4256 *Chem. Mater.* **2009,** *21,* 4256–4260
DOI:10.1021/cm901320p

CHEMISTRY OF MATERIALS
Article

Efficient Organic Solar Cells Based on Planar Metallophthalocyanines

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Received May 14, 2009. Revised Manuscript Received July 22, 2009

Organic solar cells based on planar metallophthalocyanines (MPc, M = Cu, Zn, Pd, Pc)/3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI) were investigated. PdPc/PTCBI solar cells have a peak external quantum efficiency of 30.9%, which is almost twice as those of conventional solar cells based on CuPc and ZnPc/PTCBI. Optical modeling was carried out using a transfer matrix algorithm in order to determine the exciton diffusion lengths for four MPcs. External quantum efficiency measurement and optical modeling indicate that PdPc has the longest exciton diffusion length among four different MPcs, leading to a power conversion efficiency of 1.3% and a short circuit current density of 4.0 mA/cm^2 under the illumination of AM 1.5 G 100 mW/cm^2. When fullerene (C_{60}) was used as an acceptor, solar cells based on PdPc exhibit a short circuit current density of 6.8 mA/cm^2, resulting in a power conversion efficiency of 2.2%, while solar cells based on CuPc show 1.6%.

Introduction

Organic solar cells have attracted much attention due to their compatibility with flexible substrates and low cost fabrication. The power conversion efficiency of the organic solar cells has been improving steadily by the application of the functional materials with high conductivity,[1,2] strong absorption, and large band offset energy[3] and by device engineering.[4–6]

For small molecule organic solar cells, metallophthalocyanines (MPcs) are promising donor materials owing to their high absorption coefficient, high hole mobility, and chemical and thermal stability. A versatile group of phthalocyanines with different electronic and optical properties can be synthesized by varying the centered metal in the Pc ring.[7] However, most of research has focused on planar MPcs such as CuPc and ZnPc. Recently, nonplanar phthalocyanines SnPc and PbPc have been introduced as infrared absorbing materials. However, they have much lower mobility compared to planar MPcs due to poor $\pi-\pi$ overlap of neighboring molecules leading to a low fill factor in solar cells.[8,9] Another promising nonplanar *Pc*, subphthalocyanine, was recently reported and gives large open circuit voltage and 3% of power conversion efficiency.[10]

In planar heterojunction organic solar cells, an important limiting factor for the efficiency is the short exciton diffusion length (L_d) compared to an optical absorption length. Hence, the longer exciton diffusion length is a key factor for large photocurrent and high efficiency. In general, L_d depends on the carrier mobility and the exciton lifetime.[11] It was proposed that when the heavier atoms with 4d or 5d valence electrons than Cu substitute the centered metal in the planar phthalocyanine, the intermolecular electron transfer through the centered metal is facilitated by mixing between d orbitals in the metal and π orbitals in the surrounding Pc ring, which improves the carrier mobility.[12] In addition, the coordination of the heavy metal provides a rapid conversion route of the singlet into the triplet excitons that have a longer lifetime (microsecond ~ millisecond). Recently, it was reported that Pd-porphyrin had longer L_d compared to metal-free and Zn-porphyrin derivatives, which was attributed to

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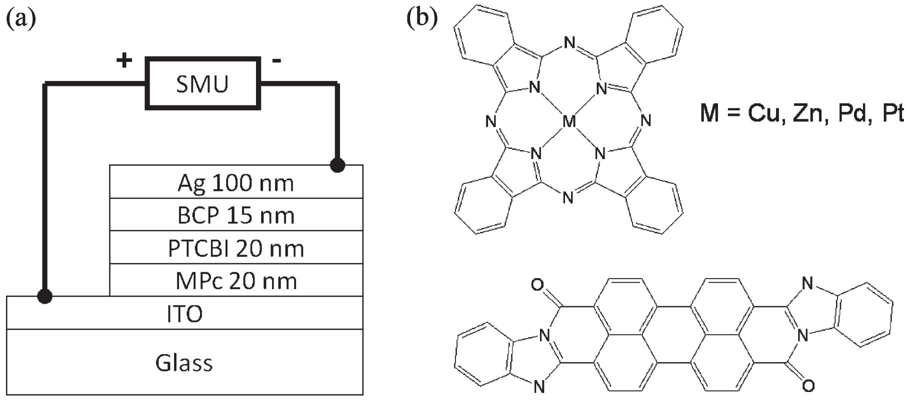

Figure 1. (a) Device structure of MPc/PTCBI solar cells and (b) molecular structures of MPcs (top) and PTCBI (bottom).

singlet−triplet mixing due to spin−orbit coupling.[11] The triplet material of Pt-porphyrin derivative (PtOEP) with long lifetime was proposed and 2.1% of power conversion efficiency was achieved.[13] While porphyrins exhibit head-to-tail molecular stacking, planar phthalocyanines show the cofacial stacking which enahances the exction transport through energy transfer.[14] On the basis of this regard, planar PdPc and PtPc are expected to have longer L_d than CuPc and ZnPc and also to have comparable carrier transport. The increase of the spin−orbit coupling effect from CuPc, PdPc to PtPc was reported in the literature.[15] However, there have been not many reports on solar cells based on the heavy metal centered phthalocyanines.[16]

Here, we demonstrate planar double heterojunction solar cells consisting of PdPc and PtPc as a donor layer and compare the results with the devices made using CuPc and ZnPc. Devices made of metal free phthalocyanine were also discussed to consider the effect of impurities in MPc cells.

The exciton diffusion lengths of MPcs were also estimated and compared. For most of devices, 3,4,9,10-perylene tetracarboxylic bisbenzimidazole (PTCBI) is chosen as an acceptor, which has been widely used and is known to have a good air stability.[17] For comparison, C_{60} was also used as an acceptor in CuPc and PdPc devices.

Experimental Section

All organic layers were deposited by thermal vacuum deposition on 150 nm thick indium tin oxide (ITO) with a sheet resistance of 15 Ω/sq. Phthalocyanines (CuPc, ZnPc, PdPc, and PtPc) and PTCBI were synthesized following previous reports.[18,19] C_{60} (99.9%) was purchased from the MER corp (Tuscon, Arizona). Bathocuporine (BCP) was used as an exciton blocking layer. All organic materials were purified using train sublimation prior to use. The films were deposited at the rate of 1−2 Å/s, with a working pressure of 10^{-7} Torr. Silver was deposited through a shadow mask to form a cathode with active device area of 0.2 cm^2. Device schematic and molecular structure of MPcs are shown in Figure 1. After the fabrication of solar cells, current density−voltage ($J-V$) characteristics were measured under an AM 1.5 G solar simulator with an intensity of 100 mW/cm^2 in a nitrogen-filled glovebox. Unless specified otherwise, all other measurements were carried out in the air. Absorption coefficients were determined using a spectrophotometer, by measuring both transmittance and reflectance of 20 nm thick MPcs on glass substrate. External quantum efficiency (EQE) was measured at varying wavelengths (280−1100 nm) with an interval of 10 nm. HOMO energy levels of MPcs were estimated in solution using a cyclic voltammetry, with an internal reference of ferrocene, assuming that the HOMO energy level of ferrocene is 4.8 eV. Optical constants used in the optical modeling of organic layers were measured by spectroscopic ellipsometry. Atomic force microscopy (AFM) height images for MPcs on glass were obtained in tapping mode. XRD (X-ray diffraction) for 100 nm thick MPc thin films on ITO glass were taken using the K_α radiation in reflection mode of $\theta-2\theta$.

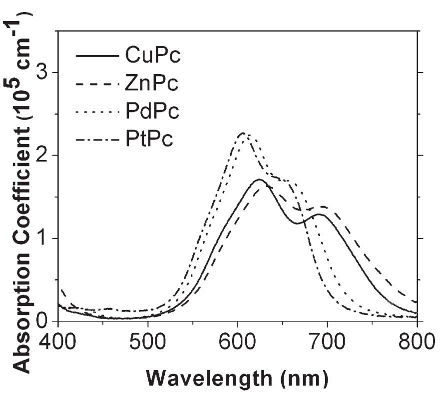

Figure 2. Measured absorption coefficient of MPcs with thickness of 20 nm on glass substrate.

Results and Discussions

Figure 2 shows optical absorption coefficients of different MPcs. The strong absorption in visible range is attributed to Q-band by $\pi-\pi^*$ transition. Absorption spectra of MPcs are sensitive to their electronic structure and molecular packing.[7] Due to excitonic coupling, the Q-band is split into two characteristic peaks. The position and intensity ratio of these peaks indicate that our MPc

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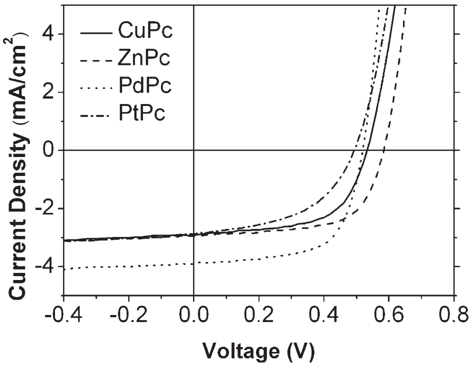

Figure 3. Current density−voltage characteristics of MPc/PTCBI cell in the AM 1.5 G solar illumination with a light intensity of 100 mW/cm^2.

Table 1. Summary of Open Circuit Voltage, Short Circuit Current Density, Fill Factor, and Power Conversion Efficiency of MPc/PTCBI Solar Cells[a]

	CuPc	ZnPc	PdPc	PtPc
efficiency (%)	0.91	1.1	1.3	0.70
J_{sc} (mA/cm^2)	2.9	3.0	4.0	2.9
V_{oc} (V)	0.53	0.58	0.52	0.49
fill factor (%)	60	63	64	50
HOMO level (eV)	5.2	5.1	5.2	5.3

[a] HOMO energy levels of MPcs are shown in the last row in the table.

thin films are of the α-form, which agrees well with the literature.[7,18] The shape of the absorption spectra of PdPc and PtPc is almost identical. The absorption peaks of PdPc and PtPc are stronger when compared with those of CuPc and ZnPc. However, the width of PdPc and PtPc absorption peaks is narrower than that of CuPc and ZnPc. The shift of the absorption peaks to shorter wavelength, by the coordination of a heavy metal to the Pc ring, is due to the strong interaction between the metal and the Pc ligand (hypsochromic shift), which induces an increased energy gap between HOMO and LUMO levels.[20]

Figure 3 shows $J-V$ characteristics of the devices with the structure of ITO/MPc (20 nm)/PTCBI (20 nm)/BCP (15 nm)/Ag (100 nm) under illumination of 100 mW/cm^2. The device parameters are summarized in Table 1. All parameters represent average values of 5 cells. Among all MPc devices fabricated in this study, PdPc/PTCBI solar cells have the highest efficiency of 1.3%, along with a high J_{sc} of 4.0 mA/cm^2 and a fill factor of 64%; while CuPc, ZnPc, and PtPc have J_{sc} values of 2.9, 3.0, and 2.9 mA/cm^2, respectively.

In order to characterize MPc devices in detail, the measurement of the EQE was made as shown in Figure 4a. The highest EQE values of CuPc, ZnPc, PdPc, and PtPc are 16.2, 17.0, 30.9, and 19.7%, respectively. The peak EQE value of CuPc devices is in accord with previous literature data.[21] The higher EQE of PdPc devices can be attributed to stronger absorption and/or a longer L_d. The optical absorption within the devices was

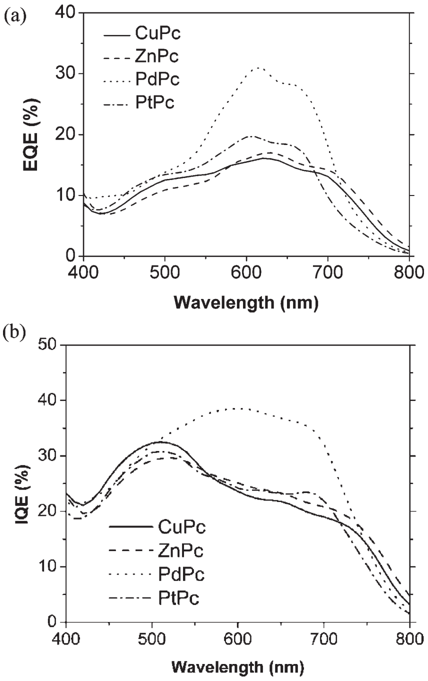

Figure 4. (a) External quantum efficiency (EQE) spectra of MPc/PTCBI solar cells: CuPc (solid line), ZnPc (dashed line), PdPc (dotted line), and PtPc (dashed−dotted line). (b) Internal quantum efficiency (IQE) of MPc/PTCBI devices: CuPc (solid line), ZnPc (dashed line), PdPc (dotted line), and PtPc (dashed−dotted line).

determined by measuring their specular reflection. The results show that 73, 71, 83, and 81% of the incident photons are absorbed in CuPc, ZnPc, PdPc, and PtPc devices at their peak EQE wavelengths of 620, 630, 610, and 610 nm, respectively. The difference in the absorption of PdPc devices from ZnPc and CuPc devices is not significant and hence cannot explain the higher EQE of PdPc devices. Internal quantum efficiency (IQE), which is normalized to absorption, supports the above statement. As shown in Figure 4b, the IQE values for PdPc in the wavelength range of 550−750 nm, where most of absorption is due to MPc, are higher than the other three MPcs. This indicates that a larger portion of absorbed photons contributes to photo current for PdPc.

Since exciton transport to donor/acceptor (D/A) interfaces is limited by shorter exciton diffusion lengths than thickness of donor and acceptor layers, larger D/A interface area leads to higher photo current, as demonstrated for needlelike CuPc morphology in previous literature.[22] The effective D/A interface could be enhanced significantly by this approach. The surface morphology of MPcs was obtained by AFM in the tapping mode, as shown in Figure 5. All four MPcs exhibit the very similar and smooth morphologies without needlelike structures with an rms (root-mean-square) roughness of 2.2−2.8 nm. Given such smoothness, a longer exciton diffusion length is expected for PdPc.

The L_d of MPcs was estimated by fitting the measured EQE to the simulated EQE values using a transfer matrix model, based upon the following assumptions; the device

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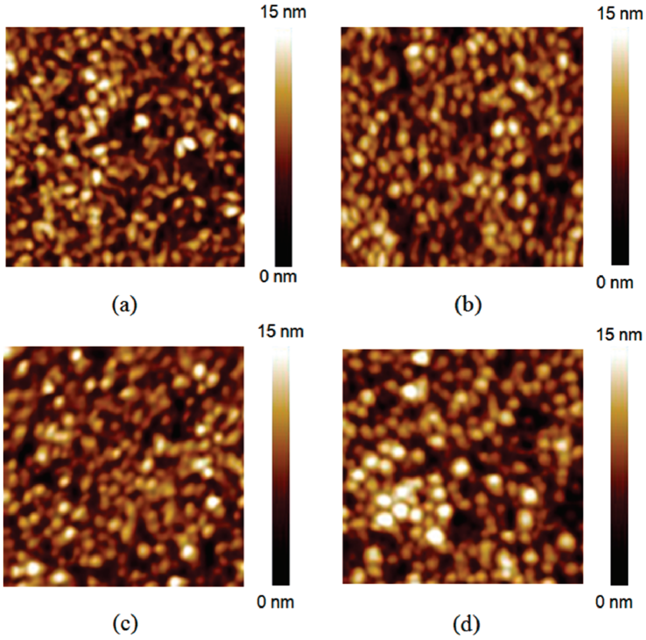

Figure 5. AFM height images of four MPcs (scan size 0.5 μm × 0.5 μm): (a) CuPc, (b) ZnPc, (c) PdPc, and (d) PtPc.

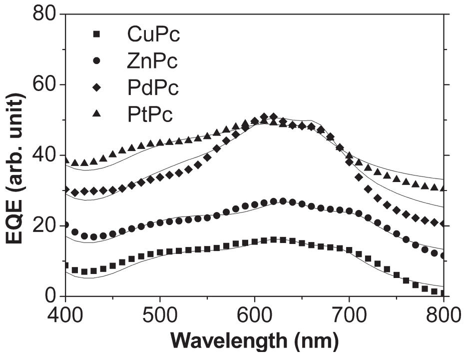

Figure 6. Calculated EQE (solid line) of MPc/PTCBI solar cells with the measured EQE (CuPc : square, ZnPc : circle, PdPc : diamond, PtPc : triangle).

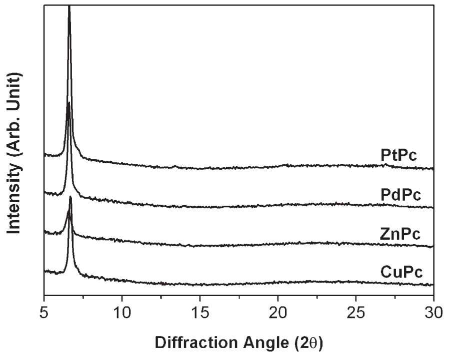

Figure 7. X-ray diffraction patterns of 100 nm thick MPc thin films on glass.

is planar, the concentration of excitons at the interface of MPc/PTCBI is zero, the flux of excitons at the interface of ITO/MPc and MPc/BCP is zero, and the carrier collection efficiency is unity.[23,24] The measured optical constants were used for calculation of the EQE values for each MPc/PTCBI device.

The L_d for each MPc and PTCBI was determined from the best fitting of EQE as shown in Figure 6. Estimated L_d values were 5.8, 6.2, 10.1, and 5.6 nm for CuPc, ZnPc, PdPc, and PtPc, respectively, and 4.5 nm for PTCBI. The longer L_d of PdPc than CuPc and ZnPc may be explained by the enhanced spin−orbit coupling due to the heavier Pd atom. However, L_d of PtPc was not longer than CuPc and ZnPc, even though it was expected to have the longest L_d among the four MPcs due to the heaviest atomic mass. The crystallite size, orientation of the molecules, and unintentional impurity may also influence the exciton transport in organic materials, and thus, affect L_d directly.[25] In this regard, XRD was used to investigate the crystallite size and orientation of MPc thin films. As shown in Figure 7, all MPcs thin films on glass exhibited one predominant peak around 6.6−6.7°, which corresponds to (100) for CuPc and (200) for ZnPc, PdPc, and PtPc. For all MPcs, the molecular stacking axis (lattice parameter, b) is parallel to the substrate and the spacing between adjacent stacking axis is in the range of 13.2−13.4 Å, based on XRD patterns. The crystallite sizes of MPcs estimated by Sherrer method are 37, 24, 39, and 41 nm for CuPc, ZnPc, PdPc, and PtPc, respectively.[26] Since XRD analysis shows that the molecular orientation and crystallite sizes of MPc thin films are all within similar range. This excludes the conjecture that the structural difference of PtPc can be a reason for its low exciton diffusion length.

The photogenerated excitons transport to the donor/acceptor interface through energy transfer mechanisms such as Förster and Dexter.[13] Thus, L_d is also dependent on the intermolecular distance and the orientation of molecules. Additionally, it was reported that the photocurrent of the solar cells made of MPc/C_{60} is linearly dependent on the hole mobility of MPcs.[27] The hole mobility of our MPcs was determined using space charge-limited current (SCLC) model.[28] ITO/MPc/Au device structures were fabricated for SCLC measurement. The thickness of MPcs is in the range of 100−150 nm. The determined zero field hole mobility of MPcs is 9.1×10^{-6}, 9.2×10^{-6}, 2.4×10^{-6}, and 1.1×10^{-7} cm^2/(V s) for CuPc, ZnPc, PdPc, and PtPc, respectively. Although the hole mobility of PdPc is comparable to CuPc and ZnPc, PtPc has the lowest mobility, almost two orders of a magnitude lower than the other MPcs.

The most dominant impurity in MPcs is known to be H_2Pc.[25] Since the sublimation temperature of H_2Pc is very close to most of planar MPcs, it is difficult to separate H_2Pc completely from MPc by thermal gradient

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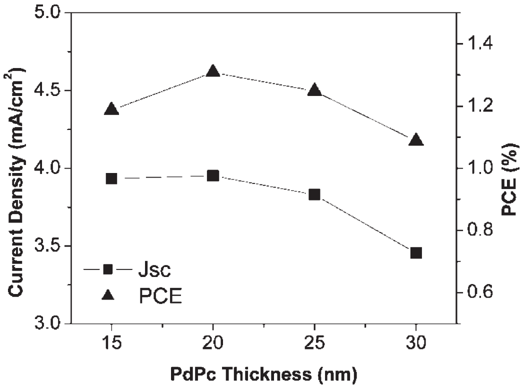

Figure 8. Measured short circuit current density and efficiency of PdPc/PTCBI devices as a function of PdPc thickness.

purification approach. In order to highlight the effect of H_2Pc on the device performances of MPc cells, we fabricated and tested solar cells made of H_2Pc/PTCBI under the same illumination conditions as the MPc cells. The V_{oc} of H_2Pc cells is 0.45 V, which is lower than any of the MPcs in this study, while J_{sc} is 2.8 mA/cm^2, which is comparable to CuPc and ZnPc. In general, V_{oc} of organic solar cells is proportional to the energy difference between HOMO of the donor and LUMO of the acceptor. From the HOMO levels measured by the cyclic voltammetry, shown in Table 1, the higher V_{oc} of PtPc than CuPc and ZnPc was expected. However, V_{oc} of PtPc is 0.49 V, which is also lower than that of ZnPc and CuPc. The incorporation of H_2Pc in PtPc during synthesis and the difficulty to remove it completely during purification may contribute to the decrease in mobility and V_{oc} of PtPc. H_2Pc impurity decreases the hole mobility of PtPc by introducing trap states, which also hinder the exciton transport, resulting in lower exciton diffusion length than expected. Detailed study on the impact of impurities on device performance is underway.

The effect of PdPc thickness on device performance was studied by varying the thickness of PdPc from 10 to 30. Devices with 10 nm thickness PdPc failed due to large leakage current. The measured J_{sc} under illumination and the efficiency are shown in Figure 8. For all devices, FF is over 60%. The best efficiency was achieved with 20 nm thickness of PdPc due to highest J_{sc} of 4.0 mA/cm^2 and FF of 64%. J_{sc} decreases with increasing thickness above 20 nm, which supports the determined exciton diffusion length.

C_{60} was used as an acceptor material for PdPc and also compared with CuPc/C_{60} devices in order to investigate the performance of PdPc on an acceptor material other than PTCBI. It is known that C_{60} has much longer exciton diffusion length (~40 nm) than PTCBI.[23] Figure 9 shows $J-V$ characteristic of two devices under illumination with device structure of ITO/MPc (20 nm)/C_{60} (30 nm)/BCP (10 nm)/Ag (100 nm). Device parameters of both cells are shown in Table 2. Due to significant photo current contribution from C_{60} as shown in inset picture of Figure 9, the photo current density is larger than that of MPc/PTCBI devices. PdPc/C_{60} devices exhibit J_{sc} of 6.8 mA/cm^2, while CuPc/C_{60} devices give 4.7 mA/cm^2, leading to an efficiency of 2.2%, compared to 1.6% of CuPc/C_{60} devices.

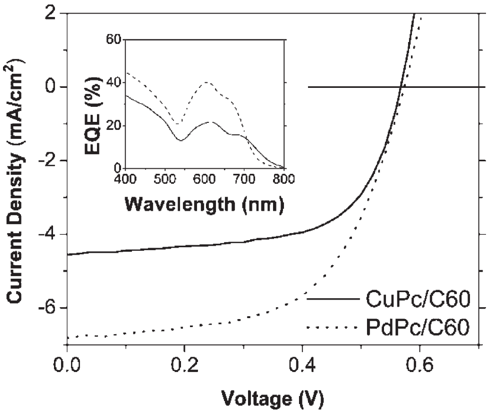

Figure 9. Current density−voltage characteristics and (inset) EQE spectra of CuPc and PdPc/C_{60} cells in the AM 1.5 G solar illumination with a light intensity of 100 mW/cm^2.

Table 2. Summary of Open Circuit Voltage, Short Circuit Current Density, Fill Factor, and Power Conversion Efficiency of CuPc/C_{60} and PdPc/C_{60} Solar Cells

	efficiency (%)	J_{sc} (mA/cm^2)	V_{oc} (V)	fill factor (%)
CuPc/C_{60}	1.6	4.5	0.56	62
PdPc/C_{60}	2.2	6.8	0.57	57

Conclusions

In conclusion, we have demonstrated that PdPc is a promising donor material with long exciton diffusion length which leads to higher efficiency of PdPc/PTCBI solar cells than CuPc and ZnPc/PTCBI devices. By using a donor material which has comparable mobility to CuPc and ZnPc but has longer exciton diffusion length, the efficiency and the photocurrent density were noticeably enhanced. This supports that the longer exciton diffusion length helps improve the device efficiency of planar heterojunction solar cells. In addition, the use of PdPc donor along with C_{60} acceptor increases the cell performance even further. It is anticipated that further device engineering based on PdPc/C_{60} tandem structure will resulting in higher efficiency than 2.2%.

Acknowledgment. We would like to acknowledge the partial support of the Advanced Photovoltaics Center and the National Science Foundation (CBET-0756148). H.M.H and G.E.J. acknowledge the FiDiPro program and the Graduate School of Modern Optics and Photonics, Finland. J.L. thanks the National Science Foundation (CHE-0748867) for partial support of this work.