

Review

Organic solar cells: An overview focusing on active layer morphology

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Abstract

Solar cells constructed of organic materials are becoming increasingly efficient due to the discovery of the bulk heterojunction concept. This review provides an overview of organic solar cells. Topics covered include: a brief history of organic solar cell development; device construction, definitions, and characteristics; and heterojunction morphology and its relation to device efficiency in conjugated polymer/fullerene systems. The aim of this article is to show that researchers are developing a better understanding of how material structure relates to function and that they are applying this knowledge to build more efficient light-harvesting devices.

Abbreviations: AFM – atomic force microscopy; C₆₀ – fullerene; FF – fill factor; HOMO – highest occupied molecular orbital; I_{sc} – short circuit voltage; IPCE – incident photon to current efficiency; ITO – indium tin oxide; KFM – Kelvin force microscopy; LUMO – lowest unoccupied molecular orbital; MDMO-PPV – poly[2-methoxy-5-(3′7′-dimethyloctyloxy)-1,4-phenylene vinylene]; MEH-PPV – poly[(2-methoxy-5-((2-ethylhexyl)oxy)-1,4-phenylene)vinylene]; MPP – maximum power point; OSC – organic solar cell; P3HT – poly(3-hexylthiophene); P3OT – poly(3-octylthiophene); Pc – phthalocyanine; PCBM – (6,6)-phenyl-C₆₁-butyric-acid methyl ester; PCE – power conversion efficiency; PEDOT-PSS – poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); QE – quantum efficiency; SEM – scanning electron microscopy; TEM – transmission electron microscopy; V_{oc} – open circuit voltage

Introduction

Interest in organic solar cells stems primarily from the promise of ease of processing. This is because, to date, many organic solar cell devices have used polymers as integral parts of their construction. For example, conjugated polymers often participate as electron donors and hole conductors in the active layer of organic solar cells. Since the science of polymer processing is well-developed, it is hoped that one day conventional processing steps, such as roll-to-roll processing and doctor-blading can be employed to make large-area, inexpensive

organic solar cells on flexible substrates. Such flexible cells, it is proposed, could be used in countless ways, from handheld electronics to commercial power production.

However, basic organic solar cell research and device development still have a long way to go to compete with inorganic solar cells. The efficiency of inorganic solar cells can top 20% and the development of inorganic thin-layer and multi-junction devices will likely lead to even better performance. In contrast, the best organic solar cells, based on the bulk heterojunction concept, operate at 3.0–3.5% efficiency. Nevertheless,

progress is being made and much research effort is being spent to better understand the operation of organic solar cells and their structure/property relationships.

This brief review aims to summarize the development and characteristics of organic solar cells and highlight recent research in the area. First, a short history of organic solar cells is presented. Pertinent definitions and device construction follow, along with materials that are commonly used. Next, recent efforts to understand the relationship between active layer morphology and device performance are highlighted.

Background

In 1959, Kallmann and Pope observed a photovoltaic effect in a single crystal of anthracene when sandwiched between two identical electrodes and illuminated from one side (Kallmann et al. 1959). While they could not completely explain the phenomenon, they postulated that different exciton dissociation mechanisms must occur at the light and dark electrodes. Later, they also observed a photovoltaic effect in a tetracene–water system (Geacintov et al. 1966). Since this device was also completely symmetrical, except for illumination, they thought that exciton dissociation via electron injection into the water, and hole transport by the organic material away from the interface, could explain the observed behavior. These studies, along with later studies on liquid crystalline porphyrins by Gregg (1989), show how a photovoltaic effect can arise in a symmetrical organic device. Furthermore, they highlight the differences between conventional (inorganic) solar cells, which are usually based on silicon or other inorganic semiconductors, and organic solar cells. According to Gregg, in a conventional device, charge carriers (electrons and holes) are generated in the bulk of the material and the electrons and holes are not tightly bound to each other (Gregg 2003; Gregg et al. 2003). The charge carriers are separated from each other by the built-in electric field of the device and travel to their respective electrode where they are transported out of the semiconducting material. Devices made from organic semiconductors do not operate this way. In contrast to the free carriers in inorganic materials, the charge carriers in organic semiconductors are tightly bound to

each other in the form of excitons. The excitons only dissociate at interfaces, such as at electrodes or, as in the case of heterojunction devices, at the interface between donor and acceptor organic materials.

In addition to, or as a consequence of, the properties outlined above, there are other differences between conventional and organic solar cells. Conventional devices are so-called minority carrier materials. The diffusion of the minority carriers in the built-in electric potential (electric field) creates the photovoltaic current. On the other hand, organic cells are majority carriers because holes exist primarily in one phase, electrons exist primarily in the other phase, and their movements result directly in current flow. This is illustrated in Figure 1 below.

Also, the distribution and diffusion of carriers within the materials operate under different mechanisms (Gregg 2003; Gregg et al. 2003). In conventional cells, holes and electrons are generated together, in the same phase of the material, and the photoinduced chemical potential gradient tends to drive them in the same direction. This effect is greater on the minority carriers than on the majority carriers. In addition, the built-in electric potential of inorganic devices drives the separation and flow of holes and electrons. In contrast, in organic heterojunction devices, excitons dissociate at interfaces. So, the hole is generated in one phase (the donor phase) and the electron is generated in the other phase (the acceptor phase). As a consequence of the free carriers being spatially separated and existing in different phases, the photoinduced chemical

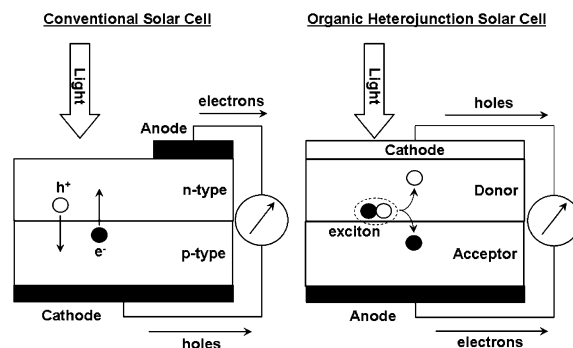


Figure 1. Schematic diagrams of a conventional p–n junction solar cell (left) and an organic heterojunction solar cell (right). The diagram highlights differences in carrier generation between the two types of devices.

potential drives them in opposite directions. In heterojunction organic devices, built-in electrical fields may play a smaller role in carrier movement, depending on device construction (solid state or dye-sensitized).

Organic solar cell basics

In this section, some basics of organic solar cells are outlined. First, device construction is outlined and the difference between a bilayer heterojunction and a bulk heterojunction is emphasized. Then, some characteristics, or properties of organic solar cells are reviewed. These properties, such as fill factor and various types of efficiencies, are often quoted in the literature. However, it is important to understand the meaning of these terms, how they arise, and what material parameters affect them. For example, the term ‘efficiency’ is regularly used to describe devices, but there are many types of efficiencies used in the literature. An attempt will be made to clear up the many definitions.

It is interesting to note that, in organic devices, a photovoltaic current can be observed even in a symmetrical device – a setup with only one photoactive material and electrodes constructed of the same material top and bottom. In this type of device, the excitons must remain intact (not relax) long enough to reach an electrode and dissociate. Since the electrons and holes are so tightly bound, only those excitons that reach an electrode can dissociate and lead to charge flow. This highlights the advantage of having a donor–acceptor heterojunction in the active layer of an organic device. Figure 2 depicts the band structure of a device that contains only one material in the active layer, while Figure 3 depicts the band structure of a device with a donor–acceptor blend. These figures highlight how exciton dissociation produces free charge carriers either at the electrode (Figure 2) or at the heterojunction (Figure 3).

Furthermore, the structure of the heterojunction – bilayer or bulk – is of great importance to the characteristics of the device. In depth studies of the structure of the heterojunction will be summarized later in the article, but the basic difference between a bilayer and bulk heterojunction is illustrated here.

Figure 4 shows that, in a bilayer device, the junction between donor and acceptor materials is

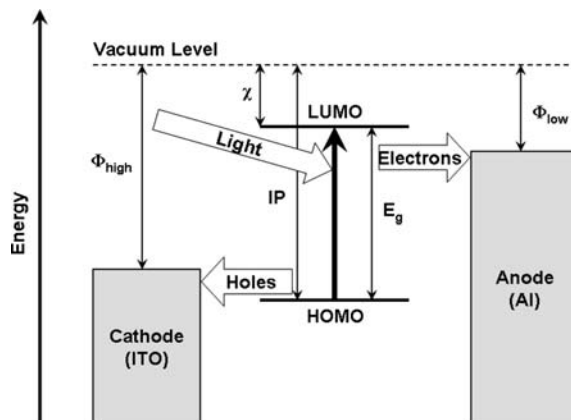


Figure 2. Schematic diagram of the band structure of an organic solar cell having only one material in the active layer and different types of metal electrodes.

planar. In a bulk heterojunction device, attempts have been made to maximize/optimize the interface between phases. In organic solar cells made from blends of conjugated polymers (donor) and fullerenes (acceptor), it is the conjugated polymer that absorbs the incident light. The absorption process generates an exciton that can either relax back to the ground state or dissociate into an electron and a hole. Since, in organic cells, exciton diffusion lengths are small and the dissociation process only occurs at the donor/acceptor interface, controlling the structure of the active layer is very important to constructing efficient devices.

A complete bulk heterojunction organic solar cell is pictured in Figure 5. Notice from the pre-

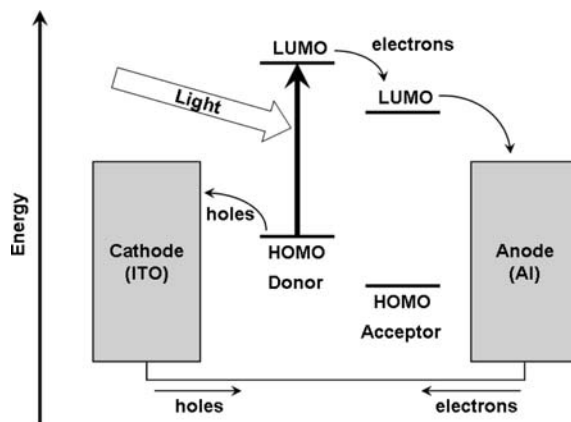


Figure 3. Schematic diagram of the band structure of a heterojunction organic solar cell. The active layer in this type of device contains a donor and an acceptor. Also, here the electrodes are short-circuited, which equalizes their work functions.

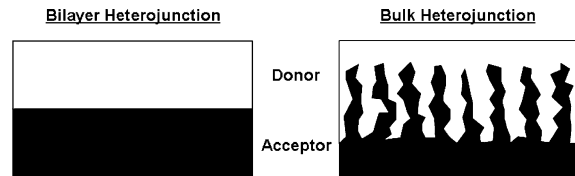


Figure 4. Illustration of bilayer and bulk heterojunction active layers.

vious section that an organic device is typically inverted relative to a conventional one. The organic device generally has a transparent cathode through which light enters. Conventional solar cells typically allow light to enter from the anode side while the anode itself consists of a grid of conductive material. The organic cell consists of at least four distinct layers, not counting the substrate, which may be glass or some flexible, transparent polymer. On top of the substrate is laid the cathode. Indium tin oxide (ITO) is a popular cathodic material due to its transparency and glass substrate coated with ITO is commercially available. A layer of the conductive polymer mixture poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT-PSS) may be applied between the cathode and the active layer. The PEDOT-PSS layer serves several functions. Not only does it serve as a hole transporter and exciton blocker, but it also smoothens out the ITO surface, seals the active layer from oxygen, and keeps cathode material from diffusing into the active layer, which can lead to unwanted trap sites. Next, on top of the PEDOT-PSS, is deposited the active layer(s). This layer is responsible for light absorption, exciton generation/dissociation, and charge carrier diffusion. The active layer in a het-

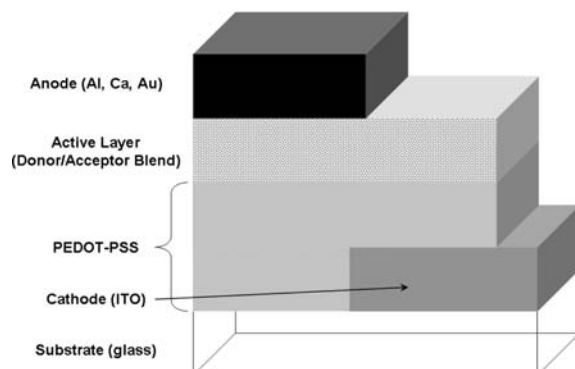


Figure 5. Diagram of the layered structure of a bulk heterojunction organic solar cell. In this illustration, the active layer is depicted as an intimate blend of donor and acceptor.

erohjunction device is made up of two materials: a donor and an acceptor. Poly-(phenylene vinylene) derivatives and poly-(alkylthiophenes) are common donors; fullerene and its derivatives are common acceptors. Other materials are also sometimes employed. These include phthalocyanines (donors) and perylene bisimides (acceptors). On top of the active layer is deposited the anode, typically made of aluminum. Calcium, silver, or gold are also used. Furthermore, a very thin layer of lithium fluoride (5–10 Å) is usually placed between the active layer and the aluminum anode. The lithium fluoride does not seem to react chemically, but does serve as a protective layer between the metal and organic material. The structures of some commonly used materials are shown in Figure 6.

Much terminology surrounds photovoltaic devices. Below are some of the important terms defined and discussed in light of organic solar cells. But first, it is useful to review what happens to a solar cell in the dark and upon exposure to illumination. A graph of current (I) versus voltage (V) is a common way to illustrate the properties of solar cells. In the dark, the I - V curve passes through the origin – with no potential, no current flows. But when the device is exposed to light, the I - V curve shifts downward, as illustrated in Figure 7.

The following terms are often used to characterize solar cells, some items are also shown in on the I - V graph:

Air Mass (AM) – A measure of how much atmosphere sunlight must travel through to reach the earth's surface. This is denoted as 'AM(x)', where x is the inverse of the cosine of the zenith angle of the sun. A typical value for solar cell measurements is AM 1.5, which means that the sun is at an angle of about 48°. Air mass describes the spectrum of radiation, but not its intensity. For solar cell purposes, the intensity is commonly fixed at 100 W/cm².

Open-Circuit Voltage (V_{oc}) – The maximum possible voltage across a photovoltaic cell; the voltage across the cell in sunlight when no current is flowing.

Short-Circuit Current (I_{sc}) – This is the current that flows through an illuminated solar cell when there is no external resistance (i.e., when the electrodes are simply connected or short-circuited). The short-circuit current is the maximum current

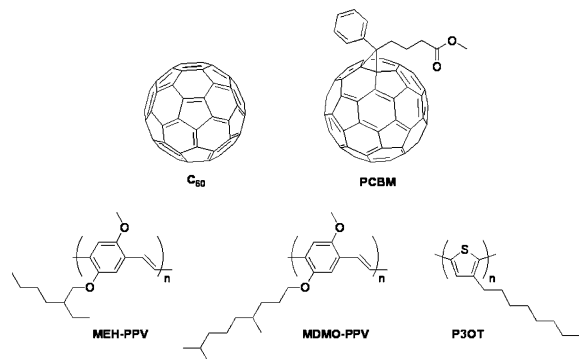


Figure 6. The structures of fullerene materials and conjugated polymers commonly used in organic photovoltaics.

that a device is able to produce. Under an external load, the current will always be less than I_{sc} .

Maximum Power Point – The point (I_{mpp} , V_{mpp}) on the I - V curve where the maximum power is produced. Power (P) is the product of current and voltage ($P = I \cdot V$) and is illustrated in the figure as the area of the rectangle formed between a point on the I - V curve and the axes. The maximum power point is the point on the I - V curve where the area of the resulting rectangle is largest.

Fill Factor (FF) – The ratio of a photovoltaic cell's actual maximum power output to its theoretical power output if both current and voltage were at their maxima, I_{sc} and V_{oc} , respectively. This is a key quantity used to measure cell performance. It is a measure of the 'squareness' of the I - V curve. The formula for FF in terms of the above quantities is:

$$FF = \frac{I_{mpp} V_{mpp}}{I_{sc} V_{oc}}$$

Power Conversion Efficiency (PCE or η_e) – The ratio of power output to power input. In other words, PCE measures the amount of power produced by a solar cell relative to the power available in the incident solar radiation (P_{in}). P_{in} here is the sum over all wavelengths and is generally fixed at 100 W/cm^2 when solar simulators are used. This is the most general way to define an efficiency. The formula for PCE, in terms of quantities defined above, is:

$$\eta_e = \frac{I_{mpp} V_{mpp}}{P_{in}} = \frac{I_{sc} V_{oc} FF}{P_{in}}$$

Quantum Efficiency (QE) – The efficiency of a device as a function of the energy or wavelength of the incident radiation. For a particular wavelength, it specifically relates the number of charge carriers collected to the number of photons shining on the device. QE can be reported in two ways: internal QE and external QE.

External Quantum Efficiency – This type of quantum efficiency includes losses by reflection and transmission. External quantum efficiency is also called IPCE (Incident Photon to Current Efficiency).

Internal Quantum Efficiency – This quantum efficiency factors out losses due to reflection and transmission of photons such that it considers processes only involving absorbed photons. By accounting for transmission and reflection processes, external QE can be transformed into internal QE.

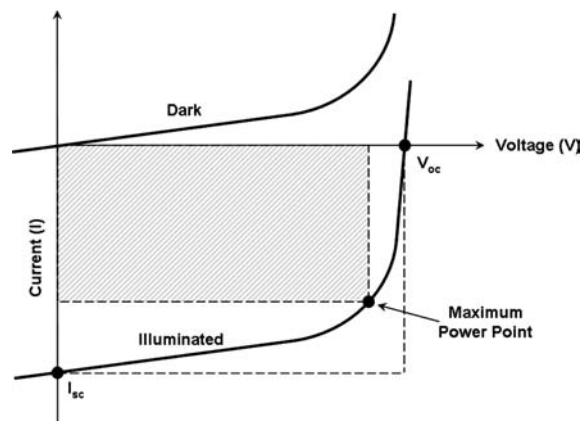


Figure 7. Graph of current versus voltage for photovoltaic devices. The figure shows how the device characteristics change upon illumination. Key points on the graph are also indicated.

The importance of the bulk heterojunction

The heterojunction was introduced by Tang in 1986 and it proved to be a great step forward for organic photovoltaics (Tang 1986). Tang described a two-layer device that employed copper phthalocyanine (CuPc) as the donor and a perylene tetracarboxylic derivative (PV) as the acceptor. The device had a power conversion efficiency of about 1%, which was an order of magnitude greater than single-material organic photovoltaics developed at that time. Furthermore, he recognized that the interface between the donor and the acceptor, not the electrode contacts, was the key to

determine the photovoltaic properties of the cell. To explain the behavior of his cell, Tang proposed that excitons diffused to the interface between the CuPc and PV and dissociated there such that the CuPc carried the holes to the ITO electrode while PV carried electrons to the Ag electrode. A consequence of this mode of operation was that the production, diffusion, and lifetime of excitons were very important to carrier generation. Exciton diffusion lengths have been estimated to range from 10 to 100 nm (Halls et al. 1996a, b; Stubinger et al. 2001). This means that only excitons generated within a short distance of the donor-acceptor interface have the possibility of dissociating into free electrons and holes. Therefore, it was recognized that the character of the interface in heterojunction devices was an important feature to control. The interface should have as high an area as possible, but the morphology of the donor and acceptor should still be such that the charge carriers have unrestricted conduction pathways to their respective electrodes. Thus, the concept of a bulk (or dispersed) heterojunction was born.

Several techniques and a variety of materials have been used to accomplish the bulk heterojunction architecture. The most common technique is simply to disperse fullerene, or one of its derivatives, in a conjugated polymer and then spincoat the solution onto the device. Yu et al. (1995) were among the first to demonstrate how such an approach greatly increased device efficiencies. Other techniques include active layers made of: 'double cable' polymers, which have fullerene derivatives attached covalently to a conjugated polymer backbone (Ramos et al. 2001a; 2001b; Cravino et al. 2003) block copolymers that have separate donor and acceptor blocks (Krebs et al. 2003; Sun 2003); and liquid crystalline assemblies comprised of segregated donor and acceptor stacks (Petritsch et al. 1999). A noteworthy example of the later was described by Schmidt-Mende et al. (2001) and consisted of a self-organized liquid crystal film containing segregated stacks of perylene and hexabenzocoronene. Most of these systems have been reviewed elsewhere (Spanggaard et al. 2004). So, here we turn our attention to a particular, but very important, aspect of bulk heterojunction devices: the morphology, or microstructure, of the active layers in fullerene/conjugated polymer systems. Specifically, the next section reviews recent work regarding the

morphology of such active layers and how the morphology affected device performance.

Morphology of fullerene-conjugated polymer active layers

Recent work on the morphology of bulk heterojunction solar cells is summarized below. Here we have mainly focused on systems that employ a conjugated polymer as the donor and fullerene, or a fullerene derivative, as the acceptor. Where possible, the method of preparation of the active layer is mentioned along with reported device efficiencies. From these studies, it is clear that active layer structure depends heavily on the processing steps and solvents used. It is also evident that the microstructure of the active layer plays a large role in determining photovoltaic properties.

Padinger and coworkers (2000) fabricated large area devices on flexible polyester substrates. They made several devices containing either MDMO-PPV or P3OT as the electron-donating conjugated polymer. They used unmodified C₆₀ or PCBM (mono-adduct) as the acceptor in the P3OT devices and C₆₀ or one of two different PCBM adducts in the MDMO-PPV devices: a mono-adduct and a bis-adduct, which was a mixture of isomers. The multi-adduct derivative was used to increase the solubility/miscibility of the fullerene. MDMO-PPV active layers were prepared by doctor-blading toluene solutions on top of PEDOT while P3OT active layers were spin-coated onto PEDOT. AFM was used to study the surface structure and revealed that, in the MDMO-PPV devices, C₆₀ produced micrometer-sized particles. The MDMO-PPV/mono-adduct and MDMO-PPV/multi-adduct devices were much smoother and homogeneous than the C₆₀ containing device, with the multi-adduct device being the most homogeneous. Meanwhile, the P3OT/C₆₀ films were homogeneous but rough on the sub-micron scale while the P3OT/PCBM (mono-adduct) mixture showed strong phase separation and pinholes about 30 nm deep. Short-circuit currents in the MDMO-PPV devices were 50, 145, and 280 $\mu\text{A}/\text{cm}^2$ for the PCBM multi-adduct, C₆₀, and PCBM mono-adduct active layers, respectively. The P3OT/PCBM device possessed a short-circuit current about half that of the other devices, but the P3OT/C₆₀ device behavior was comparable to

the MDMO-PPV/PCBM cell. The MDMO-PPV/PCBM and P3OT/C₆₀ devices exhibited power conversion efficiencies of about 1.5% under monochromatic illumination at 488 nm.

Shaheen and coworkers (2001) fabricated devices by spin-coating active layers containing 1:4 mixtures of MDMO-PPV/PCBM. They used either toluene or chlorobenzene as the casting solvent and found that the films cast from chlorobenzene were smoother than those cast from toluene. Specifically, they observed that the toluene-cast film contained horizontal features about 0.5 μm in size and had a surface roughness of about 10 nm. On the other hand, the film cast from chlorobenzene had horizontal features 0.1 μm in size but were very smooth, having height variations of 1 nm or less. The differences in morphology translated into different performance characteristics. While both devices had open-circuit voltages of 0.82 V, the more uniform chlorobenzene-cast film had a short circuit density more than twice that of the toluene-cast film (5.25 *versus* 2.33 mA/cm²). Also, the fill factor increased from 0.50 to 0.61 when comparing toluene- to chlorobenzene-cast devices. The combination of increased short-circuit density and fill factor of the chlorobenzene-cast solar cell combined to produce a 2.5% efficient device (under AM1.5) relative to the 0.9% efficiency of the toluene-cast cell. AFM images showed increased clustering of what was believed to be PCBM in the rougher film cast from toluene. This phase separation was hypothesized to lead to decreased carrier mobility. Another effect that casting solvent had on device morphology is related to the organization of the conjugated polymer chains. Optical transmission spectra revealed a red-shift in the MDMO-PPV absorption of the chlorobenzene-cast film. This was attributed to increased polymer chain interactions which led to better hole conduction by the conjugated polymer.

Martens et al. (2002) studied not only the effect of casting solvent, but also the casting method (drop-cast *versus* spin-coated) on phase separation in MDMO-PPV/PCBM layers. They used AFM to look at the surfaces and TEM to examine cross sections of films. Like Shaheen et al., they looked at toluene and chlorobenzene and found that chlorobenzene led to smaller PCBM-rich domains and smoother surfaces than toluene. In fact, their AFM measurements agreed well with those of Shaheen. The TEM studies, however, lent more

information about the films because the technique yielded information about the cross-sections of the samples and the composition of the phases in the films. Based on this and other phase studies, they proposed that the matrices of the films were a 1:1 mixture of polymer and PCBM, while the spherical domains were predominantly PCBM. Furthermore, they observed generally smaller PCBM-rich domains in spin-coated films than in drop-cast films. The reason for smaller domains was related to the faster evaporation rate in spincoating than in drop-casting. In other words, the slower evaporation rate in drop-casting allowed the PCBM-rich phase to coalesce into larger domains, but spincasting tended to freeze in smaller and more dispersed PCBM-rich domains.

Martens and coworkers (2003a, 2003b; 2004) later extended their study of the effect of casting solvent on phase behavior. They again used AFM and TEM to examine films of MDMO-PPV/PCBM cast from chlorobenzene or toluene. However, they also studied how the ratio of MDMO-PPV to PCBM affected the morphology of the resulting films. By casting solutions of MDMO-PPV/PCBM in ratios of 1:1, 1:2, and 1:4 (polymer:fullerene) they showed that toluene produced a uniform film in the 1:1 ratio, but phase separation in the 1:2 and 1:4 ratios. However, films cast from chlorobenzene were homogeneous in 1:1 and 1:2 ratios, but phase separated at the 1:4 ratio. The researchers concluded that these results show that the composition of the matrix depends on the casting solvent insofar as chlorobenzene allowed for incorporation of more PCBM into the matrix. The higher amount of acceptor in the matrix could explain why devices cast from chlorobenzene are generally more efficient than devices cast from toluene. Martens et al. also reported results of KPFM studies on similar films. These investigations showed that the phase separated domains had different local electronic properties than the matrix.

Hoppe and coworkers (2005) used KPFM in conjunction with SEM to examine active layers of 1:4 MDMO-PPV/PCBM spincast from chlorobenzene and toluene. Their results showed that casting from toluene produced a thin layer on top of the film that prevented electron propagation to the electrode.

An interesting study was done by Ltaief and coworkers (2005) on the MEH-PPV/C₆₀ system.

They studied the effect of fullerene concentration and casting solvent (THF or 1,2-dichlorobenzene) on film morphology, photoluminescence quenching, and photoelectric properties. Their research specifically examined systems with low fullerene concentrations (1–40 wt%) in an effort to differentiate effects based on charge transfer from those arising from charge transport. Lower fullerene concentrations were used so that the active layers were unlikely to have continuous fullerene pathways for electron percolation. AFM imaging of layers cast from THF showed large aggregates of fullerene, but layers cast from 1,2-dichlorobenzene were quite uniform. This suggested that aggregation of C₆₀ in the cast films was related to its solubility in the casting solvent, since C₆₀ is more soluble in 1,2-dichlorobenzene than in THF. When the photoluminescence of the films was measured, it was revealed that the THF-cast films showed increased excimer emission relative to the 1,2-dichlorobenzene-processed films. The excimer emission, which appeared around 630 nm, was attributed to the formation of polymer aggregates (MEH-PPV), which yielded information about the organization of the polymer chains in the samples – better interaction between polymer chains led to increased excimer emission. Despite the increased C₆₀ dispersion in the 1,2-dichlorobenzene samples, which is generally thought to lead to better exciton dissociation, the THF-cast samples produced better photoelectric properties. Again, this was thought to be a result of better charge transport through the matrix of the film due to the more organized polymer chains in the THF-cast film. Conversely, the uniformly dispersed fullerene in the 1,2-dichlorobenzene sample actually disrupted charge transport in the polymer matrix, producing lower short-circuit currents and fill factors than in the THF-cast film.

Outlook

As the demand for electrical power increases, producers and consumers will continue to look for alternative sources. One such source of renewable energy is, of course, the sun and researchers have been working for decades to develop devices that efficiently capture solar energy. Solar cells made from inorganic semiconductors have successfully

reached the marketplace, but those made from organic materials still need to make the leap out of the lab. As materials scientists develop a better understanding of the structure-property relationships of organic photovoltaic devices, the efficiencies of organic solar cells will improve and new device architectures will emerge. However, a firm grasp on how morphology affects performance is required in order to apply the full range of plastic processing techniques to organic solar cell fabrication.

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