Formation of Blocking Contacts at *p*-Type Porphyrin/ITO or Electrolyte Junctions

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Energetics of ITO/*p*-type porphyrin/electrolyte interfaces are discussed on the basis of photoelectrochemical and photovoltaic measurements. When sensitized by a layer of 5,10,15,20-tetraphenylporphyrinatomagnesium(II)(MgTPP), the indium-tin oxide (ITO) electrode acts as only a photocathode in an aqueous electrolyte solution. However, the ITO electrode modified with a film of ZnTPP, CuTPP or H_2TPP having oxidation potential more positive than that of MgTPP acts as not only a photocathode but also a photoanode, depending on the electrode potential and the direction of irradiation on the ITO/porphyrin electrode. The cathodic component in the photocurrents is attributed to the downward band-bending in a space charge layer at the porphyrin/electrolyte (blocking) contact and the anodic component to that at the ITO/porphyrin (blocking) contact. The upward band-bending, on the contrary, is found inefficient in producing charge carriers, because the accumulation layer is conducting (ohmic) for majority carriers (holes). The porphyrin/electrolyte junction shows certain similarities to an ITO or metal/porphyrin (semiconductor) junction. However, it should be noted that a Helmholtz double layer exists at the porphyrin/electrolyte interface. The results are rationalized from the energy levels of the porphyrin films, ITO and the redox couple solutions with due regard to the orientation of water dipoles at the porphyrin surface.

A recent interest in the dye sensitization research has centered on modelling the primary energy conversion processes in photosynthesis and on the application to conversion of solar energy into electrical and/or chemical energy.[1] The organization of dye and substrate can be varied over a wide range and can therefore be optimized with respect to the quantum efficiency of the sensitization effect. Hence, organic materials such as phthalocyanines,[2–6] merocyanines[7–10] and porphyrins[11–19] have received much attention as the promising sensitizers.

Previously we have demonstrated that the most efficient photoelectrochemical cells based on synthetic *p*-type porphyrin films on Al reach power conversion efficiencies of 1% and generate photovoltages greater than 1 V.[11,20] The dark- and photo-electrochemical properties of the cells are attributed to the MIS Schottky barrier consisting of Al–Al_xO_y–porphyrin, where conduction and valence band (CB and VB) edges of the porphyrin bend downwards under short-circuit conditions. Furthermore we have noted that a blocking contact is not formed at a *p*-type porphyrin/Ag or Pt junction. Some workers, however, have shown different views from ours.[14–16] For instance, they have attributed the cathodic photocurrents at the irradiated Pt/*p*-type porphyrin electrodes to the formation of blocking contacts at the Pt/porphyrin junctions and described that the upward band-bending in a space charge layer at the porphyrin/Pt interface is effective in producing charge carriers.

In order to build more efficient devices using porphyrin films as sensitizers it is necessary and important to solve the inconsistency and to obtain a consensus. This paper represents the energetics of ITO/*p*-type porphyrin/electrolyte interfaces and clarifies the conditions under which a blocking or an ohmic contact is formed at the junction.

Experimental

Metal-free porphyrin [5,10,15,20-tetraphenylporphyrin (H_2TPP)] and its metal derivatives (MgTPP, ZnTPP, and CuTPP) were purchased from Strem Chemicals and were purified by chromatography (Woelm alumina grade I) followed by recrystallization. These porphyrins have been characterized as *p*-type organic semiconductors.[11,14,19] *p*-Benzoquinone (BQ) from Katayama Chemicals was used after sublimation. Other chemicals used were of reagent grade. An indium-tin oxide (ITO) film was used as substrate for the porphyrin electrode because of the superiority of light-transparency and the metallic property.[21,22] An ITO film was produced on a piece of cleaned slide glass (Matsunami No. 0) by means of a Tokuda CFS-8EP closed field sputtering apparatus. O_2 partial pressure of 1.3×10^{-2} Pa and Ar partial pressure of 6.7×10^{-1} Pa were employed for fabrication of the ITO electrode. The thickness of ITO films was about 100 nm. The electric resistance was about a few hundreds ohm/square and the transparency larger than 80% in the visible region of the solar spectrum. Films of the porphyrins (100—300 nm thick) and metals (Au, Ag, and Al, *ca.* 10 nm thick) were prepared by sublimation and evaporation at pressure 10^{-4} Pa, respectively. The porphyrin-coated ITO or metal electrode was insulated from the electrolyte with epoxy resin except for the portion to be exposed to light. The photoelectrochemical measurements of the porphyrin electrodes were carried out using a two or three electrode system. For potentiostatic steady-state measurements a coiled platinum wire was used as the auxiliary electrode and a saturated calomel electrode (SCE) served as the reference. Unless otherwise stated, dissolved oxygen in solution was removed by bubbling Ar gas. A custom-built potentiostat was used to obtain the steady-state current-potential curves. Voltages and currents produced by the cells were measured with a Takeda TR 8651 electrometer. Applied voltages were provided by a Takeda TR 6141 voltage supply and monitored with a Takeda TR 6855 digital multimeter. The light source consisted of a 45 W tungsten-halogen lamp and a Baush-Lomb Cat. No. 33-86-76 monochromator. An Ushio

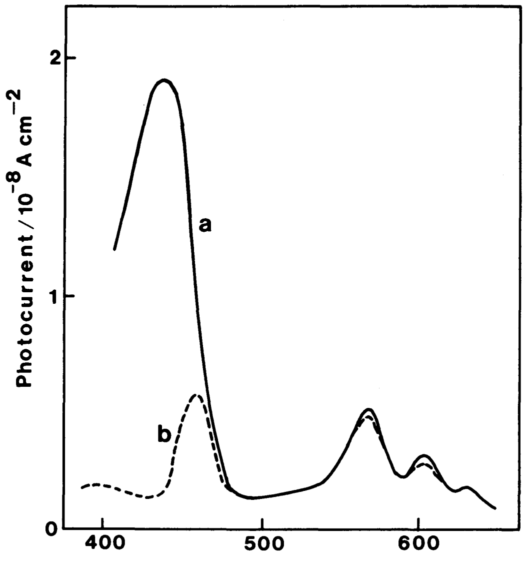

Fig. 1. Action spectra of short-circuit photocurrents of the ITO/MgTPP (*ca.* 200 nm thick)/HQ-BQ, phosphate buffer/Pt cell. (a) and (b) are obtained by irradiation of the MgTPP/electrolyte and ITO/MgTPP junctions.

500 W xenon lamp was also used as light source with a Toshiba KL-43 interference filter. Light intensity was measured with a calibrated Eppley thermopile of 16 junctions. Optical absorption spectra were recorded on a Shimadzu UV-240 spectrometer. All measurements were carried out at room temperature.

Results and Discussion

Figure 1 shows action spectra of short-circuit photocurrents for the ITO/MgTPP/electrolyte/Pt cell. The electrolyte was a phosphate buffer [0.025 M (1 M=1 mol dm^{-3}) KH_2PO_4, 0.025 M Na_2HPO_4 and 0.1 M KCl: pH 6.87], containing 1 mM hydroquinone (HQ) and 1 mM BQ. Curves (a) and (b) were obtained by irradiation of the MgTPP/electrolyte and ITO/MgTPP interfaces, respectively. The photocurrents have been normalized in such a way that the intensity of the incident light on the interface between MgTPP and ITO or electrolyte is constant (about 30 μW cm^{-2}) in consideration of the absorption of light with ITO or the electrolyte and the reflection at the glass/ITO or electrolyte interface. The photocurrents flowed from Pt to ITO through the MgTPP/electrolyte interface regardless of the wavelength and the direction of irradiation. Taking account of this and the finding that the action spectrum (a) resembles the optical absorption spectrum of a MgTPP film, the difference in shape between the action spectra (a) and (b) is attributable to an optical filtering effect of the MgTPP phase.[8] Namely it shows that the photocurrent is generated *via* the excited states of the porphyrin and that only the light absorbed near the blocking (electrolyte) contact is effective in producing charge carriers.[23,24] This was confirmed by the voltage dependence of the photocurrent action spectrum obtained under irradiation of the MgTPP/electrolyte interface (Fig. 2). When a negative bias voltage was applied to the ITO electrode, the cathodic photocurrent was strikingly enhanced. On the contrary, when a positive voltage was applied the photocurrent was reduced to zero.

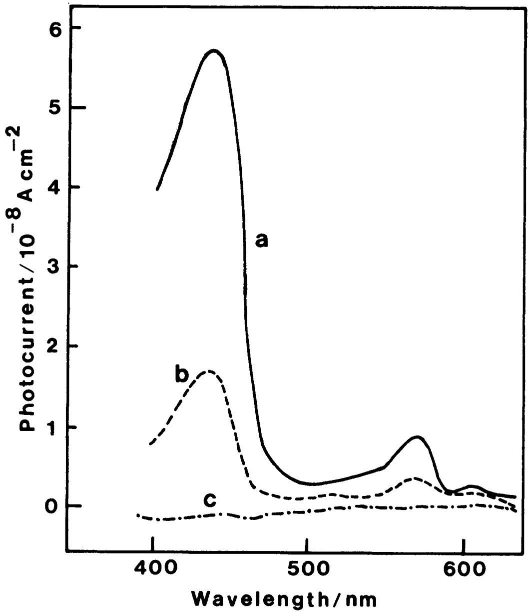

Fig. 2. Voltage dependence of the photocurrent action spectrum for the ITO/MgTPP/HQ-BQ/Pt cell. (a), (b), and (c) are obtained by irradiation of the MgTPP/electrolyte junction at voltages of −0.21 V, 0 V and +0.2 V, being applied to the ITO electrode.

In case of the ITO electrode modified with ZnTPP, which is uneasily oxidized in comparison with MgTPP, there was a wavelength region of around the peak of a Soret band (440 nm) of the ZnTPP film, where small anodic photocurrents were observed by irradiation of the ITO/ZnTPP interface under short-circuit conditions (Table 1). This shows the existence of a small Schottky barrier (blocking contact) at the ITO/ZnTPP junction and coincides with the dark current-voltage characteristics of the ITO/ZnTPP/Ag cell (Fig. 3). The observed rectification effect is due to the blocking contact at the ITO/ZnTPP junction, since the ZnTPP/Ag junction has been found an ohmic contact.[11,12]

For ITO electrodes modified with films of CuTPP and H_2TPP with oxidation potentials more positive than those of MgTPP and ZnTPP, both cathodic and anodic photocurrents were clearly observed, depending on the direction of irradiation on the ITO/porphyrin electrodes (Table 1). This indicates that blocking contacts are formed at both junctions of the porphyrin with ITO and the electrolyte and thus the ITO/porphyrin electrodes act as photocathodes and also as photoanodes. The observation of the anodic photocurrents seemingly depends on the oxidation potentials of the porphyrins.

Figure 4 illustrates energy levels of ITO, redox agents and porphyrin films studied. The free energy

TABLE 1. SUMMARY OF THE PHOTORESPONSE OF THE PORPHYRIN FILMS ON ITO IN THE ITO/ PORPHYRIN/ HQ–BQ, PHOSPHATE BUFFER/ Pt CELL

Porphyrin	λ_{max}[a]/nm	$h\nu \rightarrow$ITO/porphyrin	porphyrin/electrolyte$\leftarrow h\nu$	$E_{1/2}$[b]/V vs. SCE
MgTPP	445	~	——[c]	0.61
Zn TPP	440	+[c]	——	0.78
Cu TPP	430	++	——	0.96
H_2 TPP	445	++	——	1.04

a) Peak of a Soret band of a porphyrin solid film, at which irradiation is carried out. b) Oxidation at Pt in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate. c) Plus and minus signs denote anodic and cathodic photocurrents, respectively. Double plus and minus signs mean stronger photoresponse.

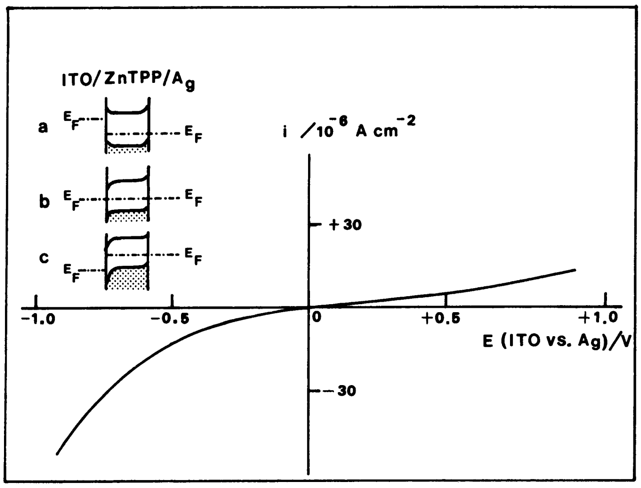

Fig. 3. Dark current-voltage curve for the ITO/Zn-TPP/Ag cell. The inset shows the band-bending at the ITO/ZnTPP/Ag contact at (a) negative, (b) zero and (c) positive bias voltages.

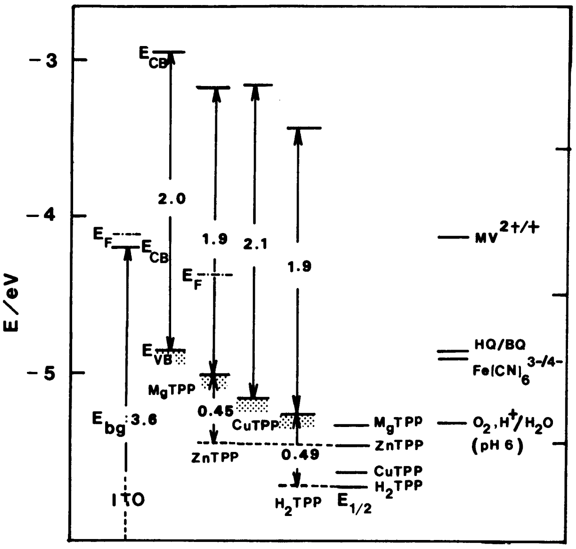

Fig. 4. Energy levels of ITO, porphyrin films and redox systems.

of electrons in a semiconductor or a metal is characterized by the Fermi level (E_F). The Fermi level in ITO lies just above the CB edge because of degeneracy of the *n*-type semiconductor. Hence, the electric behavior of ITO is similar to that of a metal. The E_F in a ZnTPP film has been found slightly closer to the VB, *viz.* E_{VB}=−5.0 eV, E_F=−4.3 eV and E_{CB}=−3.0 eV from the vacuum level.[14] The E_{VB} for a H_2TPP film is located at 5.2 eV below the vacuum level.[25] The values of E_{VB} of MgTPP and CuTPP films were estimated from the first ring oxidation potentials ($E_{1/2}$) obtained for the porphyrins in nonaqueous solutions assuming that the VB edges were situated at potentials 0.47 V higher than the oxidation potentials.[6] The energy difference of 0.47 eV was the average for experimental results (0.45 eV for ZnTPP and 0.49 eV for H_2TPP). The Fermi levels for MgTPP, CuTPP, and H_2TPP films might be about 0.7 eV higher than their respective VB edges as observed for ZnTPP film. The values of optical band gaps for the porphyrins were estimated from the spectral properties of the porphyrin films.

If a porphyrin film, whose Fermi level lies below that for ITO, is brought into contact with ITO, the Fermi levels will be equilibrated by electron transfer from the ITO to the porphyrin. This results in the formation of a space charge layer in the porphyrin, while counter charge remains very close to the interface in the ITO layer. Thus a blocking contact is formed at the ITO/porphyrin junction, where the CB and VB edges bend downwards, and leads to the production of anodic photocurrents. The anodic photocurrent at the irradiated ITO/porphyrin electrode depended upon the relative position of the Fermi levels of ITO and the porphyrin. For example, no distinct anodic photocurrent is observed by irradiation of the ITO/MgTPP electrode (Table 1), because the Fermi levels of ITO and MgTPP are almost the same. For a film of ZnTPP, CuTPP or H_2TPP having oxidation potential more positive than that of MgTPP, the Fermi level lies below that of ITO and the blocking contact must be formed at the ITO/porphyrin junction. In effect, the anodic photocurrents were observed. An upward band-bending, in principle, may be produced at a contact of ITO with a *p*-type porphyrin, of which Fermi level lies above that of ITO. However, such a contact should be ohmic for majority carriers (holes), unless surface states exist. This may be inferred from the finding that no obvious cathodic photocurrent is observed for the ITO/ZnTPP/Ag cell at negative bias voltages applied to the ITO electrode, where the upward band-bending is formed as shown in the inset of Fig. 3.

The Fermi level in an electrolyte solution corresponds to the redox potential of a redox couple involved in the electrolyte.[26] Apparently, judging from the positions of the Fermi levels for the porphyrin films studied and the redox potential of the HQ/BQ couple (Fig. 4), the porphyrin/electrolyte contacts are supposed to be ohmic because the Fermi levels of the porphyrins lie above the redox potential of the HQ/BQ couple and at equilibrium upward band-bendings are produced at the porphyrin/electrolyte junctions. However, actually the cathodic photocurrents are observed by irradiation of the porphyrin/electrolyte interfaces. In view of the fact the photoelectric behaviors of the ITO/porphyrin contacts can reasonably be explained in terms of the energy diagram of Fig. 4, the inconsistency between the prediction and the experimental result reminds us of two plausible reasons. One is an existence of surface states at the porphyrin/electrolyte interface, which causes Fermi level pinning[27] and the other is that the energy levels of the porphyrin films in aqueous solution might be different from those *in vacuo*.

At first, we consider a few points about the possibility of the Fermi level pinning at the porphyrin/electrolyte interface. The positions of the Fermi level and band edges at the surface of the porphyrin contacting the electrolyte can be estimated from measurement of the flat-band potential (E_{fb}). Figure 5 illustrates the steady-state photocurrent-potential curves for the ITO/ZnTPP electrode in aqueous electrolyte solutions. Without oxdizing agents, only small photocurrents were observed over the potential range of −0.5 V to +1.0 V *vs.* SCE under irradiation of the ZnTPP/electrolyte interface at 430 nm [curve (a)]. In this case, the ZnTPP film used was so thick (*ca.* 200 nm) that the light hardly reached the ITO/ZnTPP interface through the porphyrin phase. The cathodic photocurrents obtained by irradiation of the ZnTPP/electrolyte interface were enhanced by the addition of oxidizing agents such as O_2, $[Fe(CN)_6]^{3-}$, BQ, methylviologen (MV^{2+}), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone and $Cr_2O_7^{2-}$. The onset potential (E_{op}) of about +0.5 V *vs.* SCE was almost independent of the oxidizing species except for MV^{2+} and of pH in the range 5.5—9.0. It is well known that the surface states formed at inorganic semiconductors sometimes bring about the Fermi level pinning, which results in an output photovoltage independent of the redox potential of an electrolyte.[27] However, this may be not the case for the porphyrin electrode since the E_{op} of the ZnTPP electrode is found independent of the kind of the oxidizing species ranging in potential from +0.2 V to +0.7 V *vs.* NHE as described above. In other words, the band edges of the porphyrin films are fixed at the porphyrin/electrolyte interfaces.[28]

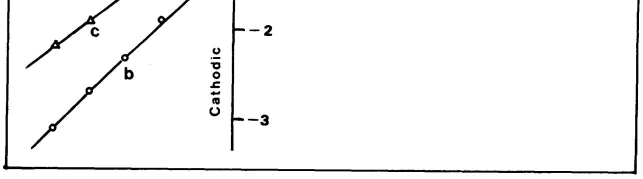

Fig. 5. Potential dependence of the steady-state photocurrent for the ITO/ZnTPP electrode. (a), (b) and (c) are obtained by irradiation of the ZnTPP/electrolyte junction, and (d) obtained by irradiation of the ITO/ZnTPP junction. (a): acetate buffer (1 M CH_3COOH and 1 M CH_3COONa, pH 4.7); (b): in (a) +0.2 mM O_2; (c) and (d): 0.1 M KCl+0.2 mM O_2.

Secondly, we discuss the difference in energy levels of the porphyrin films *in vacuo* and in aqueous electrolyte solution. The E_{op} of about +0.5 V is probably near the flat-band potential at the ZnTPP/electrolyte interface, from which the Fermi level of the ZnTPP film in the aqueous electrolyte solution is estimated to be about 0.9 eV lower than that (−4.3 eV) *in vacuo*. The contribution of the Helmholtz double layer, especially an inner Helmholtz layer, should be taken into consideration to account for the energy difference. In view of similarity between the E_{fb} for a semiconductor and the zero charge potential (E_{pzc}) for a metal, surface potential due to orientaion of water dipoles at the porphyrin is one of the plausible factors responsible for the energy difference. According to Trasatti,[29] the relationship between E_{pzc} and work function (ϕ) for a metal is written in the following form, $E_{pzc}=\phi-4.61-0.40\ \alpha$, where α is defined as the degree of orientation of water at the metal. The maximum surface potential of −0.40 V indicates that the dipole of water points the negative end (oxygen) towards the metal and forms an angle of about 34° with the metal surface. A surface potential of about 0.75 V corresponds to the perpendicular dipoles. On these bases, it may be possible to ascribe a part of the potential difference of +0.9 V to the surface potential due to the orientation of water dipoles at the porphyrin electrode. We note that in this case a water molecule must be oriented with the positive end (hydrogen) toward the porphyrin.

When the ITO/ZnTPP interface was irradiated in solution containing oxidizing agents, no evident photocurrent was observed [curve (d) in Fig. 5]. However, in the presence of reducing agents such as HQ and $[Fe(CN)_6]^{4-}$ instead of the oxidizing agents the ITO/ZnTPP electrode exhibited anodic photocurrents at potentials more positive than about −0.1 V *vs.* SCE (Fig. 6).

On these bases, the energy diagram of the ITO/ZnTPP/electrolyte interfaces is represented as shown in Fig. 7. At this time we should note the fact that the band edges are fixed at the porphyrin surfaces. It is

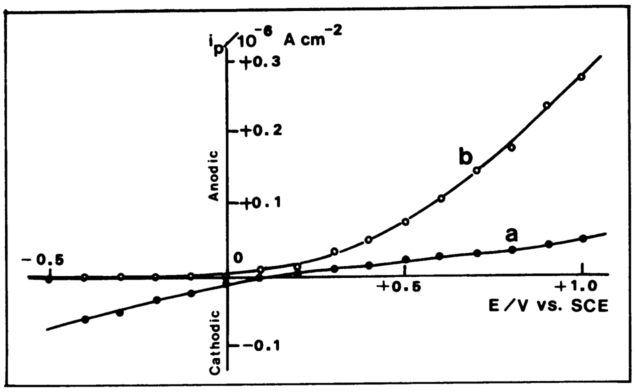

Fig. 6. Potential dependence of the steady-state photocurrent for the ITO/ZnTPP electrode in 0.5 mM $[Fe(CN)_6]^{4-}$ and 0.1 M KCl. (a) and (b) are obtained by irradiation of the ZnTPP/electrolyte and ITO/ZnTPP junctions, respectively.

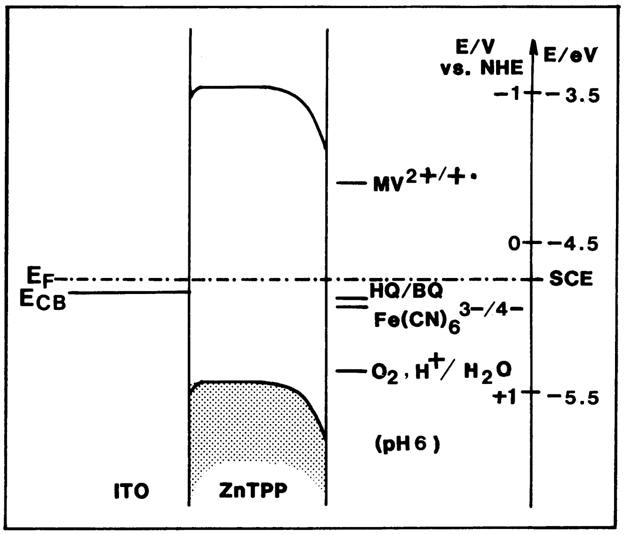

Fig. 7. Band model for the ITO/ZnTPP/electrolyte contacts at 0 V *vs.* SCE.

of great interest that photoelectrochemical reduction of methylviologen (MV^{2+}) occurs even near the flat-band potential, because such a *p*-type porphyrin electrode can be used as a photocathode for reduction of H_2O to produce H_2. The redox potential of HQ/BQ is negative so that at equilibrium the downward band-bending is produced at the ZnTPP/electrolyte interface, which brings about the cathodic photocurrent under short-circuit conditions (Fig. 8). This is in good agreement with the result for the photoelectrochemical cell with ZnTPP (Table 1). Similarly the steady-state photocurrent-potential curves of the ITO/H_2TPP electrode are understood (Fig. 9). The E_{op} for the cathodic photocurrent was negative a little more than that for the ZnTPP electrode. By all accounts it is deduced that the cathodic photocurrents observed at the Pt/ZnTPP electrode[14–16] might be due to the ZnTPP/electrolyte (blocking) contact and not to the Pt/ZnTPP contact.

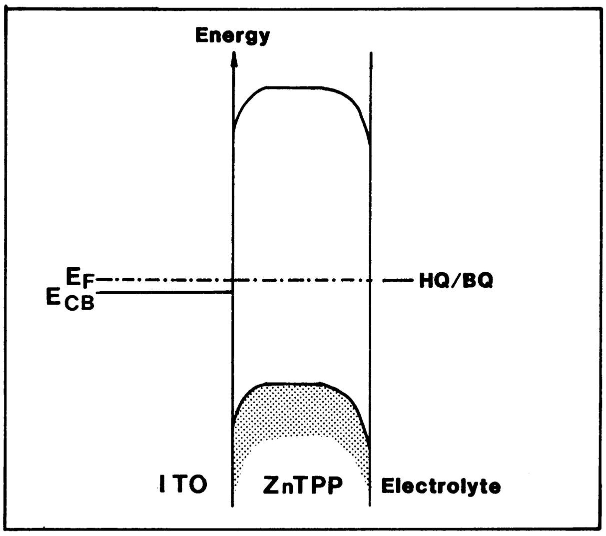

Fig. 8. Equilibrium electron energies for the ITO/ZnTPP electrode in contact with the HQ/BQ couple.

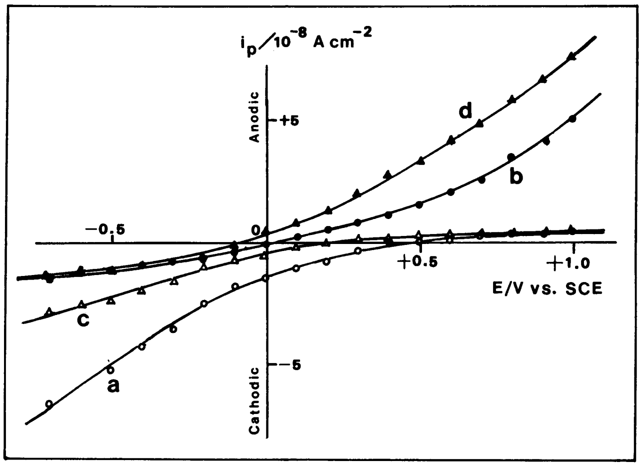

Fig. 9. Potential dependence of the steady-state photocurrent for the ITO/H_2TPP electrode in the presence of about 0.2 mM O_2 [(a) and (b)] and 0.5 mM $[Fe(CN)_6]^{4-}$ [(c) and (d)]. (a) and (c) are obtained by irradiation of the H_2TPP/electrolyte junction, and (b) and (d) obtained by irradiation of the ITO/H_2TPP junction.

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