



The effect of fullerene doping on photoelectric conversion using titanyl phthalocyanine and a perylene pigment

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Abstract

The effect of fullerene (C₆₀) doping on photoelectric conversion using titanyl phthalocyanine (TiOPc) and a perylene pigment, *N, N'*-dimethyl-3,4 : 9,10-perylenebis(dicarboximide) (MPCI), was investigated. A new three-layer cell, ITO/MPCI/C₆₀-doped TiOPc/TiOPc/Au, exhibited a higher quantum yield for charge-carrier photogeneration than a two-layer cell without the C₆₀-doped TiOPc layer, ITO/MPCI/TiOPc/Au, upon irradiation with monochromatic light which TiOPc mainly absorbs. The three-layer cell showed a high conversion efficiency of 0.63% for incident white light at an intensity of ca. 100 mW cm⁻². © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Organic photovoltaic device; Titanyl phthalocyanine; *N, N'*-dimethyl-3,4 : 9,10-perylenebis(dicarboximide); Fullerene; Doping

1. Introduction

Organic photovoltaic devices have attracted a great deal of attention not only from the scientific viewpoint but also for their applications in solar cells, photosensors, etc. Organic materials are attractive because of their light weight and processability, and

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the ease of material design on the molecular level. There have been a number of reports on organic photovoltaic devices using a variety of dyes [1–21] and semiconducting polymers [22–30]. The search for new materials with good performance characteristics as well as the improvement in device fabrication has been a subject of importance.

Titanyl phthalocyanine (TiOPc) is expected to be a promising candidate for photoactive materials for use in photovoltaic devices, because TiOPc functions as an excellent material for charge-carrier photogeneration in photoreceptors for use in electrophotography [31]. It is expected that p–n heterojunction devices using TiOPc as a p-type organic semiconductor in combination with suitable n-type organic semiconductors exhibit high conversion efficiencies. In addition, the use of TiOPc as a photoactive material for photoelectric conversion is of interest from the following viewpoints. The judicious choice of an n-type organic semiconductor in combination with TiOPc will allow the fabrication of a device that responds to light over the whole visible wavelength range. Since TiOPc exists as several different polymorphs, it is of interest to examine the effect of the morphology of TiOPc on its photovoltaic properties.

Shirota et al. have reported that photovoltaic devices consisting of the thin films of TiOPc and *N, N'*-dimethyl-3,4:9,10-perylenebis(dicarboximide) (MPCI), sandwiched between indium-tin-oxide (ITO) and gold (Au) electrodes, showed a response to light over the whole visible wavelength range from 400 to 900 nm, as expected from their electronic absorption spectra [20]. It has been shown that the cell with a structure of ITO/MPCI(500 Å)/TiOPc(500 Å)/Au exhibits a higher conversion efficiency than the cell with a structure of ITO/TiOPc(500 Å)/MPCI(500 Å)/Au, because the formation of a Schottky barrier at the interface between the MPCI layer and the Au electrode in the latter cell reduces the photovoltaic effect resulting from the p–n heterojunction between TiOPc and MPCI and that the former cell exhibits a conversion efficiency of ca. 0.35% for white light at 8–130 mW cm⁻² [20]. It was also found that the p–n heterojunction cell using the polycrystalline film of α -TiOPc exhibits a much higher conversion efficiency than the cell using the amorphous film of TiOPc under irradiation with monochromatic light which TiOPc mainly absorbs [21].

Recently, bilayer heterojunction devices or devices consisting of interpenetrated network composites using fullerene (C₆₀) and conjugated polymers, e.g., poly(*p*-phenylenevinylene), poly[2-methoxy-5-2'-ethyl-hexyloxy]-1,4-phenylenevinylene], and polythiophene derivatives, have been reported to show high conversion efficiencies due to the occurrence of efficient photo-induced charge transfer from the polymers to C₆₀ [32–38].

In the present study, we have investigated the effect of doping with C₆₀ on photoelectric conversion using TiOPc and MPCI. We have fabricated a new three-layer photovoltaic device using TiOPc, MPCI, and C₆₀-doped TiOPc and examined the performances of the device in comparison with those of a two-layer device using TiOPc and MPCI. It is expected that efficient charge separation will take place by successive electron transfer from the C₆₀ anion radical to MPCI, leading to an improvement in conversion efficiency.

2. Experimental

TiOPc was prepared by the reaction of tetra-*n*-butyl orthotitanate with 1,3-diiminoisoindoline in quinoline at 180°C for 3 h. Crude precipitates were washed with hot *N,N'*-dimethylformamide and then with hot methanol, and purified by train sublimation in vacuo (5 mm Hg, 500°C). Anal. Calcd: C, 66.68; H, 2.80; N, 19.44. Found: C, 66.76; H, 2.79; N, 19.41%. TiOPc thus prepared and purified showed X-ray diffraction peaks at $2\theta = 9.3, 10.4, 13.2, 16.1, 20.8, 23.2, 25.5, 26.3, 27.0$ and 32.6° , which were in accordance with those of a crystalline sample of β -TiOPc. MPCl (Paliogen Red L420) was purchased from BASF AG and purified by train sublimation in vacuo (5 mm Hg, 480°C). Anal. Calcd: C, 74.64; H, 3.37; N 6.70. Found: C, 74.64; H, 3.27; N, 6.71%. C₆₀ was provided by Prof. Dr. Oleg Schevaleyevsky, Semenov Institute of Chemical Physics, Moscow, Russia. Its purity was 99.95%.

Layered photovoltaic devices, ITO/MPCl(500 Å)/TiOPc(500 Å)/Au (cell (a)) and ITO/MPCl(500 Å)/30 mol% C₆₀-doped TiOPc(300 Å)/TiOPc(200 Å)/Au (cell (b)), were fabricated as follows. The organic layers of MPCl and TiOPc were successively deposited onto an ITO-coated glass substrate by vacuum deposition at ca. 10^{-5} Torr at an evaporation rate of $2\text{--}3 \text{ \AA s}^{-1}$. The C₆₀-doped TiOPc layer was deposited by simultaneous evaporation of TiOPc and C₆₀ from two different sources. A semitransparent gold electrode was then deposited onto the top organic film.

Current density–voltage characteristics in the dark and under irradiation with monochromatic visible light or white light were measured as follows. A ramp voltage with a scan rate of 10 mV s^{-1} was applied to the cell using a potentiostat equipped with a function generator and the current was recorded as a function of the applied voltage with a *X–Y* recorder. Monochromatic visible light or white light was obtained from a 500 W xenon lamp using a monochromator or a metal mesh attenuator, respectively. The intensities of monochromatic and white light were measured with a power meter (Anritsu ML 96B) and a thermopile (gentec TPM-310), respectively. Action spectra were obtained by plotting quantum yields for the photogeneration of charge carriers against the wavelength of incident light.

3. Results and discussion

The films of TiOPc and MPCl obtained by vacuum deposition of β -TiOPc and crystalline MPCl showed only a broad halo in the X-ray diffraction pattern and were assigned to be amorphous. Fig. 1 shows the electronic absorption spectra of the vacuum-deposited films of TiOPc, MPCl, and C₆₀. TiOPc and MPCl absorb light in the wavelength range from 600 to 900 nm and from 400 to 600 nm, respectively. C₆₀ shows a weak absorption in the wavelength range from 400 to 600 nm.

Fig. 2 shows the structures of layered photovoltaic cells, (a) and (b). Both cells showed a rectification behavior in the dark. The forward current flowed from the ITO electrode to the Au electrode through the outer circuit when a positive bias was applied to the Au electrode in contact with TiOPc. That is, electrons and holes moved toward the Au and ITO electrodes through the TiOPc and MPCl layers, respectively.

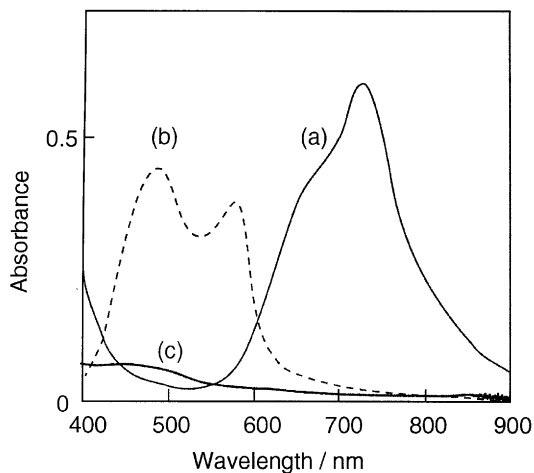


Fig. 1. Electronic absorption spectra of vacuum-deposited (a) TiOPc, (b) MPCl, and (c) C₆₀ films. Film thickness: 500 Å.

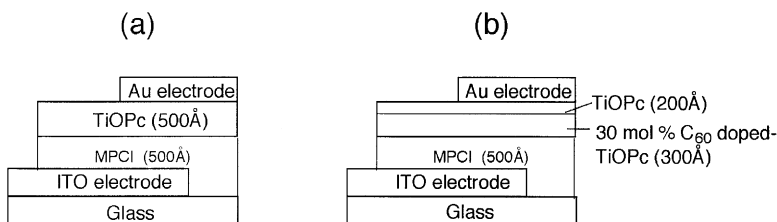


Fig. 2. Side views of layered photovoltaic devices: (a) ITO/MPCl(300 Å)/TiOPc(500 Å)/Au and (b) ITO/MPCl(500 Å)/30 mol% C₆₀-doped TiOPc(300 Å)/TiOPc(200 Å)/Au.

For both cells, photocurrent flowed from the Au electrode to the ITO electrode through the outer circuit in a direction opposite to the dark current, as a result of which photogenerated electrons and holes moved toward the ITO and Au electrodes through the MPCl and TiOPc layers, respectively.

The quantum yield for the photogeneration of charge carriers, which is defined as electrons per photon, can be calculated from the following Eq. (1) [9]:

$$\Phi = \frac{J_{sc}/e}{I_t \left/ \frac{\lambda \times 10^{-9}}{hc} \right.} = \frac{1240 \times J_{sc}}{I_t \lambda}, \quad (1)$$

where J_{sc} (A cm⁻²) is the short-circuit photocurrent, e (C) is the elementary charge, I_t (W cm⁻²) is the intensity of monochromatic light transmitted through the ITO electrode, and λ (nm) is the wavelength of irradiated light, h (J s) is the Planck constant, and c (m s⁻¹) is the speed of light in vacuum. Fig. 3 shows the action spectra

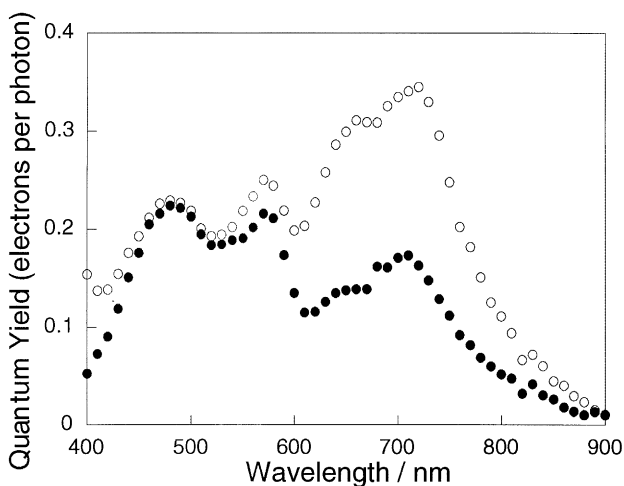


Fig. 3. Action spectra of the quantum yields for charge-carrier photogeneration for the cells upon irradiation with monochromatic light through the ITO electrode: (a) ITO/MPCl(500 Å)/TiOPc(500 Å)/Au and (b) ITO/MPCl(500 Å)/30 mol% C₆₀-doped TiOPc(300 Å)/TiOPc(200 Å)/Au.

of the quantum yields for the photogeneration of charge carriers for the cells (a) and (b) upon irradiation through the ITO electrode. The action spectra of the quantum yield for charge-carrier photogeneration for both cells (a) and (b) resemble the superposition of the electronic absorption spectra of TiOPc and MPCl. However, the comparison of the quantum yield for charge-carrier photogeneration between the cells (a) and (b) clearly shows that the efficiency of charge-carrier photogeneration upon irradiation with monochromatic light ($10\text{--}50 \mu\text{W cm}^{-2}$) in the wavelength range from 600 to 900 nm which TiOPc absorbs is improved approximately twice for the cell (b) relative to the cell (a). For example, the quantum yields for charge-carrier photogeneration were 0.16 and 0.34 for the cells (a) and (b), respectively, when irradiated with 720 nm monochromatic light.

Fig. 4 shows current density–voltage characteristics for the cell (b) under irradiation with white light of varying intensities through the ITO electrode. The performance characteristics of the cell (b) together with those of the cell (a) upon irradiation with either monochromatic light or white light are summarized in Table 1. The experimental results show that the three-layer cell (b) exhibits larger open-circuit photovoltages than the two-layer cell (a) under irradiation with monochromatic light or white light. The reason for a larger built-in potential for the cell (b) relative to the cell (a) is not clear at present. It was also shown that when the cell was illuminated with monochromatic light of 720 nm, which TiOPc mainly absorbed, the three-layer cell (b) exhibited a larger short-circuit photocurrent due to an increased quantum yield for charge-carrier photogeneration than the two-layer cell (a). The three-layer cell (b) using the C₆₀-doped TiOPc layer showed a conversion efficiency of 0.63% when irradiated with white light at an intensity of 94 mW cm^{-2} .

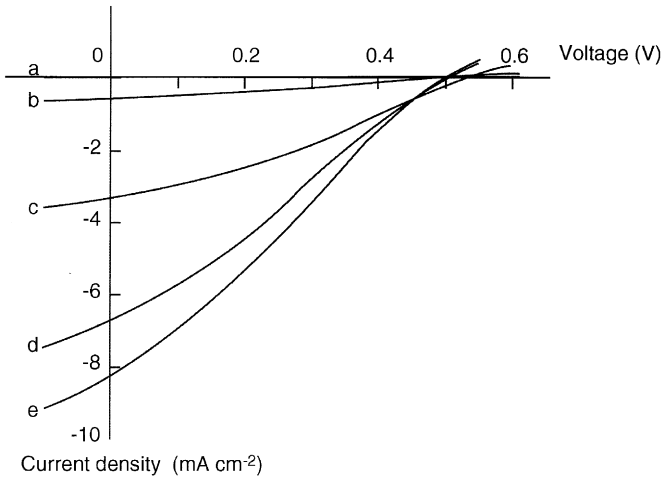


Fig. 4. Current density–voltage characteristics for ITO/MPCl(500 Å)/30 mol% C₆₀-doped TiOPc(300 Å)/TiOPc(200 Å)/Au cell: (a) in the dark and (b)–(e) under irradiation with white light through the ITO electrode. Intensity of incident light: (b) 13, (c) 94, (d) 187, and (e) 262 mW cm⁻².

Table 1

Performance characteristics of ITO/MPCl(500 Å)/TiOPc(500 Å)/Au (cell a) and ITO/MPCl(500 Å)/30 mol% C₆₀-doped TiOPc(300 Å)/TiOPc(200 Å)/Au (cell b)

	ITO/MPCl(500 Å)/TiOPc(500 Å)/Au			ITO/MPCl(500 Å)/30 mol% C ₆₀ -doped TiOPc(300 Å)/TiOPc(200 Å)/Au		
	470 nm ^a	720 nm ^b	White light ^b	470 nm ^a	720 nm ^b	White light ^b
Light intensity I_t or I_0 (mW cm ⁻²)	0.397 ^c	0.254 ^c	108 ^d	0.355 ^c	0.298 ^c	94 ^d
Open-circuit voltage V_{oc} (V)	0.25	0.27	0.34	0.42	0.43	0.53
Short-circuit photocurrent J_{sc} (mA cm ⁻²)	0.032	0.021	3.0	0.036	0.055	3.4
Fill factor FF	0.34	0.31	0.36	0.43	0.39	0.32
Conversion efficiency η' or η (%)	0.67 ^e	0.68 ^c	0.34 ^f	1.8 ^e	3.1 ^e	0.63 ^f

^aIrradiated through Au electrode.

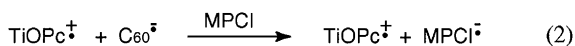
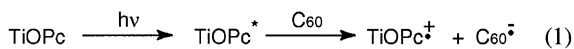
^bIrradiated through ITO electrode.

^cIntensity of transmitted light I_t .

^dIntensity of incident light I_0 .

^eConversion efficiency (η') for transmitted monochromatic light $\eta' = \frac{V_{oc}J_{sc}FF}{I_t} \times 100$.

^fConversion efficiency (η) for incident white light $\eta = \frac{V_{oc}J_{sc}FF}{I_0} \times 100$.



Scheme 1. Charge-carrier photogeneration processes for the three-layer cell (b).

Improved conversion efficiencies for the cell (b) relative to the cell (a) upon irradiation with monochromatic light or white light result from larger open-circuit voltages and larger short-circuit currents. The improvement in the quantum yield for charge-carrier photogeneration upon irradiation particularly with light which TiOPc mainly absorbs, which leads to a larger short-circuit current, may be attributed to efficient charge separation by successive electron transfer from the C_{60} anion radical, generated by photo-induced electron transfer from TiOPc to C_{60} in the C_{60} -doped TiOPc layer, to MPCI as shown in Scheme 1. That is, when the cell (b) is irradiated with light which TiOPc mainly absorbs, TiOPc in the C_{60} -doped TiOPc layer is photoexcited and electron transfer will take place from TiOPc in the electronically excited state to C_{60} in the ground state, followed by successive electron transfer from the C_{60} anion radical to MPCI at the interface between the C_{60} -doped TiOPc layer and the MPCI layer to generate the MPCI radical anion.

4. Conclusion

For the purpose of improving the conversion efficiency of the organic photovoltaic device using TiOPc and MPCI, the effect of doping with C_{60} on photoelectric conversion was investigated. A new three-layer cell, ITO/MPCI/ C_{60} -doped TiOPc/TiOPc/Au, was fabricated and its performances were compared with those of the two-layer cell, ITO/MPCI/TiOPc/Au. It was shown that doping with C_{60} in TiOPc improved the performances; the three-layer cell exhibited higher quantum yields for charge-carrier photogeneration and higher conversion efficiencies than the two-layer cell.

Acknowledgements

The authors thank Prof. Dr. Oleg Schevaleyevsky and his coworkers for the sample of C_{60} .

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