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Chain-length dependence of photoelectric conversion from a porphyrin monolayer modified electrode

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Abstract

The photoelectrochemistry of a series of porphyrins containing an alkyl chain terminated with imidazolyl, is described. Indium–tin oxide electrodes deposited with porphyrins using the Langmuir–Blodgett (LB) technique exhibit high photocurrent values under ambient condition. Action spectra of the photocurrent generation are coincident with the absorption of the LB film-modified electrodes, indicating that the dye aggregates in the LB film are responsible for the photocurrent. The bias voltages that may influence the photocurrent have also been investigated. The photocurrents varied with the side chain length; the compound with a longer chain but not with the shortest chain generated the maximum photocurrent. To interpret such a special case, a possible mechanism is suggested.

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Keywords: Porphyrin; LB-film; Photocurrent; Chain-length; Imidazole; ITO

1. Introduction

Porphyrin derivatives play an indispensable role in nature, e.g., light harvesting and electron transfer in photosynthesis and oxygen transfer in circulating system of human beings [1]. Photosynthesis has particularly attracted much attention for its potential to be applied as a model in solar energy conversion [2–7]. Many efforts have been put into mimicking photosynthesis, such as constructing the architecture of dyads or triads consisting of donors and acceptors [8–14], with bridges of varying length, to elucidate the energy/electron-transfer process and obtain high efficiency in photon-to-electron conversion. In photoelectric conversion through a wide gap semiconductor electrode, the process of photosynthesis is very similar to that of photoinduced excitation of dyes followed by the electron transfer between the conduction band of the electrode and the orbitals of dyes [15].

Porphyrins have been applied in photovoltaic cell with metal as electrode [16,17]. A few researchers have investigated the properties of porphyrins on indium–tin oxide (ITO) electrode. Yamashita et al. reported a kind of porphyrin photoelectrode which was prepared by vapor deposition of porphyrins on ITO electrode [18].

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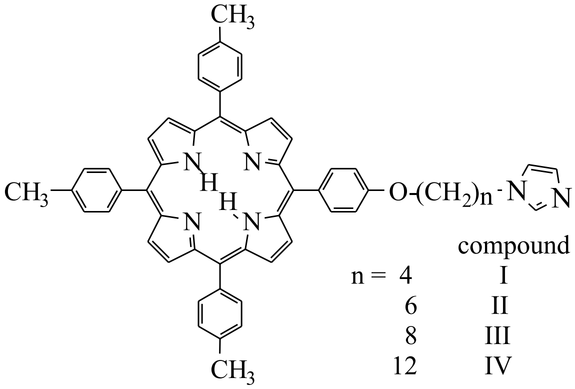
Gregg et al. built up a solar cell filled with liquid crystal porphyrins with ITO coated glass as electrodes [19]. The application of Langmuir–Blodgett (LB) technique, which has become an efficient way to fabricate organic thin films with well controlled compositions, structures, and thickness, has remarkably improved the constructing of the spatial configurationally structures, thus unusual properties can be discerned [20,21]. For formation of high quality film via LB technique, an amphiphilic structure is necessary. In this report, we chose imidazole as hydrophilic group, and a series of porphyrins containing a varied length of alkyl chain terminated with imidazolyl, respectively, were synthesized. Imidazole as functional group of histidine constitutes part of the active sites of chymotrypsin [22] and has significant buffering power near the pH of intracellular fluids and blood [23]. In view of its acid–base adjustment performance, we hope it may improve the photoelectric properties of porphyrins on electrodes such as ITO electrode and, especially, nanocrystal TiO_2 electrode.

Here we investigated their photocurrent generations on ITO electrodes fabricated through LB technique. The order of photocurrent values created from these porphyrin films of different length was not consistent with what we had expected, i.e., the compound with the shortest chain length among our synthesized compounds would have the biggest photocurrent. On contrary, the compound with a longer chain generated the maximum photocurrent. To interpret such a discrepancy, a possible mechanism for the electron-transfer process is proposed.

2. Experimental

2.1. Materials

The starting material, 5-(4-hydroxyphenyl)-10,15,20-tritolylporphyrin (P(OH)TP), was synthesized and purified as described in the literature [24]. Compounds I–IV, as shown in Scheme 1, were synthesized in the same procedure: equivalent P(OH)TP and *n*-bromoalkylimidazole (*n* = 4, 6, 8, 12, respectively) were stirred in *N*,*N*-dimethylformamide at room temperature for 24 h in the presence of a 10-fold molar excess of sodium hydride. The reaction mixture was adjusted to neutral, then the solvent was removed through evaporation, and finally the crude product was purified by column chromatography on silica gel with dichloromethane and ethyl acetate (9:1) as eluent, to give pure compounds in the yield of ca. 55%. For compound I: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): −2.68 (s, 2H), 1.83 (m, 2H), 2.05 (m, 2H), 2.74 (s, 9H), 4.05 (t, 2H), 4.07 (t, 2H), 6.98 (s, 1H), 7.18 (d, 2H), 7.58 (d, 6H), 7.64 (s, 1H), 8.10 (s, 1H), 8.15 (d, 8H), 8.92 (s, 8H); ESI-FTMS: $m/z = 398.195$ ($[C_{54}H_{46}N_6O + 2H^+]$ requires 398.195). For compound II: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): −2.70 (s, 2H), 1.46 (m, 2H), 1.64 (m, 2H), 1.92 (m, 4H), 2.72 (s, 9H), 3.96 (t, 2H), 4.19 (t, 2H), 6.95 (s, 1H), 7.13 (s, 1H), 7.24 (d, 2H), 7.56 (d, 6H), 7.63 (s, 1H), 8.12 (d, 8H), 8.88 (s, 8H); ESI-FTMS: $m/z = 412.209$ ($[C_{56}H_{50}N_6O + 2H^+]$ requires 412.210). For compound III: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): −2.72 (s, 2H), 1.45 (m, 6H), 1.62 (m, 2H), 1.83 (m, 2H), 1.96 (m, 2H), 2.72 (s, 9H), 3.98 (t, 2H), 4.22 (t, 2H), 6.94 (s, 1H), 7.11 (s, 1H), 7.25 (d, 2H), 7.53 (s, 1H), 7.57 (d, 6H), 8.13 (d, 8H), 8.90 (s, 8H); ESI-FTMS: $m/z = 426.224$ ($[C_{58}H_{54}N_6O + 2H^+]$ requires 426.226). For compound IV: ^{1}H NMR (300 MHz, $CDCl_3$) (ppm): −2.75 (s, 2H), 1.33 (m, 2H), 1.44–1.48 (m, 12H), 1.61 (m, 2H), 1.79 (m, 4H), 2.02 (m, 2H), 2.71 (s, 9H), 3.93 (t, 2H), 4.25 (t, 2H), 6.90 (s, 1H), 7.08 (s, 1H), 7.28 (s, 2H), 7.52 (s, 1H), 7.56 (d, 6H), 8.11 (d, 8H), 8.86 (s, 8H); ESI-FTMS:



n =	compound
4	I
6	II
8	III
12	IV

Scheme 1. Structures of compounds I to IV.

$m/z = 454.257$ ([$C_{62}H_{62}N_6O + 2H^+$] requires 454.257). Hydroquinone (H_2Q) was recrystallized from water before use. Methyl viologen diiodide (MV^{2+}) was synthesized by reaction of 4,4′-dipyridyl with excess methyl iodide in refluxing ethanol for 6 h. The product was filtered and washed with ethanol at least four times, and its identity was confirmed by ^1H NMR analysis.

2.2. Apparatus

^1H NMR spectra were obtained by using a Varian GEMINE 300. Electronic spectra were measured with a PE UV/Vis spectrophotometer Lambda 20. LB film-modified ITO electrodes were fabricated by using a model 622 NIMA LB trough. The light source of the photoelectrochemical studies was provided by a 500 W Xe arc lamp. The light beam was made to pass through a group of filters (300–800 nm, Toshiba Co., Japan, and Schott Co., USA) to obtain the given band-pass of light. The light intensity at each wavelength was calibrated by a power meter (Scientech, USA).

2.3. LB film preparation

Solutions of I–IV in chloroform were spread dropwise on the clean water subphase by syringe at a subphase temperature of 20 ± 1 °C. The chloroform was allowed to evaporate for 15 min, and the floating film was then compressed at a rate of 40 $cm^2\,min^{-1}$. The substrate for monolayer deposition was ITO coated borosilicate glass with a sheet resistance of 50 $\Omega\,cm^{-2}$. The ITO plates were cleaned by using the procedures described elsewhere [25].

In order to deposit the monolayer, the ITO slide was first immersed in the subphase. When the monolayer was formed, and compressed to 15 mN/m, the slide was then raised at a rate of 4 $mm\,min^{-1}$. Only monolayer films with transfer ratio of 1.0 ± 0.1 were used in all experiments.

2.4. Photoelectrochemical measurements

A conventional three-electrode glass cell (30 ml capacity) having a flat window with a 0.80 cm^2 effective light irradiation area for illumination was used. The counter electrode was a polished Pt wire, and the reference was a saturated calomel electrode. All photoelectrochemical data were recorded by a model CH600 voltammetric analyzer controlled by computer. The supporting electrolyte was an aqueous solution of 0.5 M KCl. The action spectra were obtained by irradiation with the light through a set of band-pass filters.

3. Results and discussion

3.1. Characterization of LB film and dye-ITO electrode

The surface pressure–area isotherms of the compounds I–IV are presented in Fig. 1. Although no other surfactants were added, the films show relatively high collapse pressures, which means that the group of imidazole is competent for being a hydrophilic part in an amphiphilic molecule. Compound I which contains 4C side chain has a higher collapse pressure than compounds II and III. It does not agree with the conventional notion: the longer the side chain to some extent, the more stable the monolayer [26]. But it may be due to the balance between the hydrophilic and the hydrophobic groups in the molecule to give a higher collapse pressure for compound I. While the limiting areas per molecule of compounds I–IV are about 103, 84, 82, 77 $Å^2$, respectively, which shows the monotonic decrease with the increase of carbon numbers of the side chains, suggesting that the films form more tightly as the length of side chains increases. The values of the limiting areas per

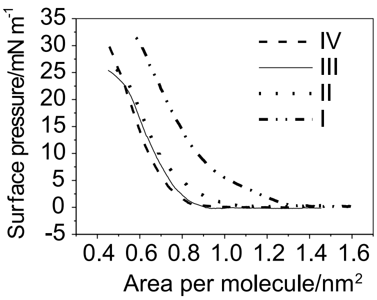


Fig. 1. Surface pressure–area (π–A) isotherms of compounds I–IV at the air/water interface (20 ± 1 °C).

molecule are much smaller than that of 5-(4-pyridyl)-10,15,20-tritertbutylphenylporphyrin [27], indicating that molecules of compounds I–IV are almost vertically oriented on a water subphase.

Because the electronic absorption spectra of all the compounds in chloroform and on ITO electrodes have similarities, the representatives in two conditions are shown in Fig. 2. The $\lambda_{\max}$ of the LB film on ITO electrode occurs at ca. 440 nm, which is significantly red-shifted from the chloroform solution ($\lambda_{\max} = 420$ nm), suggesting the presence of J-aggregate in the film [28].

3.2. Photocurrent generation from dye-ITO electrode

Steady cathodic photocurrents ranging from 620 to 2923 nA cm^{-2} (Table 1) were obtained from the compounds I–IV modified electrodes, when illuminated by a white light with 156 mW cm^{-2} light intensity without any bias voltage in 0.5 M KCl electrolyte solution. The photocurrent obtained in present experiment is visibly higher than that of porphyrins on ITO electrode reported previously [15]. The photoelectric response was very stable when switching on and off for many times.

Fig. 3 shows the action spectra of the cathodic photocurrents of compounds I–IV. The spectra responses coincide with those of the absorption spectra of LB films (Fig. 2), suggesting that the aggregate of the dyes in the LB film is responsible for the photocurrent generation. The photocurrents of ITO electrodes modified with the LB films of compound II in 0.5 M KCl electrolyte solution with zero bias voltage was up to 419 nA cm^{-2} under irradiation of 2.85×10^{14} photons/cm^2 s at 440 nm and was nearly four times higher than that of compound IV. The photocurrents generated from compounds I and IV were also inferior to that of compound II. The reason for such differences will be discussed later. In the case of compound II, photocurrent was 419 nA cm^{-2} at 440 nm, corresponding to 0.093% of IPCE yield (IPCE is defined as the number of electrons generated by light in the external circuit divided by the number of incident photons [29]). The quantum yield φ is about 0.93% for the monolayer compound II modified electrode.

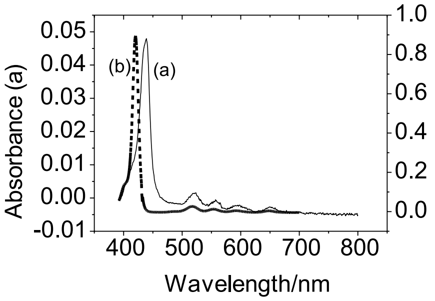


Fig. 2. Absorption spectra of compound II (a) on ITO electrode and (b) in CHCl$_3$ solution.

Table 1
Properties of the monolayer films of compound I–IV on ITO

Sample	I	II	III	IV
Photocurrent (μA cm^{-2})[a]	2.34	2.92	2.17	0.62
φ^b (%)	0.68	0.93	0.71	0.23
k^c	10.2	23.3	49.6	50.0
m^c	0.77	0.83	0.76	0.73

[a] Irradiation under a white light of 156 mW cm^{-2}.

[b] Quantum yield at 440 nm irradiation by white light of 156 mW cm^{-2} through a band-pass filter.

[c] Terms in equation $i = kI^m$.

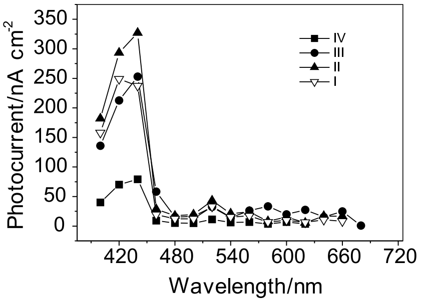


Fig. 3. Photocurrent action spectra of the dye modified ITO electrodes, upon irradiation by a white light of 156 mW cm^{-2} through a set of band-pass filters in 0.5 M KCl electrolyte solution with zero bias voltage under ambient conditions. The incident light intensities of different wavelengths were all normalized.

3.3. Bias voltage dependence of electron injection

The dependence of the photocurrent on the applied bias potential is an important evidence for determining the character of photocurrent. To

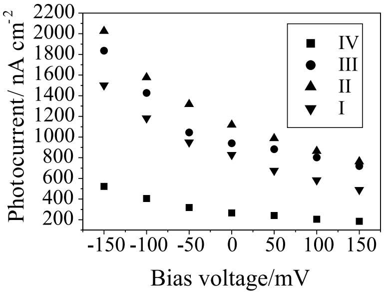


Fig. 4. Photocurrent vs bias voltage for compounds I–IV LB films–ITO electrodes in 0.5 M KCl aquous solution under ambient conditions, upon irradiation with a 46.6 mW cm^{-2} white light.

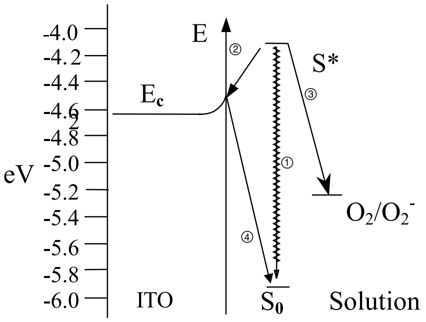


Fig. 5. An energy level diagram for the ITO electrode–monolayer interface. Arrows indicate possible directions of electron propagation.

further prove the electron-transfer process between the ITO electrode and the LB film, the effect of bias voltage was investigated. The relationship between bias voltage and the photocurrent values is shown in Fig. 4. With the increase of negative bias to the electrode, an increment of cathodic photocurrent can be seen and vice versa. This may result from the level change of the conduction band of the ITO electrode: the conduction band level increases with the application of negative bias to the electrode, thus a deeper energy gap between the conduction band and the HOMO of dyes accelerates the photoinduced separation or induces the formation of charge separation.

3.4. Effect of side chain length and a possible mechanism for photocurrent generation

The molecules on the air–water interface become more vertically oriented on the surface of water as the side chain length increases. The area of the compounds I and IV are 720 and 742 Å^2 (calculated with Insight II program, MSI Co.), respectively. Thus the dihedral angle between the surface of water and the face of porphyrins are ca. 82° and 84° for compounds I and IV, respectively. The distances between porphyrin skeletons and electrode surface are ca. 5.9, 8.6, 10.9, and 16.0 Å for compounds I–IV, respectively, indicating that compound IV has been out of the range for efficient electron transfer [30], which can be ascribed to the main cause for its poor photocurrent generation.

Fig. 5 shows a possible mechanism for photocurrent generation. An excited porphyrin molecule (S_1) on the surface of electrode may either undergo reversion to ground state (S_0) (step 1), be oxidized by electron injection directly into the bulk semiconductor (step 2), or into acceptors around the porphyrin, or be reduced by electron injection from the semiconductor (step 4). Since oxygen can act as a reasonable electron acceptor [31], which has a reduction potential of 0.57 V for O_2/O_2^- [32], the excited porphyrin may transfer one electron to oxygen (step 3). In that case, the electrons from the conduction band can reduce the oxidized porphyrins if there is not enough additional donors in aqueous to competitively reduce it, thus a cathodic photocurrent is produced (step 4). The conduction band (E_c) and valence band (E_v) edges of the ITO electrode surface are estimated to be ca. −4.5 and −8.3 eV [33], respectively. The oxidation potential of porphyrins is taken to be +1.2 V vs SHE as quoted for free base tetraphenylporphyrin in DMSO [34].

The dependence of photocurrent on the redox additives also confirms such a mechanism. All the four compounds exhibited the same characteristic and only that of compound II is shown in Table 2 for the sake of concision. The photocurrent decreased sharply when N_2 gas was used to remove O_2, indicating that O_2 acted as a dominant acceptor. The increase of photocurrent could be seen as well upon the addition of MV^{2+}, which is a strong acceptor, into the solution. The presence of H_2Q as a donor in the solution decreased the

Table 2
Effect of redox additives on the photocurrent generation of compound II on ITO electrode[a]

Redox additive	c^b (mg ml^{-1})	Ambient	N_2
–	–	966	162
MV^{2+} $2I^-$	0.13	1057	–
	0.67	1250	–
	1.13	1417	–
	1.60	1525	1152
H_2Q	0.13	332	–
	0.40	−70	–
	0.53	−210	–
	1.40	−399	−902

[a] Irradiation under a white light of 46.6 mW cm^{-2}.

[b] The concentration of redox additives in electrolyte solution.

cathodic photocurrcent and even changed the current to anodic. The anodic photocurrent was especially high when O_2 was removed from the solution. This may result from the reduction of the excited porphyrin by H_2Q and the resulting anion prompts the electron injection from reduced porphyrin into semiconductor electrode. When there is no other acceptor but mainly donor in the solution, e.g., O_2 removed, the injection becomes predominant.

The value of cathodic photocurrent as a result of the competition between step 2 and step 3 would be higher when more electrons are transferred to oxygen. Compound I whose porphyrin skeleton is more proximate to electrode surface would have higher electron-transfer rate in step 2 than that of compound II. The electrons generated in step 2 may recombine with oxidized porphyrins in step 4. The net photocurrent of compound I is lower than that of compound II because there is a great fraction of compound I excited states are deactivated through step 2 and then step 4, supposing that the rates of compounds I and II at step 3 change only slightly. It might be the primary factor for the difference of photocurrent generation between compounds I and II. The lower photocurrent of compound III compared with compound II may result from the decrease of electron-transfer rate in step 4 as the distance between the electrode surface and porphyrin molecules becomes longer than that of compound II.

4. Conclusions

A series of porphyrins containing varied length of side chain terminated with imidazolyl were synthesized and fabricated into dye modified ITO electrodes by LB technique. Noticeable cathodic photocurrents were observed under ambient condition and the values varied with the chain length. The reason for such a variance is ascribed to the different rate of electron transfer between the excited porphyrin and the conduction band of semiconductor electrode among the four porphyrin derivatives. The effects of voltage on the photocurrent had also been investigated. The quantum yield is more than 0.9% for a 6C side chain porphyrin under ambient condition. The fact that quantum yields of such porphyrins vary with side chain length suggests that, to obtain maximum photo-electric conversion efficiency, an optimal distance between dye and electrode surface should be chosen, which can be adjusted through changing the number of carbon of the side chain.

Acknowledgements

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