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Formation and characterization of MEH-PPV/PCBM-based bulk heterojunction solar cells

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Polymer/fullerene bulk heterojunction solar cells with poly[2-methoxy-5-(20-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV), zinc-phthalocyanine (ZnPc) and 6,6-phenyl C61-butyric acid methyl ester (PCBM), were produced and characterized. A device based on MEH-PPV and PCBM provided better efficiency, fill factor and short-circuit current compared to those of a device on MEH-PPV(ZnPc) and PCBM. The solar cells with a MEH-PPV and PCBM structure showed a higher photoresponse in the range of 300 to 60 nm. The energy levels of the molecules were calculated and are discussed.

Key words: Solar cells, Fullerene, Chemical synthesis, Semiconductivity.

Introduction

Various types of carbon hollow-cage nanostructures such as C_{60}, giant fullerenes, nanocapsules, onions, nanopolyhedra, cones, cubes, and nanotubes has been studied. These C structures show different physical properties, and have the potential for studying materials of low dimensionality within an isolated environment. By controlling the size, layer numbers, helicity, compositions, and included clusters, the cluster-included C nanocage structures with a band-gap energy of 0-1.7 eV and nonmagnetism are expected to show various electronic, optical, and magnetic properties such as Coulomb blockade, photoluminescence, and superparamagnetism [1].

Recently, C_{60}-based polymer/fullerene solar cells have been investigated and reported [2]. These organic solar cells have a potential for use in lightweight, flexible, inexpensive and large-scale solar cells [3-5]. However, significant improvements of photovoltaic efficiencies are mandatory for use in future solar power plants. One of the improvements is the donor-acceptor (DA) proximity in the devices by using blends of donor-like and acceptor -like molecules or polymers, which are called DA bulk -heterojunction solar cells [2, 6-10].

The purpose of the present study is to characterize polymer/fullerene bulk heterojunction solar cells using different organic polymers. In the present study, poly [2-methoxy-5-(20-ethylhexoxy)-1,4-phenylenevinylene] (MEH-PPV) and zinc-phthalocyanine (ZnPc) were used as p-type semiconductors [11,12], and 6,6-phenyl C61-butyric acid methyl ester (PCBM) was used for the n-type one. Device structures were produced, and efficiencies and spectral responsivity were investigated. The present study will indicate a guideline for polymer/fullerene solar cells with higher efficiencies.

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Experimental procedures

A thin layer of polyethylenedioxythiophen doped with polystyrene-sulfonic acid (PEDOT:PSS) (Sigma Aldrich) was spin-coated on pre-cleaned indium tin oxide (ITO) glass plates (Furuuchi-Kagaku, ~10Ω/ □). Then, semiconductor layers were prepared on a PEDOT layer by spin coating using a mixed solution of MEH-PPV (Sigma Aldrich), ZnPc (Sigma Aldrich), and PCBM (Frontier Carbon) in 1,2-dichlorobenzene. The weight ratios of MEH-PPV:PCBM and MEH-PPV:ZnPc:PCBM were 1:8 and 0.5:0.5:8, respectively. The thickness of the blended devices were approximately 150 nm. After annealing at 100 °C for 30 minutes in a N_2 atmosphere, aluminum (Al) metal contacts with a thickness of 100 nm were evaporated as a top electrode. A schematic diagram of the present solar cells is shown in Fig. 1.

The current density-voltage (J-V) characteristics of the solar cells were measured both in the dark and under illumination at 100mW/cm^2 using an AM 1.5 solar simulator in N_2. The solar cells were illuminated through the side of the ITO substrates, and the illuminated area was 0.090 cm^2. Spectral responses of the solar cells were investigated by means of UV-visible spectroscopy.

The molecular structures were optimized by CS Chem3D (CambridgeSoft) and WinMOPAC (Fujitsu Ltd.). Molecular orbital calculations were carried out by MOPAC,

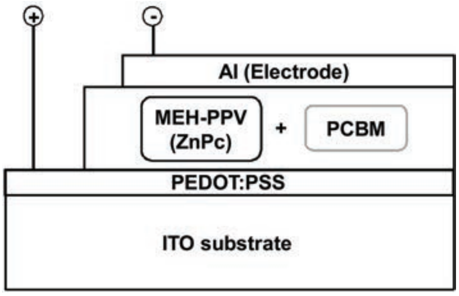

Fig. 1. Structure of bulk-heterojunction solar cells.

and the electronic structures were investigated.

Results and discussion

Measured current density-voltage (J-V) characteristics of MEH-PPV/PCBM and MEH-PPV(ZnPc)/PCBM structures in the dark and under illumination are shown in Fig. 2(a) and 2(b), respectively. Each structure shows characteristic curves for an open circuit voltage and a short circuit current. Although no photocurrent is observed in the dark for both samples, a photocurrent below -2.5 mA/cm^2 is observed under illumination for the MEH-PPV/PCBM structure. Measured parameters of these solar cells are summarized in Table 1. A solar cell with the MEH-PPV/PCBM structure provided a power convergent efficiency (η) of 0.75%, a fill factor (FF) of 0.42, an open circuit voltage (V_{OC}) of 0.70 V and a J_{SC} of 2.59 mA/cm^2, which is better than that of a MEH-PPV(ZnPc)/PCBM device.

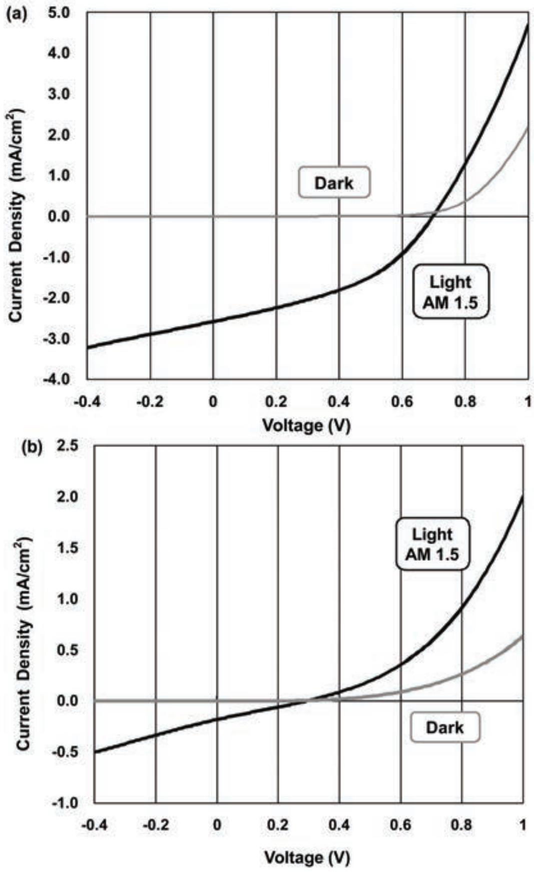

Fig. 2. Measured current density - voltage (J-V) characteristic of (a) MEH-PPV/PCBM and (b) MEH-PPV(ZnPc)/PCBM structures in the dark and under illumination.

Table 1. Measured parameters of the solar cells

	MEH-PPV + PCBM	MEH-PPV + ZnPc + PCBM
V_{OC} (V)	0.70	0.29
J_{SC} (mA/cm^2)	2.59	0.18
FF	0.42	0.25
η(%)	0.75	0.014

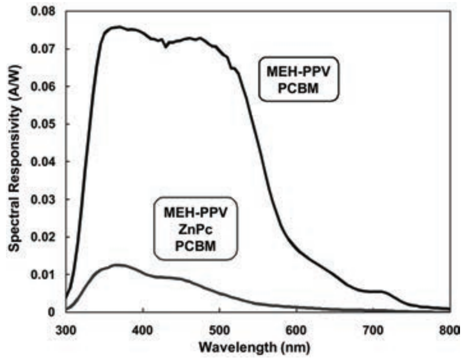

Fig. 3. Spectral photoresponses of the solar cells.

Fig. 3 gives measured spectral photoresponses of the solar cells. The MEH-PPV/PCBM structure shows a high photoresponse in the range of 300 to 600 nm. On the other hand, the MEH-PPV(ZnPc)/PCBM shows a low responsive, which is due to the low solubility of ZnPc in 1,2-dichlorobenzene. Since the ZnPc would be expected to absorb light with a wave length below ~700 nm, optimization of the nanocomposite structure with MEH-PPV (ZnPc) would increase the efficiencies of solar cells.

The structures and symmetry of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important for the prediction of the three-dimensional chemical structure in a chemical reaction, and the electronic structures of the molecules were calculated. The energy levels of LUMO of PCBM are shown in Fig. 4(a), and the LUMO levels are observed around the C_{60} molecule with a high electron negativity. The energy levels of HOMO of MEH-PPV and ZnPc are also shown in Fig. 4(b) and 4(c), respectively. HOMO levels are observed around the five- and six-membered rings in the main chain structures of the polymers, and an asymmetry of the HOMO levels of ZnPc is also observed, which is due to the charge transfer from oxygen and zinc atoms. The effective formation and separation of excitons in the MEH-PPV/PCBM system is due to the nanocomposite structure. The energy levels of HOMO

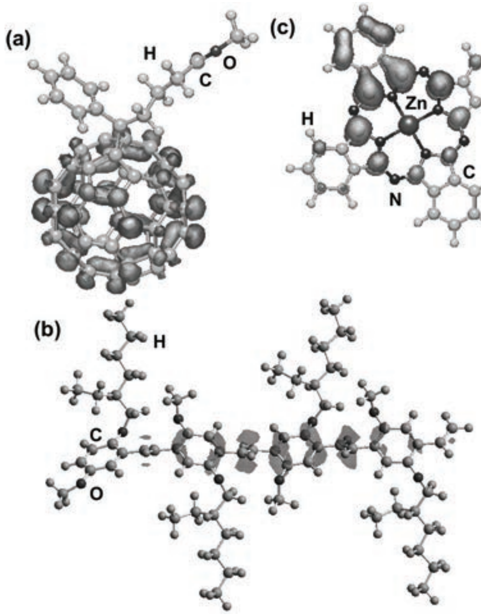

Fig. 4. Calculated (a) LUMO levels of PCBM and.HOMO levels of (b) MEH-PPV and (c) ZnPc.

of MEH-PPV are around the atoms in the main chain structures, and the separated carriers would transfer from MEH-PPV to C_{60}. Interdiffusion of PCBM into the MEH-PPV network would lead to the existence of C_{60} molecules within the exciton diffusion radius of the MEH-PPV network.

An energy level diagram of MEH-PPV /PCBM solar cells is summarized and shown in Fig. 5 Previously reported values [13-15] were used for the energy levels of the figures by adjusting to the present study. An energy gap of 2.1 eV, which is an estimated value from Fig. 3, is used for the model. A relation between V_{OC} and the polymer oxidation potential was reported as $V_{OC} = (1/e)(|E^{Donor}HOMO| - |E^{PCBM}LUMO|) - 0.3(V)$, where e is the elementary charge [14]. The value of 0.3 V is an empirical factor, and this is enough for efficient charge separation [16]. The present model agrees with this equation, and control of the energy levels is important to increase the efficiency.

A combination of the present solar cells and boron nitride nanomaterials with various direct band gaps might be effective to increase efficiencies [17]. The performances of the present solar cells would also be due to the nanoscale structures of the polymer materials, and the control and structure should be investigated further.

Conclusions

Two-types of polymer/fullerene bulk heterojunction solar cells with MEH-PPV/PCBM and MEH-PPV(ZnPc) /PCBM were produced and characterized. A device based on MEH-PPV and PCBM provided a of 0.75%, a FF of 0.42, a V_{OC} of 0.70 V and a J_{SC} of 2.59 mA/cm^2,

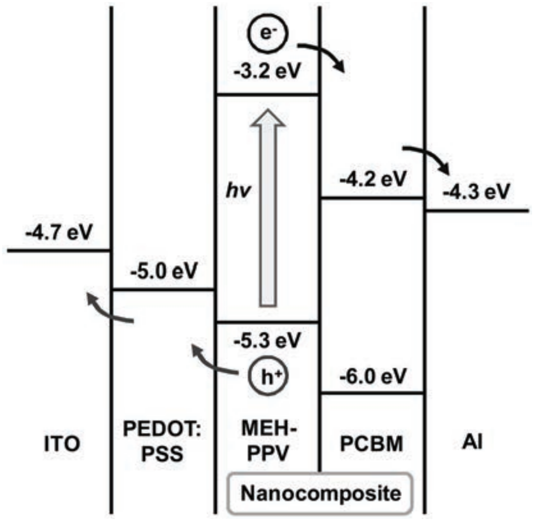

Fig. 5. Energy level diagram of P3HT/PCBM solar cells.

which are better than that of a device based on MEH-PPV(ZnPc) and PCBM. The solar cell with a MEH-PPV/PCBM structure showed a higher photoresponse in the range of 300 to 600 nm. Energy levels of the molecules were calculated, and HOMO levels were localized around the main chains of the polymers. Optimization of blended structures with MEH-PPV and ZnPc would increase the efficiencies of solar cells.

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