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Approaches to conducting polymer devices with nanostructures: photoelectrochemical function of one-dimensional and two-dimensional porphyrin polymers with oligothienyl molecular wire

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Abstract

The nanofabrication of molecular semiconductors for the construction of molecular photoelectronic devices is an important area of research; to this end, we have constructed porphyrin polymers possessing a tailor-made structure. In this paper, we report the photoelectronic function of the porphyrin polymers connected by oligothienyl bridges. One-dimensional porphyrin polymers with various lengths of oligothienyl bridge in the axial direction were synthesized by the electrochemical polymerization of symmetrical bis(oligothienylalkoxy)phosphorus(V)-porphyrin. The conductivity of the polymer was strongly enhanced by photoirradiation, indicating photoinduced carrier formation. The layered sandwich cell of the polymer with polybithiophene showed electric rectifying properties in the dark. Interestingly, photovoltage and photocurrent were observed on photoirradiation. On the basis of these results, a microscopic polymer junction chip was constructed. Two-dimensional porphyrin polymers containing oligothienyl bridges in the lateral direction were prepared by similar electrochemical oxidation of *meso*-tetrakis(oligothienyl)porphyrin metal complexes and were fabricated as layered diodes.

Keywords: Conducting polymer devices; Nanostructure; Photoelectrochemical function; Porphyrin polymers; Oligothienyl molecular wire

1. Introduction

The nanofabrication of molecular semiconductors for the construction of molecular photoelectronic devices is an important area of research [1]. The incorporation of multiple redox centres into conducting molecular systems is a useful approach for trial construction. For example, the incorporation of a photosensitizer and a suitable electron donor and/or acceptor into a polymeric chain has been proposed as a molecular system based on photoinduced electron transfer [1a]. However, the production of such polymers containing a number of large aromatic moieties or metal complexes is difficult because of the intractable solubility and flexibility, which limit the possibilities for controlled fabrication on terminal electrodes. In order to overcome these difficulties, electrochemical polymerization is useful, since the polymer is deposited directly on the terminal electrode. With this in mind, we have synthesized a series of porphyrin derivatives (Fig. 1) which can be polymerized by normal electrochemical oxidation [2]. On polymerization, one- or two-dimensional polymers, with porphyrin moieties separated by ordered oligothienyl molecular wire, can be obtained. In addition, lateral polymerization can be combined with axial polymerization to afford three-dimensional molecular systems. In this paper, we report the construction and photoelectronic function of highly ordered porphyrin polymers with one- and two-dimensional structures. The electron transfer process of the metalloporphyrin polymers and their hybridization with certain conducting polymers are also reported.

2. Experimental details

2.1. Materials

In this study, the oligothiophenes, which can be easily dimerized by electrochemical oxidation, were used as coupling elements [3].

The phosphorus(V)porphyrin can form two stable axial bonds on the central phosphorus atom. The phosphorus(V)-porphyrin derivatives containing two thienylalkoxy or oligothienylalkoxy groups at the axial positions of the central

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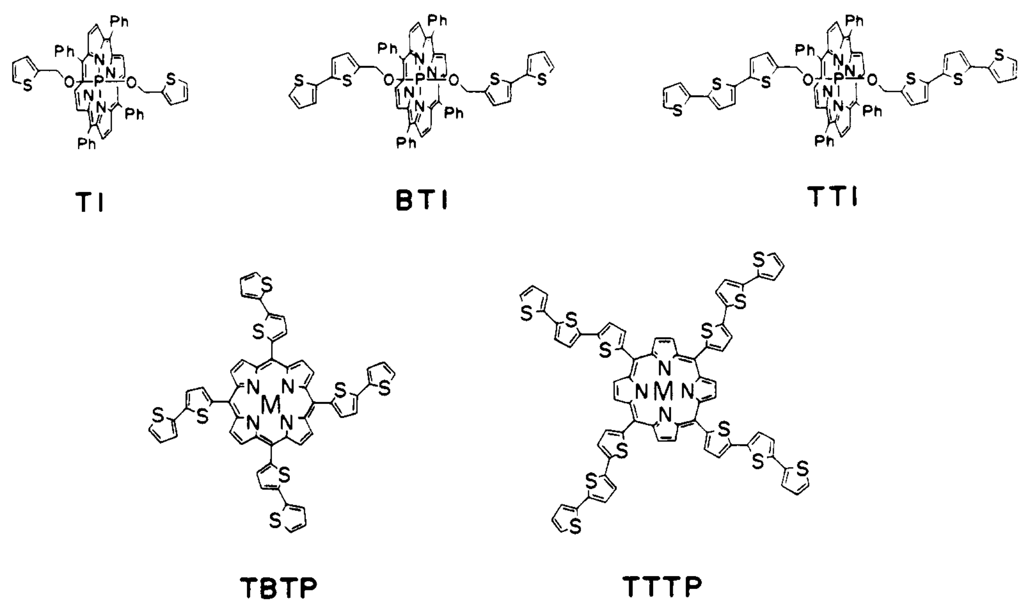


Fig. 1. Structures of porphyrin derivatives with thiophene or oligothiophene moieties. M ≡ 2H, Zn, Pd.

phosphorus atom (T1, BT1 and TT1) were synthesized by the reaction of dichlorophosphorus(V)tetraphenylporphyrin with the corresponding thienyl or oligothienyl alcohols according to Ref. [2a].

Bithiophenecarboxaldehyde and terthiophenecarboxaldehyde were synthesized from the corresponding oligothiophene by Vilsmeyer reaction according to the literature [4]. Free base porphyrins (*meso*-tetrakis(bithienyl)porphyrin (TBTP) and *meso*-tetrakis(terthienyl)porphyrin (TTTP)) were synthesized by refluxing the thiophenecarboxaldehyde derivatives with pyrrole in propionic acid, and were purified in the usual way [5]. Zinc and palladium complexes of the porphyrins were obtained by the metallation of the free base porphyrins with an excess amount of the appropriate metal complex in the usual way [6]. UV–visible absorption data of the derivatives (λ_{max} (nm) in pyridine): TBTP, 448, 531, 579, 668; ZnTBTP, 451, 575, 621; PdTBTP, 442, 537, 579. ^{1}H NMR data of the derivatives (δ relative to $SiMe_4$ in $CDCl_3$): TBTP, δ 9.19 (s, 8H, pyrrole-β), 7.82 (d, 4H, J = 3.5 Hz, thienyl), 7.60 (d, 4H, J = 3.5 Hz, thienyl), 7.44 (dd, 4H, J = 1.3, 3.5 Hz, thienyl), 7.36 (dd, 4H, J = 1.3, 5.1 Hz, thienyl), 7.13 (dd, 4H, J = 5.1, 3.5 Hz, thienyl), −2.54 (S, 2H, pyrrole-NH); ZnTBTP, δ 9.22 (s, 8H, pyrrole-β), 7.76 (d, 4H, J = 3.5 Hz, thienyl), 7.55 (d, 4H, J = 3.5 Hz, thienyl), 7.40 (dd, 4H, J = 1.3, 3.5 Hz, thienyl), 7.31 (dd, 4H, J = 1.3, 5.1 Hz, thienyl), 7.10 (dd, 4H, J = 5.1, 3.5 Hz, thienyl); PdTBTP, δ 9.17 (s, 8H, pyrrole-β), 7.78 (d, 4H, J = 3.5 Hz, thienyl), 7.57 (d, 4H, J = 3.5 Hz, thienyl), 7.5–7.3 (m, 12H, thienyl). Fast atom bombardment mass spectrometry (FABMS) data of the derivatives (m/z, parent peak): TBTP, 967 (MH^+); ZnTBTP, 1029 (MH^+); PdTBTP, 1071 (MH^+).

2.2. Measurements

Cyclic voltammograms were measured with a Nikko Keisoku NPGS-301 potentiogalvanostat and an NFG-6 function generator. CH_2Cl_2 solution with 0.1 M n-Bu_4NBF_4 supporting electrolyte was used. A three-electrode system (platinum working electrode, platinum counter-electrode and saturated calomel reference electrode (SCE)) was employed. All the solutions were purged with nitrogen before electrolysis.

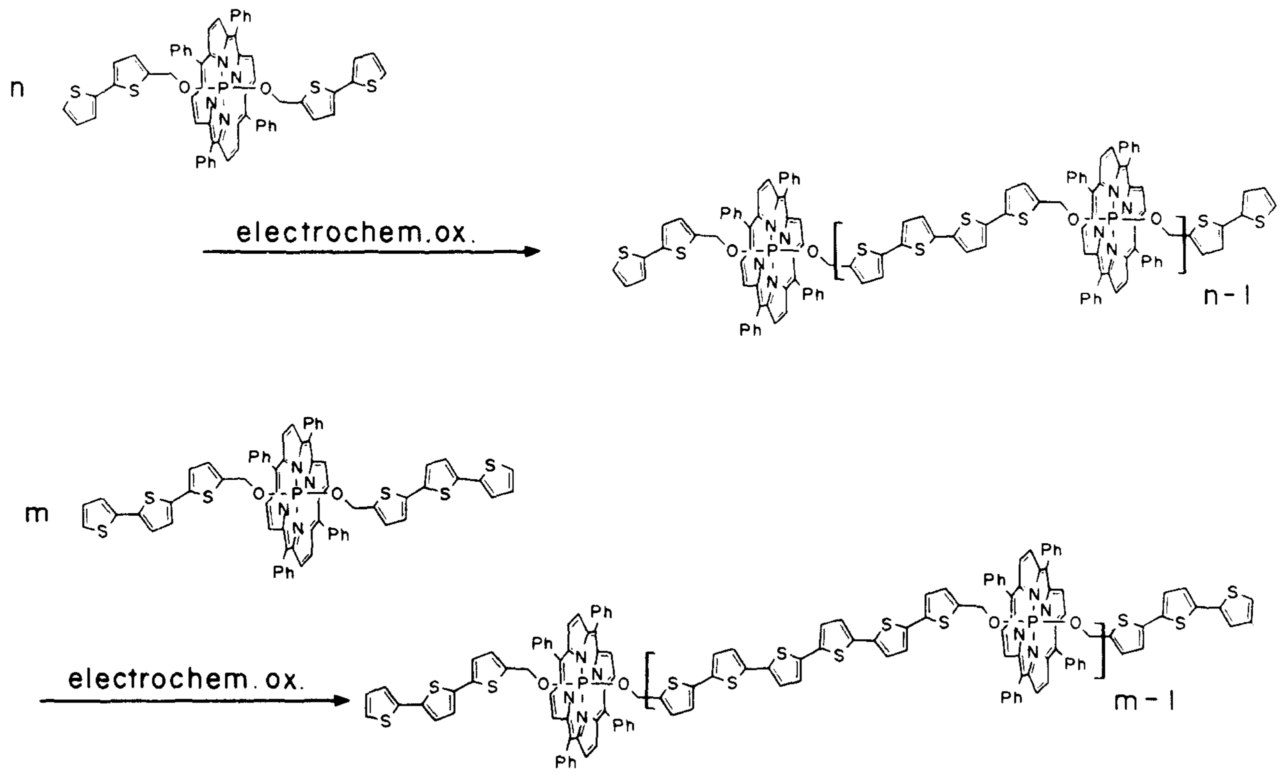
The current–voltage (I–V) curves of the polymers were measured using a sandwich cell of ITO/polymer/Au (ITO, indium tin oxide) under a nitrogen atmosphere. For the construction of the sandwich cell, each polymer was deposited on the ITO working electrode, and then the polymer was covered with Au by the sputtering method. For measurement of the I–V curves of the polymers on photoirradiation, a 500 W Xe lamp was used and the incident light was passed through a UV cut-off filter (Toshiba, L39) and an IR cut-off filter (Toshiba, IR25S) with a water jacket.

The absorption and emission spectra of the monomers and polymers were measured with a Shimadzu UV-2200 spectrophotometer and a Shimadzu RF-503A spectrofluorometer respectively.

3. Results and discussion

3.1. Electrochemical construction of one-dimensional porphyrin polymer

The phosphorus(V)porphyrin derivatives BT1 and TT1 were polymerized by electrochemical oxidation (working electrode, ITO; counter-electrode, Pt; reference electrode, SCE; solvent, 0.1 M $TBABF_4$–CH_3CN), whereas T1 was scarcely polymerized [2a]. As a result, on electrochemical oxidation of BT1 and TT1, poly-BT1 and poly-TT1 were deposited on the ITO electrode at potentials above 1.2 V and 0.9 V vs. SCE respectively. At the same time, the peak current around −0.4 V vs. SCE, assigned to the redox reaction of



Scheme 1.

the phosphorus(V)porphyrin moiety, was increased. In the absorption spectrum of the polymer obtained, the UV absorptions assigned to bithiophene (310 nm) and terthiophene (357 nm) (from the starting monomers) completely disappeared. In addition, the IR absorption peaks due to C–H out-of-plane vibrations at the α-positions of the terminal thiophenes of the axial substituents disappeared on polymerization. Consequently, it was concluded that the polymers obtained are one-dimensional with an alternating structure of phosphorus(V)porphyrin and oligothiophene moieties as shown in Scheme 1.

3.2. Photoconductivity of one-dimensional porphyrin polymer

The *I–V* curves of the porphyrin polymers were measured using the sandwich cell ITO/polymer/Au (Fig. 2). The *I–V* curves of poly-BT1 and poly-TT1 showed that the contact

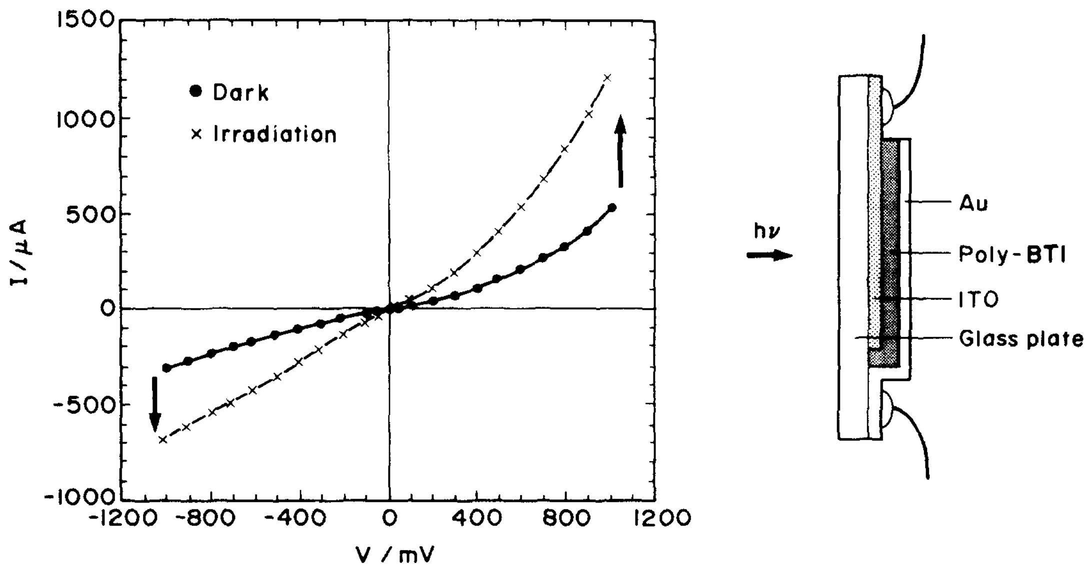


Fig. 2. *I–V* curves of poly-BT1 in the dark and on photoirradiation.

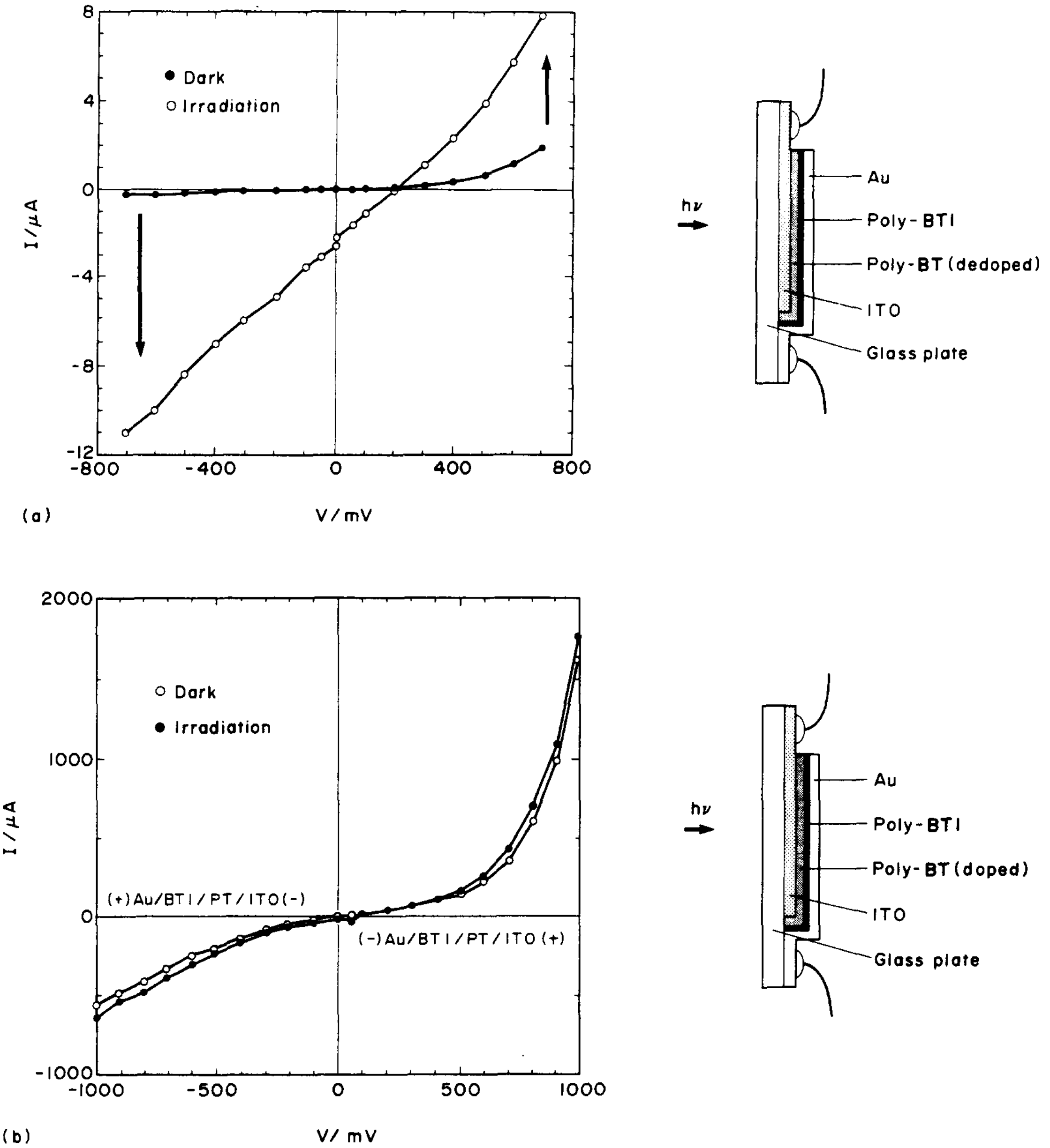


Fig. 3. *I–V* curves in the dark and on photoirradiation of the layered polymer sandwich cell (ITO electrode/poly-BT/poly-BT1/Au electrode): (a) for dedoped state of poly-BT; (b) for doped state of poly-BT.

between the polymer and the electrode was ohmic. A Schottky junction was not formed in the contact with ITO or Au. The d.c. conductivity of the polymer in the dark was 1.2×10^{-9} S cm^{-1} for poly-BT1 and 5.1×10^{-8} S cm^{-1} for poly-TT1. Interestingly, the conductivities of poly-BT1 and poly-TT1 were strongly enhanced by photoirradiation (Fig. 2). During photoirradiation by the 500 W Xe lamp, the enhancement was more than threefold, and dependent on the light intensity.

As described previously [2a,2b], the lifetime and relative quantum yield of fluorescence of the monomers depend on the length of the oligothienyl moieties, where photoinduced electron transfer from the oligothienyl moieties to the porphyrin ring occurs according to their energy levels. For the electropolymerized polymers studied here, the fluorescence originating from the porphyrin ring was not detected because of a low quantum yield. The strong quenching of the fluorescence in the polymer suggests that efficient photoinduced electron transfer occurs. Photoinduced carrier formation on electron transfer results in an increase in the conductivity in the one-dimensional polymer on photoirradiation.

3.3. Photoswitching device using one-dimensional polymer

The present photoactive porphyrin polymers containing oligothienyl molecular wire are useful for fabrication and for hybridization with other conducting polymers. In this study, photoswitching devices were made by hybridization of the one-dimensional porphyrin polymers and polybithiophene (poly-BT). Firstly, a simple layered polymer sandwich cell

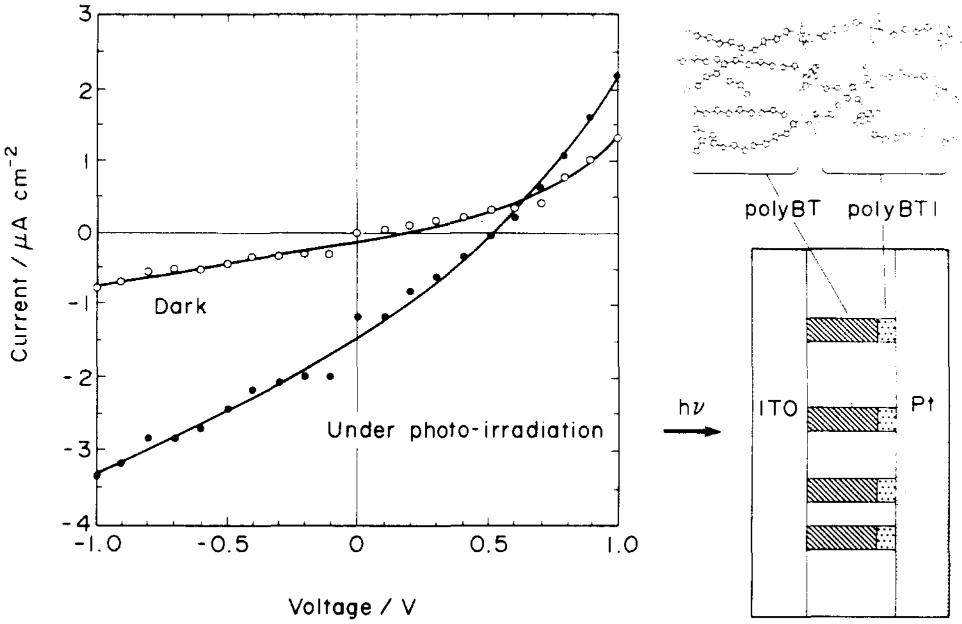


Fig. 4. *I–V* curves in the dark and on photoirradiation of the polymer sandwich chip (poly-BT/poly-BT1) prepared in the nucleopore (5 μm) of a membrane filter.

(ITO electrode/poly-BT/poly-BT1/Au electrode) was constructed by successive electrochemical polymerization of bithiophene (BT) (50 mC cm^{-2}) and BT1 (100 mC cm^{-2}). In the *I–V* profiles of the poly-BT/poly-BT1 cell for the dedoped state of poly-BT, electric rectifying properties were observed in the dark as shown in Fig. 3(a). Considering that contacts ITO/poly-BT and poly-BT1/Au were ohmic, the rectifying properties are considered to arise from the molecular interface between poly-BT and poly-BT1. Interestingly, the *I–V* profile of the layered polymer sandwich cell of poly-BT and poly-BT1 was changed significantly on photoirradiation (Fig. 3(a)). During photoirradiation with the 500 W Xe lamp, a photovoltage up to 200 mV and a photocurrent were observed. It is suggested that the hole generated in the poly-BT1 layer can migrate to the poly-BT layer efficiently. However, the *I–V* profiles of the poly-BT/poly-BT1 cell for the doped state of poly-BT were completely different. As shown in Fig. 3(b), the conductivity was strongly increased because of the higher carrier density in poly-BT, and a quasi-MIM profile was observed instead of a rectifying profile because of the presence of the low conducting poly-BT1 layer. Furthermore, the *I–V* profile of the doped cell changed only slightly on photoirradiation. It is suggested that the hole generated in the poly-BT1 layer cannot be transferred to the doped poly-BT layer. Consequently, it can be concluded that the efficient photoresponse can be attributed to photoinduced electron transfer from dedoped poly-BT to the one-dimensional polymer (poly-BT1).

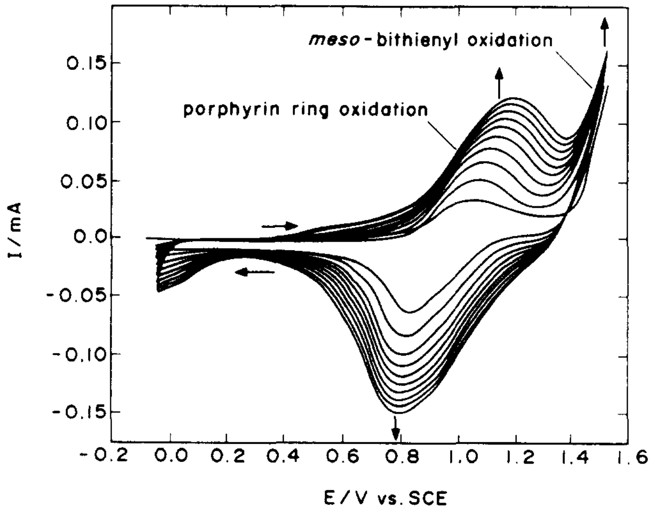
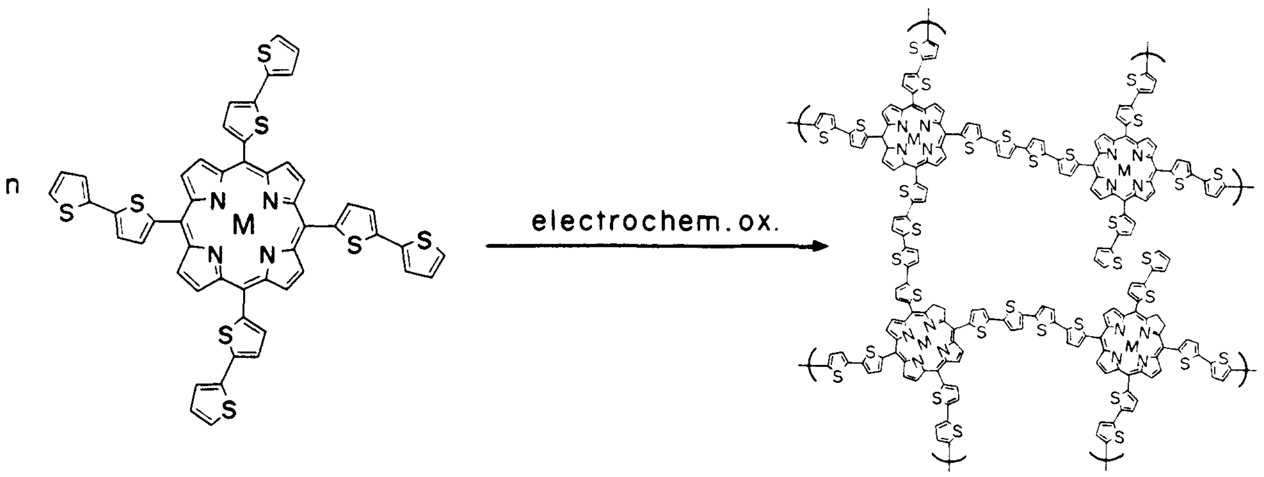


Fig. 5. Cyclic voltammograms for the electrochemical polymerization of ZnTBTP.

On the basis of the above results, a microscopic polymer junction chip (Pt electrode/poly-BT/poly-BT1/Au electrode) was constructed by successive electrochemical polymerization of BT and BT1 in a nuclepore membrane with 5 μm pores. As shown in Fig. 4, this device acts as a photodiode.

3.4. Electrochemical construction of two-dimensional porphyrin polymers

Metal complexes of TBTP and TTTP were polymerized by the electrochemical oxidative coupling of *meso*-oligothienyl groups (working electrode, ITO; counter-electrode, Pt; reference electrode, SCE; solvent, 0.1 M TBABF$_4$–CH$_2$Cl$_2$). Fig. 5 shows the cyclic voltammogram during the electrochemical polymerization of ZnTBTP. According to repeated oxidation above 1.4 V vs. SCE, at which the *meso*-bithienyl groups can be oxidized, polymer was deposited on the working ITO electrode, and the peak current assigned to the redox reaction of the first oxidation of the porphyrin ring



Scheme 2.

(around 1.0 V vs. SCE) was increased. For the other metal complexes of TBTP and TTTP, electrochemical polymerization was accomplished in a similar manner. In the IR spectra of the polymer films, the peak broadens and there is a decrease in the α-CH out-of-plane vibrations (694 and 842 cm^{-1}) of the terminal thiophene. These results suggest that α–α coupling of the *meso*-oligothienyl groups occurs to form a quasi-two-dimensional polymer. In an ultrathin film of ZnTTTP prepared on an Au(111) substrate by a single sweep from 0 V to 0.8 V, the quasi-two-dimensional structure was confirmed by STM, although some extent of disorder was included [7]. In this case, the film thickness is within 0.5 nm, which suggests planar orientation of the porphyrin rings. Consequently, it was concluded that the polymers obtained are quasi-two-dimensional with an alternating structure of porphyrin and oligothiophene moieties as shown in Scheme 2.

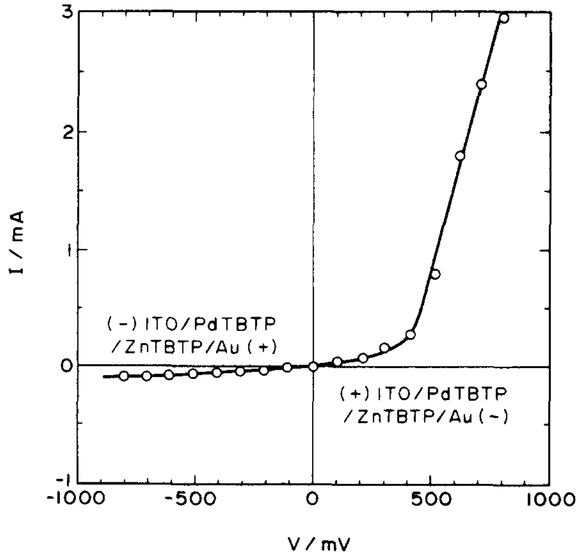


Fig. 6. I–V curves of the layered polymer sandwich cell (ITO electrode/poly-PdTBTP/poly-ZnTBTP/Au electrode).

3.5. *Electric properties of two-dimensional porphyrin polymers*

The d.c. conductivities of the polymer films measured by a sandwich cell (ITO electrode/porphyrin polymer/Au electrode) were 3×10^{-7} S cm^{-1} for poly-ZnTBTP and 2×10^{-7} S cm^{-1} for poly-PdTBTP. In these cases, each contact was ohmic. Interestingly, the layered polymer sandwich cell (ITO electrode/poly-PdTBTP/poly-ZnTBTP/Au electrode) constructed by successive electrochemical polymerization of PdTBTP (20 mC cm^{-2}) and ZnTBTP (20 mC cm^{-2}) showed electric rectifying properties as illustrated in Fig. 6. Considering that contacts ITO/poly-PdTBTP and poly-ZnTBTP/Au are ohmic, the rectifying property is considered to arise from the molecular interface between poly-PdTBTP and poly-ZnTBTP. From the rectifying direction of the current, it is suggested that the electronic flow direction is regulated from poly-ZnTBTP to poly-PdTBTP at the molecular interface. This is considered to be analogous to the p–p′ junction of organic semiconductors [8]. The oxidation potentials of the Pd porphyrins are higher than those of the Zn porphyrins; the difference is induced by their central metals [9]. However, in the I–V profile on photoirradiation, photovoltage and photocurrent are not observed, suggesting that charge recombination is rapid in the present cell. These rectifying properties at the interface of the quasi-two-dimensional porphyrin polymers suggest that the rectifying function may also be applied to the three-dimensional porphyrin system when it is constructed. The present systems, with energetic and structural tunability, may be promising candidates for organic electronics materials.

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