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Efficient Organic Heterojunction Photovoltaic Cells Based on Triplet Materials**

By *Yan Shao* and *Yang Yang**

Much effort has been expended during the past two decades in the search for organic photovoltaic materials and related device architectures since the donor–acceptor heterojunction interface was demonstrated to be an effective exciton-dissociation structure.[1–8] The effective organic photovoltaic materials include small molecules and polymers with relatively high conductivity or mobility. The power-conversion efficiencies of organic photovoltaic devices are dependent on three key processes: light absorption, exciton dissociation, and charge collection.[4] The external quantum efficiency can be estimated as $\gamma_{\text{total}} = \gamma_{\text{absorption}}\gamma_{\text{dissociation}}\gamma_{\text{collection}}$, where γ_{total} stands for total external quantum efficiency, $\gamma_{\text{absorption}}$ for light absorption, $\gamma_{\text{dissociation}}$ for exciton dissociation, and $\gamma_{\text{collection}}$ for electrode collection.

To gain high power-conversion efficiency, firstly, organic layers should be thick enough to ensure high light absorption, even though many organic photovoltaic materials possess better light-absorption capabilities compared with their inorganic counterparts with similar bandgap and thickness. However, due to the poor exciton mobility, the organic layer in the device has to be sufficiently thin, allowing the photogenerated excitons to reach the junction. In other words, their exciton diffusion lengths cannot match the respective optical absorption lengths.[3] The exciton diffusion length is dependent on two factors: exciton mobility and lifetime.[5] In order to improve exciton diffusion length we can adopt high-mobility organics, as has been demonstrated for many high-performance photovoltaic devices,[2,6,8] or, on the other hand, we can introduce materials with long exciton lifetimes. In this case, triplet materials might be excellent candidates as they often possess much longer exciton lifetimes compared with singlet ones. Fullerenes (C_{60}) are one of the best acceptor materials for organic photovoltaics owing to excellent exciton mobility, a relatively stable triplet state, and, therefore, a relatively large exciton diffusion length,[9,10] which has been reported to be as long as 400 Å.[3] Combined with its high electron affinity (EA), C_{60} and its derivatives have received much attention and have been adopted extensively in organic solar cells.[2,5,6,8]

There are two general types of organic photovoltaic structure: heterojunctions and bulk heterojunctions (or so-called interpenetrating network structures for the case of polymer blends), which provide respective advantages. Heterojunction devices often have multilayer structures and are formed by layer-by-layer material deposition. Bulk heterojunctions are fabricated via blending or codeposition methods.[11,12] The interpenetrating networks have proven to be very efficient exciton-dissociation systems, especially for recently reported high-efficiency polymer-based devices.[5] The exciton- and charge-transport properties are altered after the formation of bulk heterojunctions, since phase separation and film morphology play more important roles compared to in the respective pure materials, so that the mixtures might be considered as whole systems and their properties must be determined after fabrication.[10,13] On the other hand, heterojunctions are relatively simple systems and the transport properties, crystalline order, and film morphology can be preserved relatively well. Therefore, materials can be characterized independently before device fabrication and the different components can be substituted conveniently. Many valuable parameters can be determined experimentally in heterojunction systems.[3] In this case, heterojunctions are well suited to the investigation of new materials and theoretical approaches for photovoltaic devices.[7,11,14]

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In this communication, we demonstrate a new type of organic photovoltaic device by utilizing materials with long exciton lifetimes. Heterojunction structures were selected for demonstration. Organic triplet materials are promising candidates for long-exciton-lifetime materials. It is well known that such triplet materials possess excellent emitting characteristics and they have been extensively adopted in many phosphorescent organic light-emitting diodes (OLEDs) in recent years.[15-18] Typical exciton lifetimes for fluorescent organic materials are in the order of $\sim 10^{-9}$ s[19] while for phosphorescent organic materials lifetimes are in the order of $\sim 10^{-6}$ s.[15,19] This difference of three orders of magnitude could be utilized to extend exciton diffusion length greatly, if proper triplet materials are available.

The physical processes occurring in photovoltaic devices can be considered to be opposite to those in OLEDs, therefore the criteria of selecting materials should be different. The many phosphorescent materials used in OLEDs that are now available commercially. Therefore, it is convenient to select some triplet materials from OLED materials and use them in demonstrating photovoltaic devices. The first consideration is the light-absorption ability, which is often the weak point for many triplet materials owing to the relatively high ionization potential (IP) of their first excited single state. The second consideration is appropriate energy levels to form efficient heterojunctions with proper energy-level offset.

Here, 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphineplatinum(II) (PtOEP) was selected for the electron-donating material and C_{60} was used as the electron acceptor. Both possess strong triplet electron states, excellent thermal stability, and good ability to form thin films.[20] Unlike triplet materials adopted in phosphorescent OLEDs, where they are often used as dopants, neat PtOEP thin films were employed for photovoltaic heterojunctions because exciton diffusion and carrier mobility would be affected by the energy-trapping structures of doped thin films. 2,9-Dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) served as the hole/exciton blocker between C_{60} and the Al electrode. Indium tin oxide (ITO) glass coated with poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) film was adopted as the substrate. Figure 1 shows the configuration of the device structure, the chemical structures of the organic materials, and a schematic energy-level diagram. The energy-level values of PtOEP are taken from the literature.[15,21,22] The dashed line shows the approximate energy level of triplet energy level for the EA of PtOEP. The energy-level offset for the junction between PtOEP and C_{60} is nearly perfect for exciton dissociation and the electron affinity of PtOEP should match the ITO/PEDOT very well for hole transport.

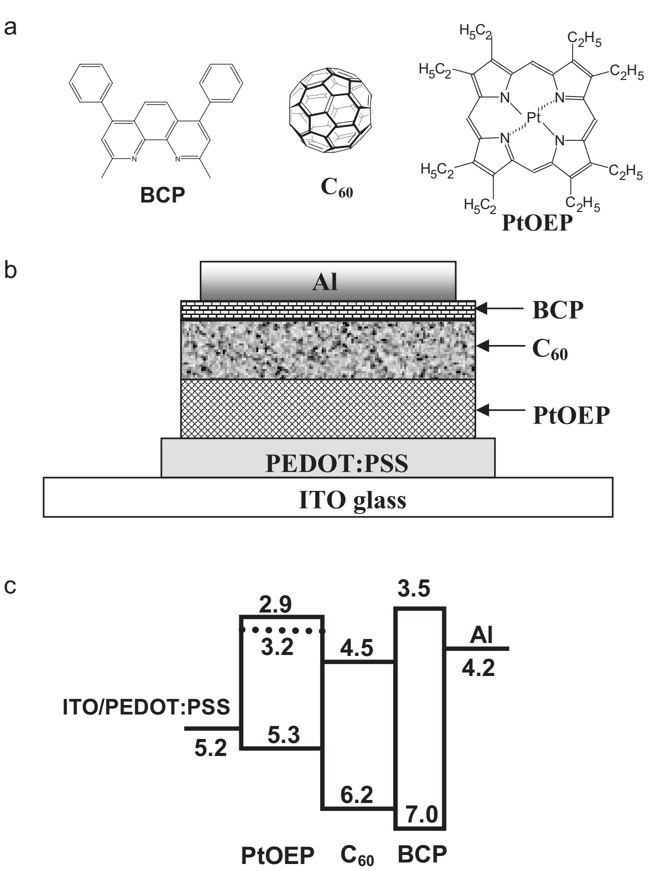

Figure 1. a) The chemical structures of the organic materials, b) the configuration of the device structure, and c) a schematic energy-level diagram.

The detailed photovoltaic device structure and thickness for each organic functional layer are described as ITO/PEDOT/PtOEP(300 Å)/C_{60}(300 Å)/BCP(80 Å)/Al(1000 Å). The series resistance can be calculated from the nearly linear part (over 1.2 V) of the dark current and it was about 43 $\Omega\,cm^{-2}$ for devices consisting of 300 Å PtOEP and 300 Å C_{60} layers. In our experiment, when the thicknesses of the PtOEP layer was beyond 400 Å, the photovoltaic devices showed lower power conversion efficiencies. Tests of the material in transistor experiments suggest that the mobility of PtOEP in the microcrystalline state is no more than 10^{-5} $cm^2\,V^{-1}\,s^{-1}$ (which is consistent with literature references[23]), and in the future a higher mobility material may result in better device performance. Figure 2 shows the device performance under 100 $mW\,cm^{-2}$ AM 1.5G illumination. The open-circuit voltage

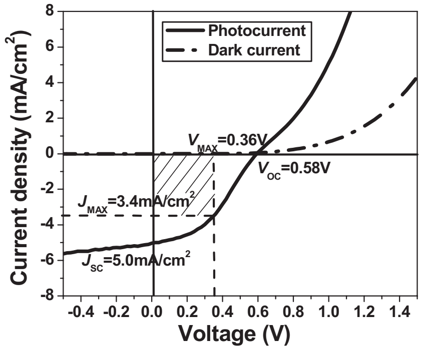

Figure 2. Dark-current and photocurrent density versus voltage curves of the photovoltaic device with the structure ITO/PEDOT/PtOEP(300 Å)/C_{60}(300 Å)/BCP(80 Å)/Al(1000 Å).

(V_{OC}) is 0.58 V and the short-circuit current density (J_{SC}) is 5 mA cm^{-2}. Figure 2 also shows the maximum power output by the shadowed rectangle with V_{MAX} of 0.36 V and J_{MAX} of 3.4 mA cm^{-2}, which gives a fill factor of 0.42 and a power conversion efficiency of 1.2 %. It was noticed that this device had a relatively high resistance and poor fill factor, and that the photocurrent was much higher than the dark current in the first quadrant. The reason for this difference can be attributed to the phenomenon of photoenhanced current.

Figure 3 shows the performance of the device after being treated for 60 min at 100 °C in a glove box under a nitrogen environment. The device performance is much better when compared to the device without heat treatment. The series resistance was calculated to be about 5.3 Ω cm^2, which is much smaller than that of the same device without heat treatment. All three important characteristics, the V_{OC}, J_{SC}, and fill factor, were improved. Here, the V_{OC} is 0.66 V and the J_{SC} is 5.6 mA cm^{-2}. Additionally, Figure 3 shows the maximum power output with V_{MAX} of 0.48 V and J_{MAX} of 4.4 mA cm^{-2}, which gives a fill factor of 0.57 and a power-conversion efficiency of 2.1 %. The conductivities in both illuminated and dark conditions were enhanced greatly, which might be ascribed to crystallization of PtOEP caused by heat treatment and consequent mobility enhancement. This kind of performance enhancement has been reported in several different photovoltaic devices.[4,24]

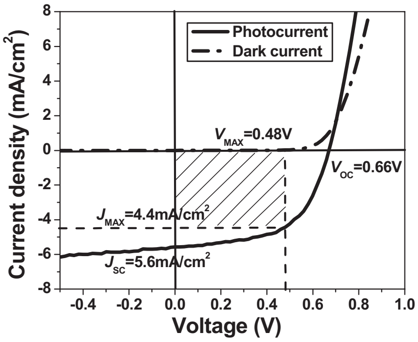

Figure 3. Dark-current and photocurrent density versus voltage curves of the photovoltaic device with the structure ITO/PEDOT/PtOEP(300 Å)/C_{60}(300 Å)/BCP(80 Å)/Al(1000 Å) after 60 min heat treatment at 100 °C under nitrogen in a glove box.

Figure 4 shows the UV-vis spectra for a 30 nm neat PtOEP film and a 30 nm PtOEP/30 nm C_{60} heterojunction film. It can be seen that the absorbance of PtOEP at long wavelengths provides a necessary contribution to the total heterojunction absorption. The contribution of PtOEP for photon absorption is almost comparable to that of C_{60} and the thickness of each layer in the device is equal, while the thickness of the donor materials used in organic photovoltaic devices often thinner compared to that of typical acceptor materials such as C_{60}.[3] Therefore, the absorption abilities of our heterojunction have been enhanced by using relatively thick layers of the donor materials. Nevertheless, the absorbed photons are still less than that of some highly efficient bulk heterojunctions with same active area, such as the blend of poly(3-hexylthiophene) (P3HT) and methanofullerene [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM).[5]

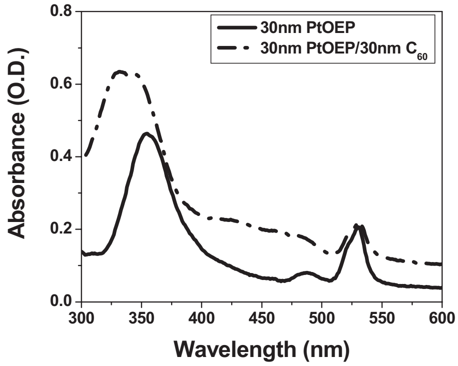

Figure 4. UV-vis spectra for a 30 nm neat PtOEP film and a 30 nm PtOEP/30 nm C_{60} heterojunction film.

To estimate the exciton diffusion length, we have carried out a thickness-dependence experiment.[3] Figure 5a shows the dependence of power-conversion efficiency on PtOEP

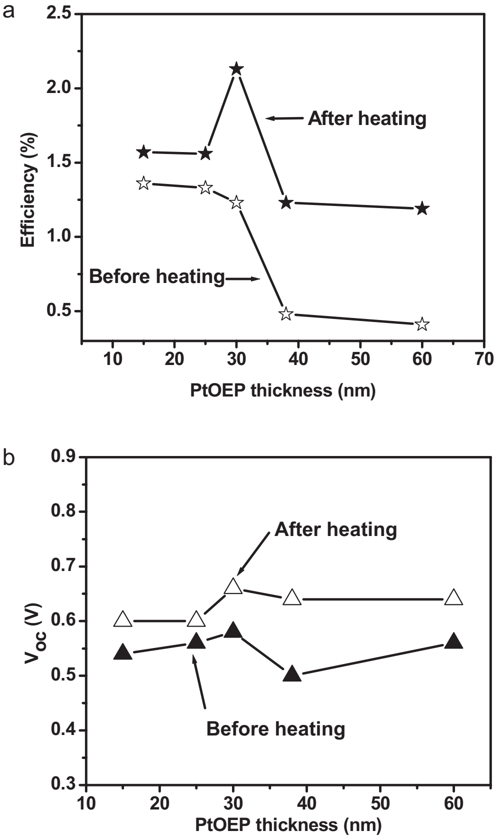

Figure 5. a) The dependence of the power-conversion efficiency on PtOEP thickness with the photovoltaic device structure ITO/PEDOT/PtOEP/C_{60}(300 Å)/BCP(80 Å)/Al(1000 Å). b) The V_{OC} dependence on PtOEP thickness for devices with the same structure.

thickness with the photovoltaic device structure ITO/PEDOT/PtOEP/C_{60}(300 Å)/BCP(80 Å)/Al(1000 Å). From this diagram, the exciton diffusion length is estimated to be around 30 nm, which is comparable to that of many other organic materials used in photovoltaic devices, such as copper phthalocyanine(CuPc) (~ 10 nm), zinc phthalocyanine (ZnPc) (~ 30 nm), and C_{60} (~ 40 nm).[3] The exciton diffusion length is mainly determined by the carrier mobility and exciton lifetime. While the mobility of most triplet materials is fairly low, in the range of 10^{-5} $cm^2 V^{-1} s^{-1}$ or lower[23], the 30 nm diffusion length can only result from the long exciton lifetime. In the future, the device efficiency can be further improved by triplet materials with better carrier mobility. Figure 5b shows the dependence of the V_{OC} on the PtOEP layer thickness with the same device structure. All the V_{OC} values have been improved after the 100 °C heat treatment.

Compared with other high-performance photovoltaic devices,[3,11,12] devices based on PtOEP showed relatively larger electrical resistance, which significantly affected our device performance. The exciton diffusion lengths for many organic materials are proportional to their mobility–lifetime product.[5] In other words, a similar mobility–lifetime product will result in a similar exciton diffusion length. Based on this principle, the great contribution of exciton lifetime in PtOEP can be confirmed by estimating mobility–lifetime products, since PtOEP shows similar exciton diffusion length compared with CuPc, ZnPc, and C_{60}. The relatively low conductivity of the PtOEP photovoltaic devices might be mainly ascribed to the low charge mobility of PtOEP (~ 10^{-5} $cm^2 V^{-1} s^{-1}$)[23] since C_{60} has been demonstrated as a high-mobility material with an electron mobility of 0.5 $cm^2 V^{-1} s^{-1}$ in the single-crystal state [25] and a mobility-lifetime product of 4×10^{-10} $cm^2 V^{-1}$ in microcrystalline film.[26] It is also known that PtOEP possesses a triplet lifetime of about 91 μs,[15,27] which would be greatly helpful to extend the mobility–lifetime product of PtOEP to the order of 10^{-10} or 10^{-9} $cm^2 V^{-1}$, which is comparable to the value of C_{60} or CuPc.

In conclusion, an effective organic photovoltaic heterojunction based on the typical triplet material PtOEP was demonstrated. Relatively high performance and 2.1 % power-conversion efficiency were obtained in a simple multilayer heterojunction structure. It is believed that introducing appropriate organic materials with long exciton lifetime is a very promising way to improve photovoltaic performance. The mobility of current triplet materials used in OLEDs might be relatively low- and high-mobility triplet materials with improved absorption matching the solar spectrum are desired for next-generation devices. With the help of triplet materials purposely designed for photovoltaics, devices based on triplet materials could be greatly improved in the future.

Experimental

The organic photovoltaic devices were fabricated on patterned ITO-coated glass substrates, which had been cleaned by successive ultrasonic treatment in acetone and isopropyl alcohol. The ITO glass was then subject to UV–ozone treatment. A thin layer of PEDOT:PSS film was spin-coated onto the ITO glass with a speed of 4000 rpm (rpm: revolutions per minute) for 1 min and then baked at 115 °C for 50 min in ambient. The fabrication process for the organic materials was carried out under a base pressure of ~ 7×10^{-7} Torr and the deposition rates for PtOEP, C_{60}, BCP, and Al were ~ 0.1 Å s^{-1}, ~ 0.1 Å s^{-1}, ~ 0.8 Å s^{-1}, and ~ 7 Å s^{-1}, respectively. The organic materials used in the device fabrication were used as received without further purification. The Al cathode was evaporated through a shadow mask with an active area of approximately 0.12 cm^2. All the electrical measurements were performed under nitrogen in a glove box at room temperature. The current-density–voltage (*J–V*) characteristics were recorded by a computer controlled Keithley 2400 source–measure unit (SMU). The photocurrent was measured under AM 1.5 solar illumination at 100 mW cm^{-2} (1 sun) supplied by a ThermalOriel 150W solar simulator and the light intensity was monitored by a calibrated silicon photodiode for the AM 1.5 spectrum. The absorption spectra were measured on Varian Cary 50 UV-visible spectrophotometer.

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