of photons in the polymer layer. The standard way to overcome this problem is to make a tandem solar cell, where two single-layer devices with different band gaps are “sandwiched” together. Given the right polymers, it is possible to absorb across the visible spectrum using this method [4]. However, current between the layers must be matched for efficient output, and a transparent cathode must be used; this sacrifices simplicity of design, and makes production more expensive [5].

In order to produce a single layer device that retains the broad spectral response of tandems, our group blended poly [3-hexylthiophene] or P3HT, and poly [2,1,3-benzothiadiazole-4, 7-diy][4,4-bis(2-ethylhexyl)-4H-cyclopenta [2,1-b:3,4-b’[dithiophene-2, 6-diyl]] or PCPDTBT into a single layer solar cell. These devices produced efficiencies over two percent, 33% higher than pure P3HT/PCBM devices fabricated under identical conditions. Furthermore, the EQE and IQE of the blend show that P3HT aids PCPDTBT with charge transport. The result of this study is exciting; it proves the feasibility of multi-polymer, single layer devices.

II. THEORY

Our lab produces bulk heterojunction (BHJ) solar cells, which generate current via the disassociation of electrons and holes at a P-N junction. The term Bulk refers to the active region of a solar cell, and heterojunction refers to the interface between two substances, in this case N-type polymer donor (P3HT or PCPDTBT) and P-type fullerene acceptor (PCBM) materials in the active layer. This type of architecture is used to control the size of microscopic regions of each material within a device. For example, in P3HT:PCBM blends, the ideal region size is about 20nm across (Fig. 5 has an artists representation) [6].

When a photon strikes the polymer, if absorbed, it excites an electron from its Highest Occupied Molecular Orbital (HOMO) state to the Lowest Unoccupied Molecular Orbital (LUMO) state, where it diffuses along the polymer chain for a finite distance; this energetic electron/hole pair is called an exciton. At this point it may de-excite and emit thermal energy, or another photon, which is called recombination. However, if it encounters an interface between donor and acceptor materials, the electron “dissociates” from its hole, flows to the lower energy acceptor (PCBM in our case), and onto the equipotential aluminum cathode. The resulting positive charge moves through the polymer to the conducting

Figure 1: Energy levels for materials used in solar cells, and the path electrons and holes take at a polymer:PCBM interface. All energies are negative, with bandgaps included in green.
PEDOT layer, and then the Indium Tin Oxide (ITO) anode. PEDOT and ITO have higher ground state energy than our polymers, making the transition favorable for a hole (see Fig. 1). This multi-step process is how BHJ solar cells generate current.

P3HT has an exciton diffusion path length of about 10 nm, which is the maximum distance excitons may travel before recombining. This means that for charge extraction to even be possible, the distance between any light absorption occuring and a polymer/PCBM interface cannot exceed 10 nm. Thus an optimally structured P3HT/PCBM device has regions no larger than 20nm across, so excitons in all locations can reach a P3HT/PCBM interface [6]. A main goal of BHJ architecture is to fine-tune these region sizes for optimal charge transport and absorption.

Combining PCPDTBT, P3HT and PCBM into one thin film does several things to device performance. Most importantly, the presence of two donor polymers broadens the absorption of the active layer, capturing more photons that can be converted into electricity. Fig. 2 shows the absorption of both polymers used, as well as the available energy in the solar spectrum. PCPDTBT also has a lower HOMO energy level and a higher Open Circuit (OC) voltage than P3HT, properties also observed in blended devices (Fig. 1) [7].

Hole mobility is a very limiting factor in charge extraction from pure P3HT [13,17]. In PCPDTBT, hole mobility is even less due to low charge lifetime and exciton dissociation efficiency (~70%) [7,17]. Optimized devices have electron and hole mobility on the same order, so efficiency can greatly improve by increasing positive charge extraction in our polymers [17]. Since P3HT’s homo level is in between that of PCPDTBT and the PEDOT conducting layer (Fig. 1), it is favorable for PCPDTBT to locally transfer holes to both P3HT and PEDOT [15]. This increases the probability of hole extraction from PCPDTBT regions where charge would normally collect, reducing recombination rates and boosting short circuit current densities [6,7,15,17].

A useful parameter in solar research is EQE, or external quantum efficiency. It is the ratio of charge carriers collected to incident photons, and can be measured per wavelength, or over a desired spectrum. It is calculated as follows:

$$\text{EQE} = \frac{\text{current}/(\text{charge of 1 electron})}{(\text{total power of photons} \cdot \text{area of cell})/(\text{energy of one photon})} \quad (1)$$

EQE cannot exceed unity, a device with 100% EQE converts every photon striking its surface into harvestable electrical energy. Another useful measure is IQE, or internal quantum efficiency. This quantity is easily calculated by dividing EQE values by the absorbance of the polymer per unit wavelength. This gives the ratio of charge carriers collected to photons absorbed in the polymer. IQE is useful when investigating internal processes during charge generation, since it only considers photons contained in the polymer layer rather than reflected, scattered or transmitted ones. It is also useful for investigating extremely thin films, because of their low absorption and EQE values. Juxtaposing EQE and IQE gives clues about charge carrier dynamics based on how the shapes of the graphs differ, this concept is explained further in the Results and Discussion section.

III. PROCEDURES

A. Device Fabrication

To fabricate polymer solar cells, obtain glass substrates that have an Indium Tin Oxide (ITO) conducting layer pre-deposited onto the surface (Fig. 3). The first procedure is unpackaging the substrates in the dust free area, and cleaning them of all dust, water, and oxygen. After donning gloves, goggles, and a lab coat, remove the wrapper from the substrates and wipe away any large dust particles with a cue tip. Then submerge the substrates in acetone, set in the ultrasonic bath for three minutes, and blow dry with pressurized nitrogen. Repeat the above step with isopropyl alcohol. With a continuous stream of nitrogen blowing across the substrates, transport them over to the dust free area, being careful not to blow air into the dust free area. After donning clean gloves, load the substrates into the UV Ozone machine and let run for fifteen minutes. This completes the cleaning process.

Submerging the substrates in isopropyl and acetone assures there are no organic materials on the substrate that would react with and damage the polymer layer. The ultrasonic bath adds kinetic energy to the process and increases the likelihood of dislodging particles. The nitrogen escort assures that dust does not fall on the substrates on the way to the dust free area, where we use ozone to react with any organics that may be stuck to the substrate. It also diffuses oxygen into the ITO layer, which improves conductivity. Now the substrates are ready for anode application.

After opening the vacuum valve for the spin coater, remove a substrate from the UV Ozone machine and place it in the chuck securely. Draw some unfiltered PEDOT solution into a
A smooth, unblemished polymer layer makes better contact with the metal electrodes and performs consistently across the device. Our lab applies thin films via spin coating, but many other application methods exist, including drop casting and dip coating, which produce films with different characteristics [17]. Swabbing the edges allows charge to freely flow between the ITO and metal electrode, a pathway that would otherwise be blocked by the polymer/PCBM film.

The substrates are now ready for cathode deposition. First, assure that the “hi-vac” valve is closed before opening the vent valve to the bell jar, which is kept under vacuum. Close the valve when the jar comes to pressure (a slight pop will occur). Carefully lift up the bell jar and remove the top shield. After removing the substrate holder, open the shudder and remove the chimney so the calcium and aluminum boats are visible. Make sure there is enough good calcium for an evaporation. Then, if necessary, replace the aluminum boat and fill it with nine aluminum pellets. Replace the chimney, close the shudder, replace the substrate holder (with substrates oriented up side facing downward) and tighten it down with an Allen wrench. Vacuum around the seal and lower the bell jar.

You may now begin pumping on the chamber. Turn on the diffusion pump, and set the mechanical pump to depressurize the foreline for at least an hour while the diffusion pump oil heats up. Don’t forget to turn on the cooling water! If the diffusion pump overheats it is a big pain to fix. Close the foreline valve, open the roughing valve, and wait until the chamber pumps down to 30 microns. Close roughing and open foreline again, the diffusion pump relies on this suction to operate. Open the hi-vac valve to begin low pressure pumping, when the thermocouple gauge is out of range (∼10⁻³ Torr) engage the ionization gauge. Pump down to around ∼10⁻⁶ Torr which is good evaporation pressure [8]. Turn on the thickness monitor and note the evaporating metal acoustic impedance, material density, and crystal usage level. Turn on the variac and set to boat one for calcium evaporation. Slowly ramp up current until the ammeter reads 70 amps, and maintain this for a minute before opening the shudder. Continue increasing current over the next few minutes, or until the thickness monitor reads 200 to 300 Å, then close the shudder and slowly bring the current down to zero (to prevent boat cracking). Switch to boat two, aluminum, and carefully ramp up the current again. Wetting occurs when the aluminum pellets melt in the boat, and the variac current increases. Allow the current to return to a stable level before continuing.
to increase. When the thickness monitor starts to show a rate, proceed with caution. Rates above 1-2 Å/s may damage the active layer. Deposit 800 to 1000 Å of aluminum for maximum conductivity. All devices received cathodes as described except for the third and last blend, which lacks the calcium layer. After removing the substrates, return the chamber to low pressure.

Calcium is deposited for its small work function, which improves OC voltage, and aluminum is a cap to keep the calcium from corroding (this happens quickly, even inside of the glove box with ~1ppm H₂O). When calcium sublimes (or aluminum evaporates), the most energetic particles leave the surface of the metal at high velocity. In order for these particles to reach a cathode, they must have a clear, line-of-sight path to the substrates. Air molecules in the bell jar obstruct this path, and their presence could result in a “dirty evaporation.” For this reason the evaporation process is completed under high vacuum. A stenciled mask traces the desired cathode pattern onto the substrates [8]. Our mask produces four solar cells per substrate, two large pixels (labeled A and D, 42 µm²) and two small pixels (labeled B and C, 3.75 µm²).

The mechanical pump achieves vacuum using a cyclic system of mechanically rotating parts. The diffusion pump uses a jet of hot oil vapor pointed downward to alter the normal distribution of gas molecule velocities in the direction of the jet, where rapid expansion is happening. This moves gas out of the low-pressure zone to the foreline, where the mechanical pump removes it (Fig. 4).

A thermocouple gauge is used for initial pressure readings above 30 microns. It uses a shielded wire filament, whose conductivity increases with temperature, which is dependent on the rate that the filament transfers heat to the surrounding air particles. This may be measured with an ammeter. For readings below 30 microns, a Bayard-Alpert ionization gauge is used. This is based on the phenomenon of residual gas ionization. High-energy electrons are injected into the low-pressure gas, and some electrons make collisions with gas molecules. The probability of collision is based on the number of molecules present. When a collision happens it ionizes a gas molecule, which is drawn to a conducting wire, creating a small current. This is easily measured [8].

Pure, untarnished cathodes give electrons an equipotential path to flow along, so they may be efficiently extracted from the active region. Cathode deposition is the last step in the device synthesis process, an illustrated cross section of a completed P3HT/PCBM device is available in Fig. 5. Now the devices are ready for testing.

B. Testing the devices

Move the substrates over to the testing area for J-V testing. Load the substrate into the testing jig with the up side facing down, and the two smaller pixels closest to the wires extending from the jig. Push the substrate onto the gold pins with the locking black piece that fits over the substrate. Then replace the black top of the jig. Turn on the light source, ours is a Dolan-Jenner that emits visible/NIR light. Turn on the Keithley 2400 and run the Labview testing program, which sweeps incrementally between −1V and 1V and records the current through each pixel. Do this on all four pixels of each device in light and dark. This information may be used to determine power conversion efficiency, OC voltage, fill factor (actual power / max power), and other useful data. Once the devices are removed from the nitrogen environment they begin to degrade immediately; the in-glove box testing setup enables multiple treatments and tests on a single device over the course of weeks, months, and even years.

In order to obtain EQE, IQE, and full light data, package the devices and take them out of the glove box. Cut aluminum tape squares 8.5mm across and carefully apply to the surface of each substrate, covering the active area but not the contacts. Bring the substrates through the antechamber to the dust free area, and mix quick dry (5 min.) epoxy in a paper bowl under the fume hood. Before the epoxy gets too viscous, apply to the edges of the aluminum tape making sure to seal all gaps. This
protects the active layer from outside air long enough to complete EQE and full sunlight tests. However, in this state devices degrade quickly, so testing must be completed during the hours subsequent to packaging.

To test in full sunlight, wheel a separate, mobile testing apparatus to the nearest sunny location on a clear day. Test devices as close to air mass 1.5 (AM 1.5) as possible, when the sun is 48.15° from zenith and the earth’s surface receives 1000 W/m² incident radiation. This is the standard testing condition for solar cells. Take a reading with the silicon diode reference, at AM 1.5 it will produce exactly 1.97 mA. Then run the Labview J-V program on each device, with surfaces aligned perpendicular to the sun’s radiation. AM 1.5 testing utilizes intense sunlight, which is far more powerful than the light sources in the lab. This is important in determining a device’s actual energy conversion capabilities, which may be greater or less than theoretical calculations based on low intensity light.

EQE testing requires monochromatic light, so it is completed in a separate lab. Run fiber optic cables between the solar light simulator, monochromator, and testing jig. Set the EQE testing program to step size 2nm, sweep 350nm to 900nm, 15 samples and 0.25s spacing. Take reference readings on each pixel of the jig using the 4-diode array. Then test all pixels on all devices without jostling the fiber optic cables, for sake of accurate comparison between tests. This completes the testing process.

C. Troubleshooting

The Spring 2012 Physics/EE 422 Polymer Lab made the third run of devices, so there were several differences between this batch and the other device runs. First and foremost, the small ITO pads were not wiped of PEDOT, so there is a small conducting pathway between the anode and the cathode. This caused most of the small pixels to be completely shorted out. A characteristic “leaky” J-V curve from this run is available in Fig. 6. In addition, the PCPD TBTPCBM control group from this run did not perform whatsoever (PCE < 0.1%); we suspect that the higher OC voltage of these devices created a larger electric field, so the PEDOT conducting pathway redirected more current back into the cell, shorting out the devices completely. However, this hypothesis remains un-tested. As a result, the only usable data from this run was collected from the large pixels of the P3HT:PCBM and blended devices. Furthermore, every student is assigned just one substrate, so each device from this run is different in its own way.

The second run of devices, with equal parts PCPD TBTP and P3HT, was actually the third run. It was preceded by a run of blended devices that we thought had failed. We had never annealed devices above 105°C with positive results, so we abandoned the batch, attributing their poor performance to a dirty evaporation. When the next run of devices showed the same behavior, we did a high temperature kill test. By the time we came back to anneal the first set of devices, months had passed, and PCE did not significantly enhance with anneals. However, the P3HT portion of the absorption showed the characteristic rise after hot anneals (>130°C).

Lastly, at some point *someone* left the diffusion pump on all weekend, and it overheated. The cooling system got clogged, and it took a long time to figure out how to fix the thickness monitor. This event postponed a device run for a few weeks.

IV. RESULTS AND DISCUSSION

Our original goal was to fabricate a blended solar cell with PCPD TBTP and P3HT absorption peaks of equal amplitude in order to attain the broadest absorption possible. Our initial attempt used mass ratio 1:0.6:1 P3HT:PCPD TBTP:PCBM and annealed for 25 minutes at 105°C. The blended devices peaked at 1.6% efficiency in full sunlight, with clearly identifiable absorption peaks from each polymer. This was a relative success, considering that the best PCPD TBTP:PCBM devices our lab has ever produced peaked at 1.6% efficiency. Fig. 7 has the EQE, IQE and absorption from this run, with different regions of absorption indicated by arrows.

The goal for the next run of devices was to equalize the amplitude of these two peaks, in order to maximize absorption. We linearly scaled the ratio of each polymer by the height of its peak in the last run so that PCPD TBTP and P3HT would be represented equally in the new blend. The final ratio was 1:1:3 P3HT:PCPD TBTP:PCBM with 2K, 4K, and 5K RPM spin speeds. Once the devices were completed however, efficiencies were terrible (average from the run was 0.578%), and the resulting absorption is available in Fig. 8.

Note the lack of P3HT optical signature in this blend, where we expected there to be one of equal amplitude to the PCPD TBTP peak. With heat treatment, P3HT usually forms a crystalline nanorod structure, increases absorption and region
P3HT:PCPDTBT:PCBM Multi-polymer single layer solar cells, by Ted Andreas

P3HT:PCBM films are mostly a result of their crystalline morphology, in fact pure crystalline P3HT has charge carrier mobility over three orders of magnitude larger than that of amorphous P3HT [9,10,12,13,14]. However, the addition of amorphous PCBM in a P3HT thin film disrupts its crystallinity [14]. Since PCPDTBT is also amorphous in comparison to P3HT, the addition of large amounts of PCPDTBT or PCBM in a P3HT film prevents it from crystallizing normally. This significantly degrades performance, since P3HT is the main charge carrier and absorber in our blended devices, and these properties depend on its morphology.

Since blended devices with significant PCPDTBT presence do not work, creating a solar cell that absorbs equally from each polymer is pointless. At this point our goals shifted to using small amounts of PCPDTBT to broaden the absorption of P3HT, while sacrificing as little crystallinity and charge mobility as possible. This technique has been fruitful for other groups [3,15]. The next run had mass ratio 1:0.25:1 P3HT:PCPDTBT:PCBM, with pure PCPDTBT:PCBM and P3HT:PCBM control groups in ratios of 1:4 and 1:1 respectively, to match the ratio of the blend. All active layers were spun out at 4000 RPM. The contacts on these devices are pure aluminum and PEDOT was not wiped during fabrication, but the blended devices still ended up achieving the highest PCE of all runs, 2.0% in full sunlight. The maximum PCE achieved by pure P3HT:PCBM devices is 1.5%, the main difference from the blend being lower open circuit (OC) voltages (0.47V P3HT, 0.6V blend), the blend also has broader absorption and slightly greater short circuit current density (2%). All devices discussed here were subjected to a ten minute anneal at 105°C. Fig. 9 has a comparison of EQE, IQE and absorption from this run. The blend absorbs 32% more light than pure P3HT devices, and achieved efficiencies 33% greater. Note that for the pure P3HT and pure PCPDTBT devices, IQE and EQE track fairly well. However, for the blended device, the PCPDTBT portion shows significant

Pure PCPDTBT:PCBM devices do not respond to thermal anneals, they are known to have a far less crystalline structure than P3HT, and annealing at high temperatures degrades device performance significantly [10,18]. It is likely that the high temperature anneals required to initiate spinodal decomposition in P3HT damaged the PCPDTBT regions of the device, resulting in a diluted active layer interspersed with regions of inactive PCPDTBT. This explains the low efficiencies of this run compared to the others.

The large short circuit currents and high absorption of P3HT:PCBM films are mostly a result of their crystalline morphology, in fact pure crystalline P3HT has charge carrier mobility over three orders of magnitude larger than that of amorphous P3HT [9,10,12,13,14]. However, the addition of amorphous PCBM in a P3HT thin film disrupts its crystallinity [14]. Since PCPDTBT is also amorphous in comparison to P3HT, the addition of large amounts of PCPDTBT or PCBM in a P3HT film prevents it from crystallizing normally. This significantly degrades performance, since P3HT is the main charge carrier and absorber in our blended devices, and these properties depend on its morphology.

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enhancement in comparison to its EQE. IQE measures how efficiently photons absorbed in the polymer are turned into extractable charge; if the PCPDTBT portion of the IQE is unproportionally higher than the rest, it means that the device converts photons absorbed by PCPDTBT better than photons absorbed in the rest of the device. We hypothesize that this is a result of P3HT helping PCPDTBT with charge extraction, but more data should be collected to confirm this hypothesis.

V. CONCLUSION

Our group successfully created PCPDTBT:P3HT:PCBM solar cells that outperform their pure P3HT:PCBM control group, the most widely used OPV in the industry. While most multi-polymer systems are used to broaden absorption specifically, blended P3HT:PCPDTBT:PCBM is unique because it also improves charge extraction from the PCPDTBT portion of the device. These devices achieve the broad absorption of tandems without the difficulty of construction, and with further optimization may obviate the need for tandem architecture.

An active, high band gap polymer doped with a supplemental absorber produces more free charge carriers, leading to higher PCEs. This concept would be easy to apply to existing systems with little extra effort; it shows that innovative approaches to device design can yield appreciable advances in this burgeoning field.

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Ted Andreas (B.S. June 2012) completed his undergraduate degree in physics at California Polytechnic State University in San Luis Obispo. He was born in Manhattan Beach, California in 1989.

Summer of 2011, Ted started working in the Polymer Lab with Dr. Robert Echols, synthesizing multi-polymer solar cells for testing and development. He has been a board member of the Society of Physics students for the past year, and is looking towards a career in the solar industry.

REFERENCE

APPENDIX

EQE, IQE, absorption


- IQE P3HT
- IQE PCPDTBT
- IQE blend
- EQE P3HT
- EQE blend
- absorbed/incident P3HT
- absorbed/incident PCPDTBT
- absorbed/incident blend

Wavelength (nm)