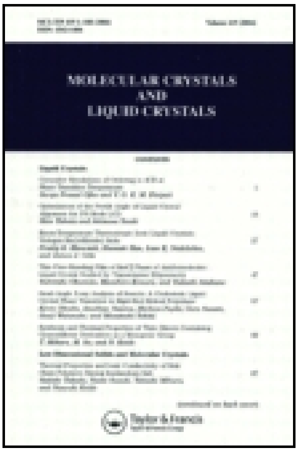

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An Optimal Design for Photovoltaic Properties of Two-Layer Organic Solar Cells Using Phthalocyanine and Perylene Derivatives

Hisao Yanagi [a] , Nobumasa Tamura [a] , Shinichi Taira [a] , Hiroyuki Furuta [a] , Shinya Douko [a] , Günter Schnurpfeil [b] & Dieter Wöhrle [b]

[a] Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe, 657, Japan

[b] Org. und Makromol. Chemie, Universität Bremen, D-28334, Bremen, Germany

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AN OPTIMAL DESIGN FOR PHOTOVOLTAIC PROPERTIES OF TWO-LAYER ORGANIC SOLAR CELLS USING PHTHALOCYANINE AND PERYLENE DERIVATIVES

HISAO YANAGI, NOBUMASA TAMURA, SHINICHI TAIRA,
HIROYUKI FURUTA, SHINYA DOUKO, GÜNTER SCHNURPFEIL[†]
AND DIETER WÖHRLE[†]
Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657, Japan
[†]Org. und Makromol. Chemie, Universität Bremen, D-28334 Bremen, Germany

Abstract Photovoltaic properties of two-layer organic p/n junction solar cells were studied for vacuum-deposited films of p-type phthalocyanine derivatives having different π-electron conjugating macrocycles and n-type N,N'-substituted 3,4:9,10-perylenebis(dicarboximide) having different peripheral groups. The power conversion efficiency was optimized by controlling the film thickness, morphology and contact with top-electrodes. The film morphology of the perylene derivatives changed depending on their peripheral alkyl groups, and higher photocurrents were obtained for the cell with a homogeneous layer of perylene derivatives. The molecular modification in p-type phthalocyanine derivatives changed the cell photovaltage. A substitution with electron-withdrawing groups, which lowered the highest occupied molecular orbital (HOMO) energy of the p-type molecules, increased the photovoltage. On the other hand, an extention of the macrocyclic ring from phthalocyanine to naphthalocyanine lowered the photovoltaic efficiency.

INTRODUCTION

Solar energy conversion has already been achieved by photovoltaic cells using inorganic (silicon) semiconductors. A practical use of these solar cells depends on a reduction in price of the devices. Since Tang[1] has reported organic p/n junction solar cells using two-layer films of phthalocyanine/perylene derivatives, molecular semiconductors[2] have attracted attetion as materials for photovoltaic devices because of their low material cost and easy processing into thin films. Semiconducting properties of organic meterials can be modified by tailoring the molecular structure, so that different kinds of p-type and n-type molecular semiconductors have so far been experimented for organic p/n junction solar cells.[3-5] However, the energy conversion efficiency of those cells has not been beyond the value, 1%, reported by Tang.[1] For improvement of their photovoltaic performance, further investigations are required to optimize the cell architecture and also to make clear the semiconducting nature in molecular materials such as doped impurities, space-charge formation, and charge-carrier generation.

In this work, different derivatives of metal phthalocyanine (MPc) and N,N'-substituted perylenebis(dicarboximide) (R_2P) were prepared for the p-type and n-type semiconductor layers, respectively. The photovoltaic efficiency of the two-layer p/n junction cells was optimized by controlling the layer structure, thickness, and electrical contact with top-

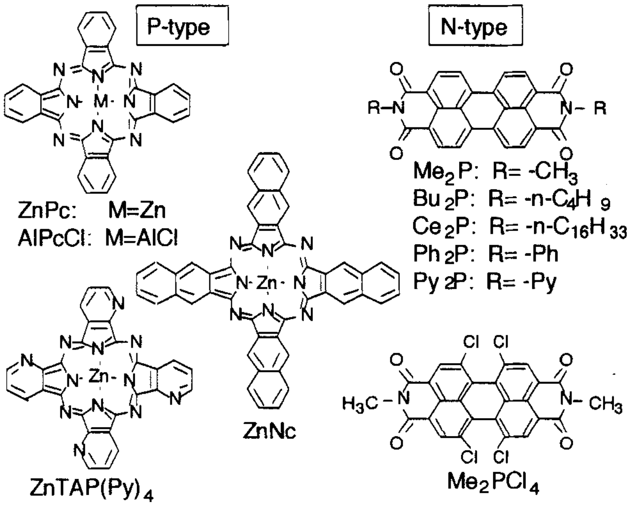

FIGURE 1. Molecular structures of p- and n-type dyes.

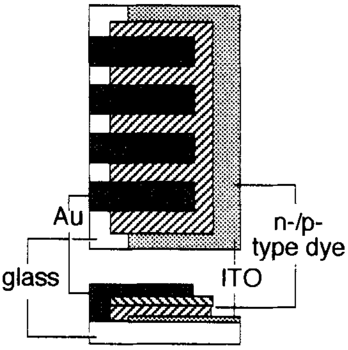

FIGURE 2. Structure of p/n junction cell.

electrodes. The junction characteristics of the cells were discussed in terms of the electronic energy-band configuration depending on the modified molecular structures.

EXPERIMENTAL

Figure 1 shows the molecular structure of used p-type MPc and n-type R_2P derivatives. As shown in the cell configuration in Fig 2, the photovoltaic cell was constructed by a successive vacuum-deposition of n-type, p-type materials or vice versa, and a top-electrode of Au or In onto indium tin oxide (ITO) coated glass substrate (25x50mm) under a vacuum of 5×10^{-4} Pa. The thickness of the organic layers was controlled to be 30-150 nm by a quartz crystal microbalance.

Photovoltaic responces of the cells were evaluated from current-voltage (I-V) characteristics in the dark and under illumination of white light (100 mW/cm^2) and short-circuit photocurrent action spectra under monochromatic illumination (normalized at 1 mW/cm^2). The illumination was made through the ITO side. Morphology of the deposited organic layers was observed by a scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Thickness Dependence in the ITO/Me$_2$P/AlPcCl/Au Cell

The two-layered films of MPc and R_2P derivatives absorb solar light efficiently in the visible wavelength region. MPc derivatives exhbit the Q-band absorption[6] in the longer wavelength region, which shifts depending on the π-conjugating macrocyclic structure. On the other hand, R_2P derivatives indicate absorption bands in the shorter wavelengths, which are not significantly affected by the peripheral substituents. For constructing p/n junction solar cells, the cell architecture such as the film thickness and sequence of the p- and n-layers should be considered for an efficient energy conversion.

In Fig.3, typical I-V curves in the dark and under illumination for the ITO/Me$_2$P/AlPcCl/Au

TABLE I. Thickness dependence of photovoltaic parameters for ITO/Me2P/AlPcCl/Au cells.

Thickness[a] (nm)	Isc (mA/cm^2)	Voc (V)	ff	η (%)
30/70	0.58	0.41	0.39	0.090
50/50	0.67	0.37	0.35	0.086
70/30	0.52	0.42	0.28	0.060
100/100	0.50	0.40	0.38	0.075
150/150	0.42	0.36	0.33	0.050

[a] Thickness of Me2P(nm)/AlPcCl(nm).

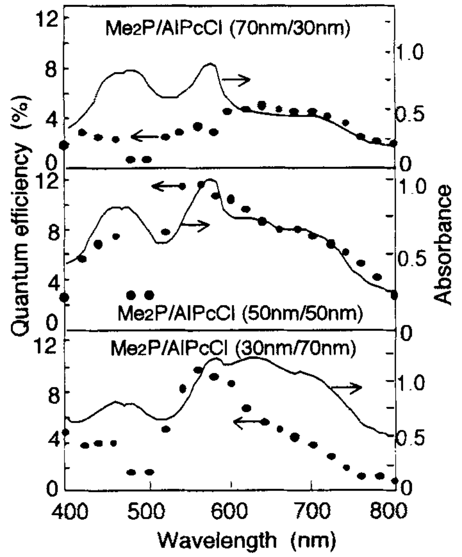

FIGURE 4. Thickness dependence of photocurrent action spectra for the ITO/Me$_2$P/AlPcCl/Au cells.

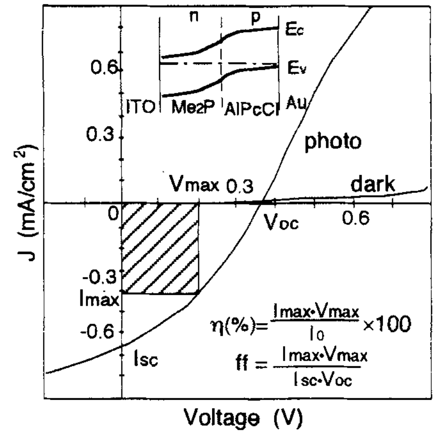

FIGURE 3. I-V curves of the ITO/Me$_2$P/AlPcCl/Au cell in the dark and under illumination.

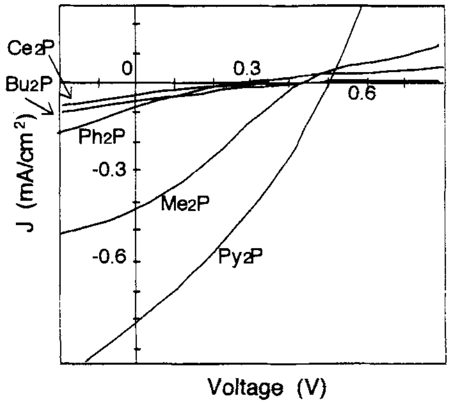

FIGURE 5. I-V curves under illumination for the cells with AlPcCl and different R$_2$P derivatives.

cell, in which Me$_2$P, subsequetly AlPcCl, with thickness of 50nm respectively, were vacuum-deposited onto ITO substrate, and the Au top-electrode was deposited with 30nm thickness. It shows a typical rectification where the dark currents increase at a positive voltage is biased at the Au electrode. The curve under illumination indicates short-circuit photcurrents (I_{sc}) of -0.67 mA/cm^2 and open-circuit photovoltage (V_{oc}) of 0.37V. This photoresponce is demonstrated by a band-structure at the p/n junction of p-type AlPcCl and n-type Me$_2$P, as illustrated in the figure.

The photovltaic parameters of I_{sc}, V_{oc}, fill factor (ff) and power conversion efficiency (η) changed depending on the thickness of the Me$_2$P and AlPcCl layers, as summarized in TABLE I. When thicker layers are deposited, the values of I_{sc} and η decrease due to an increase of series resistance of the organic layers. When the photovoltaic efficiency is compared among cells having the same total thickness of Me$_2$P/AlPcCl, the thinner Me$_2$P layer produces higher η. In Fig 4, dependence of photocurrent action spectra on the thickness ratio of the p/n layers is shown for the ITO/Me$_2$P/AlPcCl/Au cells with a total thickness of 100nm. The cell with a thicker Me$_2$P layer (Me$_2$P/AlPcCl=70nm/30nm) exhibits a low quantum efficiency at the absorption region (400-600nm) of Me$_2$P. The cell with a thickness ratio of 50nm/50nm shows the action spectrum which well matches with the absorption spectrum of the two-layered film. When the Me_2P thickness is decreased to 30nm, the action spectrum shows a peak around 600nm where both absorption bands of Me_2P and AlPcCl overlap. This thickness dependence of action spectra suggests that the photovoltaic response is attributed to the space-charge layer formed at the Me_2P/AlPcCl interface, and a thick Me_2P layer decreases photocurrents due to the filtering effect of the incident light.[7]

Morphological Effect of the Organic Layer

Morphology of the vacuum-deposited organic layers should be considered to compare the photovoltaic efficiecy of the cells. Previous photovoltaic studies on MPc derivatives have shown a significant effect of the film morphology such as homogeneity and grain size.[8] The vacuum-deposited films of R_2P derivatives used in this work exhibited different morphology depending on the substituted peripheral groups. The SEM observations showed that the films of Me_2P and Py_2P grew homogeneously in densely packed grains of ~40nm in size, whereas the films of Bu_2P, Ce_2P and Ph_2P were inhomgeneous with larger grains of various sizes. These morphological difference of the R_2P films significantly affected the photovoltaic efficiency of the p/n juction cells with AlPcCl, as shown in Fig.5. The ITO/Me_2P/AlPcCl/Au and ITO/Ph_2P/AlPcCl/Au cells show higher I_{sc} and V_{oc} values than the other ones. The high photocurrents for Me_2P and Ph_2P can be attributed to their higher carrier mobility through the densely packed grains. The homogeneous surface of the Me_2P and Ph_2P also seems to contribute a better contact with the AlPcCl layer at the p/n junction interface to produce higher V_{oc}. A change of electronic energy levels due to the substituted groups in the R_2P derivatives should also be considered to compare their photovoltage. However, such an energetic change by the substituted groups seems to be less effective, because the molecular characteristics of the R_2P derivatives are much dependent on the π-electron conjugating system of the perylene framework.

Effect of Cell Architecture

Generally, in the two-layer p/n junction cells, the n-type R_2P derivative is first deposited onto the ITO substrate,1) and the incident light is illuminated onto this R_2P layer through the ITO substrate because of the use of Förster radiationless energy transfer from the shorter wavelength absorbing R_2P to the longer wavelength absorbing MPc.[9] As shown in Fig. 6, an inversion of the Me_2P and AlPcCl layers resulted in different wavelength dependence of photocurrents. The ITO/Me_2P(100nm)/AlPcCl(100nm)/Au cell shows the filtering effect where the photocurrents decrease in the absorption region of Me_2P at the shorter wavelength. On the other hand, the inversed ITO/AlPcCl(100nm)/Me_2P(100nm)/Au cell exhibits no photocurrents at the longer wavelength region because of the filtering effect of the AlPcCl layer which is illuminated through the ITO substrate. It clearly suggests that the photocarriers are generated in the space-charge layer spread at both sides of the Me_2P/AlPcCl interface.

The inversion of the p/n layers affected the photovoltaic efficiency as shown in Table II. Due to disadvantage for Förster energy transfer the inversed cell results in a lower I_{sc} value. For the inversed ITO/AlPcCl/Me_2P/Au cell, the contact of the n-type Me_2P layer with the Au top-electrode having a high work function possibly forms the Schottky contact. The potential barrier at this contact opposes to the potential gradient formed at the AlPcCl/Me_2P junction, so that the V_{oc} value of the inversed cell is reduced. From these findings, V_{oc}, and consequently η, of the inversed cell can be improved when the top-electrode of Au is replaced with In having a lower work function which forms an ohmic contact with the Me_2P layer, as shown in Table II.

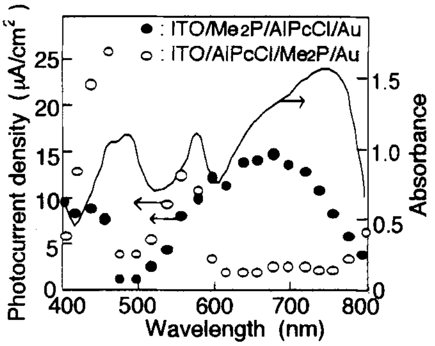

FIGURE 6. Photocurrent action spectra for the ITO/Me2P/AlPcCl/Au and ITO/AlPcCl/Me2P/Au cells.

TABLE II. Influence of cell structure on photovoltaic parameters for Me2P(100nm)/AlPcCl (100nm) cells.

Cell	Isc (mA/cm²)	Voc (V)	ff	η (%)
ITO/Me2P/AlPcCl/Au	0.41	0.43	0.28	0.049
ITO/AlPcCl/Me2P/Au	0.23	0.40	0.31	0.028
ITO/AlPcCl/Me2P/In	0.36	0.65	0.38	0.088

TABLE III. Photovoltaic parameters of the p/n junction cells using different perylene and phthalocyanine derivatives.

Cell	Isc (μA/cm²)	Voc (V)	ff	η (%)
Me2P/ZnNc	6.1	0.10	0.28	2.4×10^{-4}
Me2P/ZnPc	33.7	0.31	0.40	8.0×10^{-3}
Me2P/ZnTAP(Py)4	23.2	0.47	0.23	6.0×10^{-3}
Bu2P/ZnNc	1.36	0.09	0.21	5.0×10^{-6}
Bu2P/ZnPc	7.75	0.11	0.21	1.9×10^{-3}
Bu2P/ZnTAP(Py)4	1.15	0.23	0.21	7.5×10^{-5}
Me2PCl4/ZnNc	0.55	0.09	0.29	2.5×10^{-5}
Me2PCl4/ZnPc	6.00	0.12	0.24	4.1×10^{-4}
Me2PCl4/ZnTAP(Py)4	1.22	0.15	0.24	6.7×10^{-4}

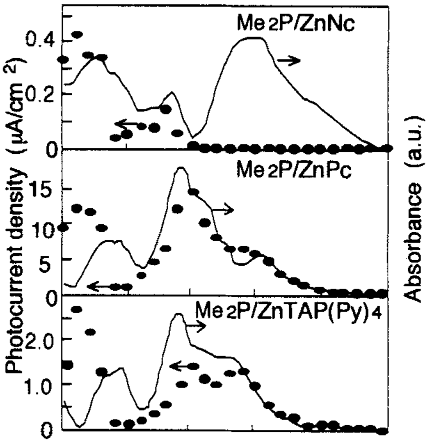

FIGURE 7. Photocurrent action spectra for the ITO/Me2P/ZnNc/Au, ITO/Me2P/ZnPc/Au and ITO/Me2P/ZnTAP(Py)4/Au cells.

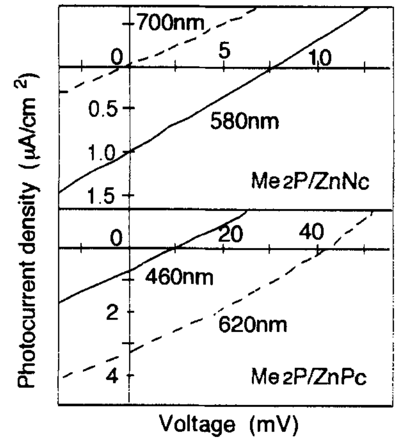

FIGURE 8. I-V curves of the ITO/Me2P/ZnPc/Au and ITO/Me2P/ZnNc/Au cells under monochromatic illuminations.

Dependence of Modified Molecular Characteristics

For development of molecular semiconducting abilities, a systematic relation should be established between the molecular structure and their semiconducting properties. A general tendency suggests that a molecular modification with electron-withdrawing substituents makes organic materials n-type-like, whereas a substitution with electron-donating groups makes them p-type-like.[10,11] Previous investigations have revealed that ambient oxygens act as acceptors for p-type MPc's,[12] and doping with electron donors like H_2 and NH_3 increases n-type semiconduction.[10,13]

In this work effects of molecular modification on photovoltaic behaviors of p/n junction cells were studied using zinc complexes of different π-electron conjugating macrocycles as p-type materials and R_2P derivatives with different peripheral groups as n-type materials. Their photovoltaic parameters are shown in Table III. The Me_2P/ZnPc cell shows the highest photovoltaic efficiency among these cells. Replacing the R_2P derivatives with Bu_2P and Me_2PCl_4 decreases both I_{sc} and V_{oc} values. Among the p-type zinc complexes, $ZnTAP(Py)_4$ gives higher V_{oc} values while ZnNc shows a low phtovoltaic efficiency. Photocurrent action spectra in Fig.7 show a comparison of the three Zn-complexes for the cells with Me_2P. The cells using ZnPc and $ZnTAP(Py)_4$ exhibit photoresponses in the light absorption region of both p- and n-type layers. However, the Me_2P/ZnNc cell indicates photocurrents only in the absorption region of Me_2P.

Fig.8 shows I-V curves of the Me_2P/ZnPc and Me_2P/ZnNc cells under monochromatic illumiations (1mW/cm^2) at the absorption maxima for the respective layers. The Me_2P/ZnPc cell shows photovoltaic effects under both illuminations for the Me_2P (460nm) and ZnPc (620nm) absorptions, where the latter illumination exhibits a higher response. On the other hand, the Me_2P/ZnNc cell exhibits no photorespose at the absorption maximum of ZnNc (700nm). It suggests that the space-charges in the Me_2P/ZnPc diffuse more in the ZnPc layer at the p/n interface, and that in the Me_2P/ZnNc cell the space-charges are not formed in the ZnNc layer or only formed at the ZnNc surface in contact with Me_2P.

The molecular orbital calculation revealed that the highest occupied molecular orbital (HOMO) energy of the compounds used here changes as follows; Me_2PCl_4 (-9.32eV) < Me_2P (-8.90eV) < Bu_2P (-8.88eV) < $ZnTAP(Py)_4$ (-7.12eV) < ZnPc (-6.70eV) < ZnNc (-6.34eV). It demonstrates that the n-type R_2P derivatives are in low HOMO energy, while the p-type Zn complexes are in high HOMO energy. The substitution with electron-withdrawing chlorine in Me_2PCl_4 and pyridyl groups in $ZnTAP(Py)_4$ lowers the HOMO energy of molecules, which is unfavorable for n-type materials, but preferable for p-type ones, to produce a high photovoltage in the p/n junction cell. On the other hand, the substitution with electron-donating alkyl groups in R_2P derivatives and the extention of the macrocyclic system from ZnPc to ZnNc, which result in an increase of their HOMO energy, decrease the photovoltaic efficiency of the cells.

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