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Improvement of Porphyrin Photovoltaic Cells in Panchromaticities and Quantum Yields by Use of Tetrabenzoporphyrin Skeleton

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Synopsis. Expansion of the porphyrin π electron system by using a tetrabenzoporphyrin (TBP) skeleton leads to better spectral match to the solar spectrum and high quantum yields when the porphyrins are used as sensitizers. Metallotetrabenzoporphyrins such as MgTBP and ZnTBP rank among the most efficient organic photoconducting materials studied so far.

Solar cells that utilize the photoelectric properties of organic materials stand still far from practical use because of conversion efficiencies much lower than those of traditional inorganic solar cells as well as no long-term stability.[1] However, solar cells made from organic compounds have some unique advantages compared with the inorganic devices in respect of low cost, ease of fabrication, flexibleness etc.

Several years ago, we found that the more easily oxidized porphyrins exhibited the higher quantum yields and that peripheral substitution could modulate the oxidation potential of the porphyrin and that long aliphatic chain substituents decreased the quantum yields, presumably by acting as insulators towards electron transport.[2] These results suggest that expansion of the porphyrin π electron system may lead to lower oxidation potentials as well as facilitate energy and electron transfer by increasing π-π interactions between neighbouring molecules and result in the increase of photocurrents and thus the quantum yields.[3]

In the present paper we show evidence that metallotetrabenzoporphyrins such as (tetrabenzoporphyrinato)magnesium (II) (MgTBP) and ZnTBP are indeed oxidized very easily in comparison with other porphyrins studied and act as most efficient sensitizers in simple photovoltaic devices based on Al/porphyrin Schottky barriers and organic *p-n* junctions.

Experimental

Porphyrins and metalloporphyrins used were prepared and purified by the methods in references.[4–6] Phthalocyanine (H_2Pc) and (phthalocyaninato)zinc(II) (ZnPc) were purchased from Tokyo Kasei Co. and purified by sublimation before use. Polycarbonate resin Panlite® (Pnl) used as a polymer binder was kindly supplied by Teijin Chemicals Ltd. Dichloromethane and dichloroethane were redistilled after dessication with calcium hydride. An amount of 10 mg of the dye was dispersed in 5 ml of 1 %(W/V) Panlite-dichloroethane solution by using a TomySeiko Handy Sonic UR-20P. A particulate dye film was prepared by casting a suitable amount of the dye-polymer mixture prepared above on an indium-tin oxide(ITO)-coated glass plate. Preparation of an ITO film, fabrication of a M/porphyrin/M′ sandwich-type cell, in which M or M′ denotes an ITO or a metal electrode, and measurements of dark and photoelectric properties of the photovoltaic cells were carried out as described previously.[7,8] Photocurrents were normalized in such a way that the intensity of monochromatic light incident on the interface of the dye film with the illuminated metal was constant at 10 μW cm^{-2} unless otherwise specified.

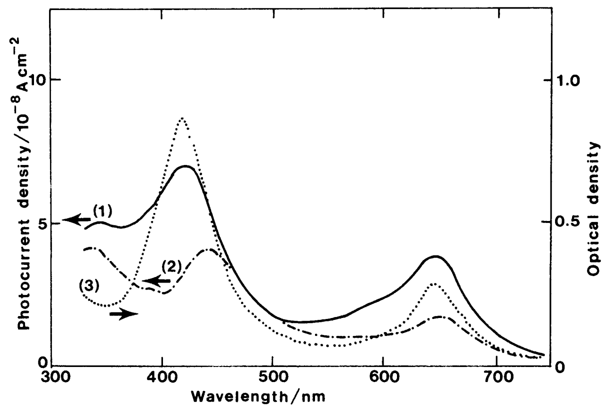

Fig. 1. Action spectra of short-circuit photocurrents for the Schottky barrier cell of Al(8 nm)/CdTBP (60 nm)/Au(9 nm). Curves (1) and (2) are obtained on illumination of the Al and the Au electrodes, respectively. Curve (3) shows the optical absorption spectrum of the CdTBP film used in the sandwich cell.

Results and Discussion

Figure 1 displays short-circuit photocurrent action spectra for the Al/CdTBP/Au Schottky barrier cell with an optical absorption spectrum of the CdTBP film. Currents passing from Al to Au through the cell were taken to be positive. For thin CdTBP films the shapes of the action spectra almost were the same for light incident on both sides. For thick films, however, the action spectra agreed well to the absorption spectrum only when the Al side was illuminated. Similar results were observed with other tetrabenzoporphyrin derivatives and can be explained in terms of an optical filtering effect[9] due to the interposed porphyrin phase on the basis of a band model of *p*-type semiconductors. Namely, only photons absorbed near the Al blocking contact are effective for generation of charge carriers, resulting in the photoresponse, while the Au contact is inert for illumination owing to the ohmic contact.

We further note that the tetrabenzoporphyrins absorb throughout the range of visible light and the light absorbing properties approach those found for chlorophylls in vivo (λ_{max}=680 and 700 nm for Photosystems II and I of green plants, respectively). The maximum fraction of the solar spectrum that can be collected by ZnTBP molecules increases to about 47%,

Table 1. Summary of Photocurrent Quantum Yields of Porphyrin and Metalloporphyrin Films with First Ring Oxidation Potentials

Compound$^{a)}$	$E_{1/2}$$^{b)}$/V vs. SCE	Cell configuration$^{c)}$	Wavelength/nm	Quantum yield$^{d)}$	References
MgTBP	0.23	B	445	8.5×10^{-2}	(3)
		C	447	1.5×10^{-1}	(3)
MgOMTBP	0.26	A	390	3.4×10^{-2}	
ZnTBP	0.40	A	390	1.5×10^{-1}	
		B	460	4.5×10^{-2}	(3)
		C	440	1.2×10^{-1}	(3)
CdTBP	0.44	A	402	4.5×10^{-2}	
MgTPP	0.61	B	440	5.2×10^{-2}	(3)
		C	445	9.8×10^{-2}	(2)
MgP	0.68	C	420	2.0×10^{-1}	(2)
ZnTPP	0.78	B	440	3.2×10^{-2}	(3)
		C	440	3.0×10^{-2}	(3)
ZnP	0.80	C	420	9.1×10^{-2}	(2)

a) Abbreviations used; OMTBP 1,4,8,11,15,18,22,25-octamethyltetrabenzo[*b*,*g*,*l*,*q*]porphyrin; P porphyrin; TBP tetrabenzoporphyrin; TPP 5,10,15,20-tetraphenylporphyrin. b) First ring oxidation potentials at Pt in CH_2Cl_2 with 0.1 mol dm^{-3} tetrabutylammonium perchlorate. c) A Al/Porphyrin/Au; B Al/Porphyrin/Ag; C Al/Porphyrin/0.1 mol dm^{-3} $K_3[Fe(CN)_6]$ and 0.1 mol dm^{-3} $K_4[Fe(CN)_6]$/Pt. d) Quantum yield is defined as the number of the electrons produced per photon incident on the dye film at 10 μW cm^{-2}.

which is about 10 or 15% larger than that for (2,3,7,8,12,13,17,18-octaethylporphyrinato)zinc(II) (ZnOEP) or (5,10,15,20-tetraphenylporphyrinato)zinc(II) (ZnTPP) molecules.[10] Thus the expansion of the porphyrin π electron system by using the TBP skeleton is very effective to improve the panchromaticity of the porphyrin, resulting in the increase of conversion efficiency as shown below.

The first ring oxidation potentials of 0.23 and 0.40 V vs. SCE found for MgTBP and ZnTBP rank these macrocyclic compounds as the easiest to oxidize among a large variety of Mg and Zn porphyrins (Table 1 and see Felton's review[11]). Judging from the oxidation potentials and the exponential correlation previously found between the oxidation potential of the porphyrin and the photocurrent quantum yield, it is expected that both MgTBP and ZnTBP are effective more than MgP. However, the fact is that MgTBP and ZnTBP show photocurrent quantum yields somewhat smaller than MgP. At this time it is necessary to recall the previous finding that for a given porphyrin ligand the quantum yields parallel the first ring oxidation potentials of the porphyrins, but all porphyrins do not fall on the same curve.[2] This might be attributable to a combination of various factors such as the ease of charge carrier formation relating with the oxidation potential of the porphyrin, the packing of porphyrin molecules in solid films and the extent of π-π overlap between the porphyrin rings, which facilitates energy and electron transfer.[12] The quantum yield of MgTBP may be greater than that of MgP under illumination of polychromatic lights such as solar rays, because the maximum fraction of the solar spectrum that can be collected by the tetrabenzo compound is larger than that by MgP. The photocurrent quantum yields for the sandwich-type Schottky barrier cells made from the metallotetrabenzoporphyrins are in the range from 10^{-2} to 10^{-1}. Comparison of the photocurrent quantum yields found here with those obtained for other porphyrins shows distinctly that tetrabenzo compounds fall within the most efficient organic light converters investigated so far.

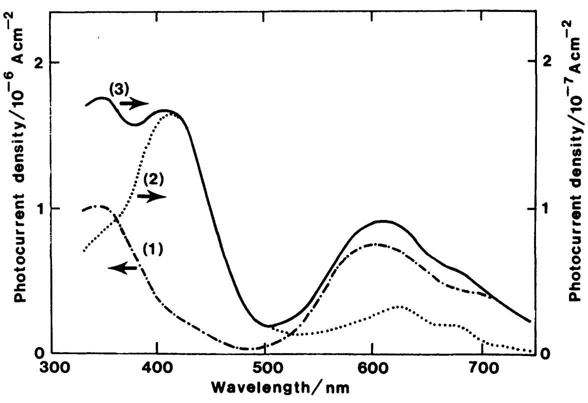

Fig. 2. Action spectra of short-circuit photocurrents for the particulate-type Schottky barrier cells of (1) ITO/H_2Pc–Pnl/Al, (2) ITO/TPTBP–Pnl/Al and (3) ITO/H_2Pc, TPTBP–Pnl/Al. Illumination is made through the Al electrode.

In more recent years photovoltaic cells prepared by dispersing fine particles of pigment in a polymer binder have received much attention as promising devices.[13,14] In particular polar polymers such as poly(vinylidene difluoride) and polyacrylonitrile have been found to give high quantum efficiencies.[15] Up to date, however, there has been no report concerning the particulate-type photovoltaic cells using the porphyrins.

Figure 2 illustrates short-circuit photocurrent action spectra for three kinds of particulate-type Schottky barrier cells. The photocurrents observed with the particulate-type cells are corrected roughly for the reflection and the absorption of light at the Al/dye-Pnl interface. Because, it was very hard to measure precisely the intensity of light incident on the dye-polymer film through the Al phase owing to the complex reflection of light, scattering etc. due to the roughness of the Al/dye-polymer interface. The first and the

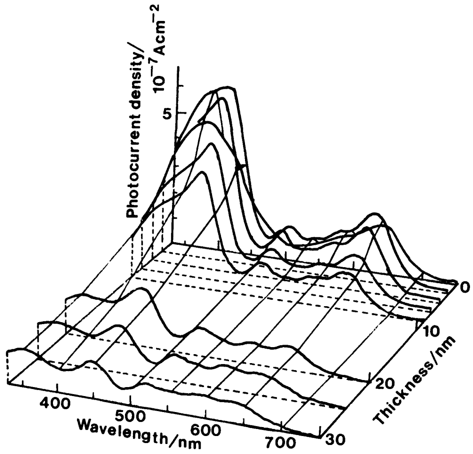

Fig. 3. Dependence of short-circuit photocurrent action spectra for the Au/ZnTBP(40 nm)/T(4-Py)P/Al cells on thickness of the T(4-Py)P film, when illuminated through the Al electrode.

second cells were prepared by dispersing H_2Pc and 5,10,15,20-tetraphenyltetrabenzoporphyrin (TPTBP) in Pnl-dichloroethane solutions, respectively. The third cell was made by dispersing equivalent amounts of H_2Pc and TPTBP in the polymer binder. It is noteworthy that TPTBP is only one sample giving a fairly good photoconducting film with Pnl among porphyrins studied. The shapes of action spectra (1) and (2) resemble those of optical absorption spectra of H_2Pc and TPTBP films. It is clear that combination of TPTBP and H_2Pc brings about the best spectral match to the solar spectrum among them. Unfortunately, however, magnitudes of the photocurrents observed with the third cell are about one tenth as large as those for the ITO/H_2Pc-Pnl/Al cell, though both cells generate photovoltages greater than 1 V.

Figure 3 illustrates short-circuit photocurrent action spectra for the Au/ZnTBP(40 nm thick)/5,10,15,20-tetra(4-pyridyl)porphyrin [T(4-Py)P]/Al *p*-*n* junction cell with varying thickness of the T(4-Py)P film. The photovoltaic spectral cosensitization effect[16] is clearly observed with the cell having a thin T(4-Py)P film. The optimum thickness of the T(4-Py)P film for the quantum yield seems to be around 2 nm, being somewhat smaller than that (about 7 nm) for the analogue T(3-Py)P in the case of a Au/ZnPc(50 nm thick)/T(3-Py)P/Al cell.[16] Such a thin film of T(4-Py)P may be composed of insular sublimates of the porphyrin. The fraction of the solar spectrum that can be collected by the ZnTBP/T(4-Py)P *p*/*n* phases becomes 1.3 times as great as that by the ZnTBP phase alone in the Al/ZnTBP Schottky barrier cell. The photocurrent quantum yield and the power conversion efficiency reach about 20 and 2 % respectively for monochromatic incident light (10 μW cm^{-2}) at 430 nm.

Thus the facile, chemical stability (ZnTBP can be heated in air without decomposing), light absorption properties and high quantum yields of the metallotetrabenzoporphyrins suggest that these macrocycles are attractive potential candidates for solar energy conversion devices.

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