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Electrochemical fabrication of one-dimensional porphyrinic wires on electrodes

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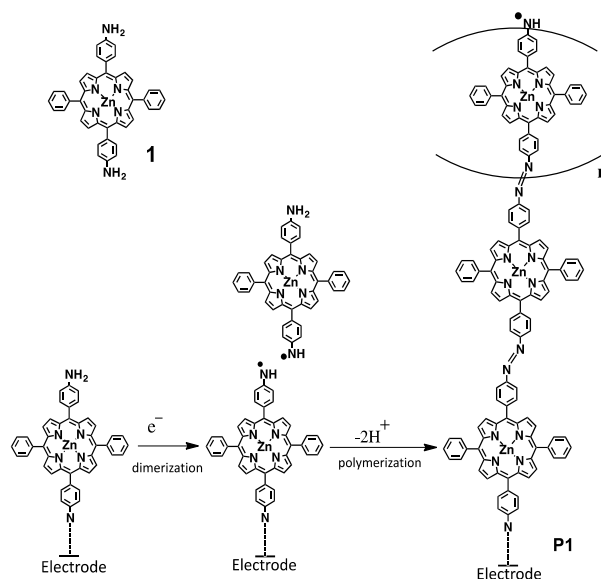
[5,15-di(4-aminophenyl)-10,20-diphenylporphyrinato]zinc(II) was found to electropolymerize on electrodes such as glassy carbon (GC), indium tin oxide (ITO), and tin oxide, to form a redox-active, stable, and reproducible π -conjugated polymer. Electrochemical and UV/vis spectroscopic studies showed that the electropolymerization involves azobenzene linkage formation via radical intermediates. The electrode modified with the porphyrinic wire featured strong light absorptions in the visible region, thereby serving as a photoanode for a photocurrent generation system

Introduction

A series of valuable characteristics, such as developed π -conjugation, intense color, rigid structure, and high chemical stability, allows porphyrins to be utilized in broad application areas like electronics,¹⁻⁴ medicine,⁵⁻⁷ catalysis⁸⁻¹⁰ and so on. Especially, because of their versatility in light absorptions and redox activities, porphyrins are frequently used in optoelectronics and photovoltaics applications. With adequate electron transfer ability and capability in acquiring light in wide wavelengths, porphyrins become eminent in light-induced electron donating systems, leading to applications in dye-sensitized solar cells¹¹⁻¹³ and bulk heterojunction solar cells.¹⁴⁻¹⁶ Moreover, the redox properties of porphyrins can be tuned at will by introducing various types of substituents and metal centres.

Synthesizing porphyrinic polymers on electrode surfaces is an important technique for applications.¹⁷ Such polymer structures may be accomplished by coordination reactions between porphyrin-containing bridging ligand molecules and metal ions,¹⁸ or by oxidative radical coupling of functionalized porphyrins.¹⁹ The electropolymerizable substituents include vinyl, amino, hydroxylphenyl, pyrrolyl,²⁰ carbazoyl²¹ and thienyl²² groups. In the present work, we show a new procedure to form a porphyrinic

polymer on various electrode surfaces, including glassy carbon (GC), indium tin oxide (ITO), and tin oxide (SnO₂). [5,15-di(4-aminophenyl)-10,20-diphenylporphyrinato]zinc(II) (**1**, Scheme 1 and Fig. 1) is electrooxidized to form a *N*-radical, such that porphyrinic oligomers linked by azobenzene (**P1**) are attached on an electrode surface (Scheme 1). The polymer film is characterized by means of electrochemistry, Raman, and UV/vis spectroscopy. The photoelectric conversion ability of the modified electrode is also reported.



Scheme 1 Proposed mechanism of the oxidative electropolymerization of **1** to form **P1**.

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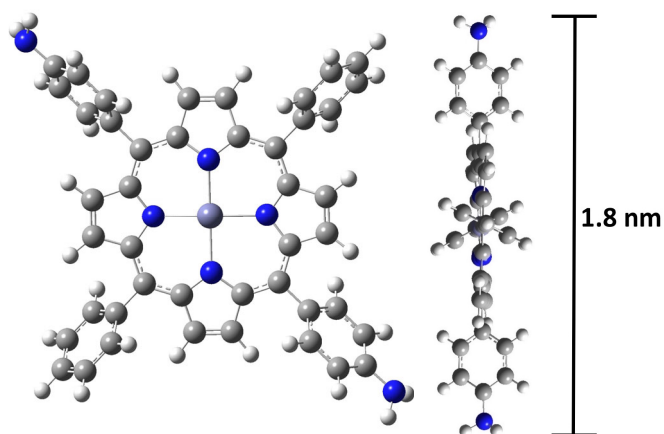


Fig. 1 Molecular size of **1** estimated by means of DFT calculation.

Experimental Section

Reagents and instrumentation

All chemicals were purchased from Kanto Chemical Co., Tokyo Chemical Industry Co., Ltd., or Wako Pure Chemical Industries, Ltd., were used as received, unless otherwise stated. **1** was synthesized according to previous literatures^{23–26} with a few modifications. Tetra-*n*-butylammonium perchlorate, Bu_4NClO_4 , employed as a supporting electrolyte was purified by recrystallization from ethanol, and dried in vacuo. A Milli-Q purification system (Merck KGaA) was used to gain pure water. ITO was treated before use upon sonication in acetone (10 min) and nonionic detergent in water (30 min \times 2) and, and purified water (10 min). The cleaned substrate was stored in water, and dried by nitrogen blow just prior to use. All ^1H NMR data were recorded on a Bruker-DRX500 using CDCl_3 as solvent and tetramethylsilane ($\delta_{\text{H}} = 0.00$) as an internal standard. High-resolution fast atom bombardment mass spectrometry (HR-FAB-MS) was conducted using a JEOL JMS-700 MStation mass spectrometer. UV/vis spectra were obtained with a JASCO V-570 spectrometer. Raman spectra were taken using JASCO NRS-5100. AFM measurements were carried out using an Agilent Technologies 5500 scanning probe microscope in the high-amplitude mode (tapping mode) with a silicon cantilever Nano World PPP-NCL probe. FE-SEM images were recorded using JEOL JSM-7400FNT with an acceleration voltage of 1.5 kV. All experiments were carried out under an ambient condition unless otherwise stated. The molecular size of **1** was determined by DFT calculation. The DFT calculation was carried out using Gaussian09 Revision D.01 program package. The geometry optimization was performed using B3LYP functional with LANL2DZ basis set for Zn and 6-31g(d) basis set for the other atoms and the result was visualized using GaussView 5.0.8 software.²⁷

Photoelectric conversion measurement

The modified ITO electrode was assigned as a working electrode (photoanode) with an Ag^+/Ag electrode (0.01 M AgClO_4 in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{acetonitrile}$) acted as a reference electrode and a Pt wire

as a counter electrode. All three electrodes were engaged in an acetonitrile solution of 0.1 M Bu_4NClO_4 containing triethanolamine (TEOA, 0.05 M) as a sacrificial donor reagent. The cell was sealed and deoxygenized by argon bubbling for 5 min.²⁷ Monochromatic light for an action spectrum (400–500 nm in every 10 nm) was extracted from a xenon lamp (MAX-302, Asahi Spectra Co., Ltd) and a monochromator (CT-10, JASCO Corporation) was utilized to monochromate the photon flux while the size of the electrode active area was approximated from a fluorocarbon rubber o-shaped ring; 0.264 cm^2 . An electrochemical analyser (ALS 750A, BAS Inc.) was used to control the electrode potential and photocurrent acquisition of the photoelectric conversion system. A photon counter (8230E and 82311B, ADC Corporation) was engaged in quantifying photon flux of the incident light. The insignificant dark current was observed when the potential of the photoanode fixed close to the open circuit potential (-0.22 V vs Ag/Ag^+). The calculation for quantum yield of photocurrent generation was made according to a previous literature.²⁹

Results and discussion

Porphyritic polymer wire **P1** was synthesized by the electrochemical oxidation method. Fig. 2 shows a cyclic voltammogram of **1** (2.0 mM)

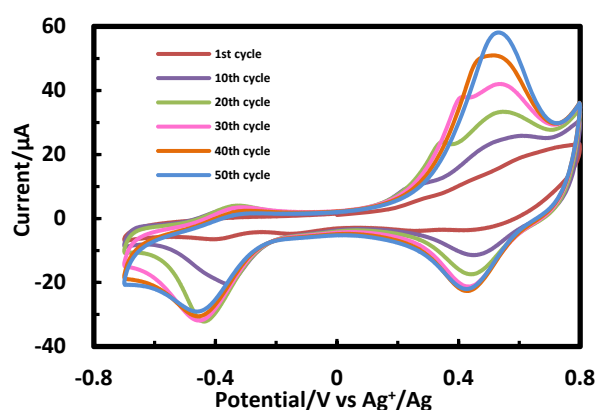


Fig. 2 Cyclic voltammogram for **1** (2 mM) upon repetitive scans (from 1st to 50th cycles) in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ at GC.

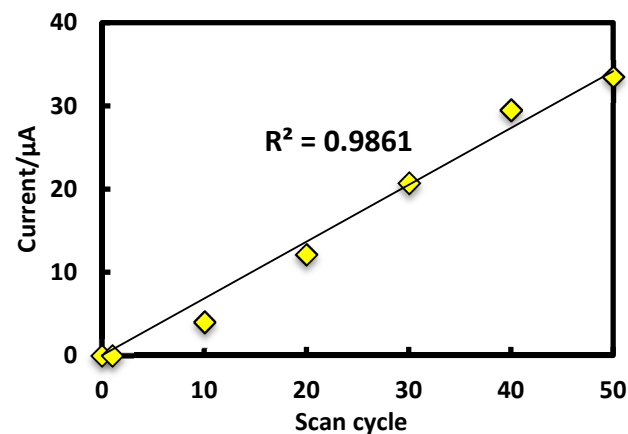


Fig. 3 Plot of anodic peak current vs. scan cycles.

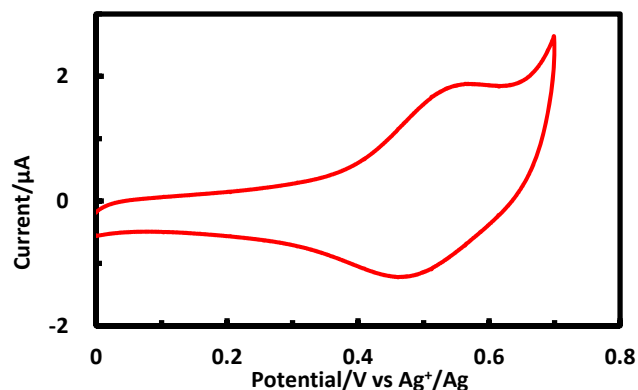


Fig. 4 Cyclic voltammogram of **P1** on GC in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$.

at GC in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$ in a repetitive redox process. An anodic peak appears at around 0.52 V vs. Ag^+/Ag , corresponding to the oxidations of both amino group³⁰ and porphyrin moiety.³¹ This argument is strongly supported by the disappearance of the shoulder peaks in Figure 2 after the electropolymerization finished (Fig. 4). Its peak current as shown in Figure 3 increases with the number of the oxidation cycles, indicative of a formation and growth of an electroactive film on the GC surface.³² In general, the oxidation of aromatic amines is likely to afford either polyaniline or azobenzene.³³ In the present case, the azobenzene linkage is responsible to elongate porphyrinic polymer wire **P1** (Scheme 1). Fig. 4 shows a cyclic voltammogram of **P1** on GC in 0.1 M $\text{Bu}_4\text{NClO}_4\text{-CH}_2\text{Cl}_2$, displaying a quasi-reversible redox wave due to the [porphyrinato]zinc(II) moiety at ca. 0.52 V. The surface coverage of the porphyrin unit was calculated to be $2.7 \times 10^{-9} \text{ mol cm}^{-2}$ from the area of the anodic redox wave.

The electropolymerization of **1** to form **P1** was also conducted on transparent electrodes such as indium tin oxide (ITO) and tin oxide (SnO_2) in order to allow spectroscopic studies. Practically identical electrochemical behaviour was observed (Fig. S1).

The morphology of **P1** was investigated by AFM and SEM. In order to observe the edge of the electropolymerized film, the modified electrode was scratched using a metal spatula, and the border of the scratched region was inspected. From the cross-sectional profile in AFM (Fig. 5), the average thickness of **P1** was calculated to be 112 nm. The surface coverage of the [porphyrinato]zinc(II) unit was estimated from the average thickness and size of **1** (Fig. 1), giving a value of $3.6 \times 10^{-9} \text{ mol cm}^{-2}$. This value was consistent with the calculated value from the cyclic voltammetry (Fig. 3). On the other hand, SEM also gave a concrete evidence for the polymer formation, showing distinguishable domains (Fig. 6): Bare ITO surface as a lower part was rather smooth, while the area modified with **P1** as the higher part displayed a creased texture.

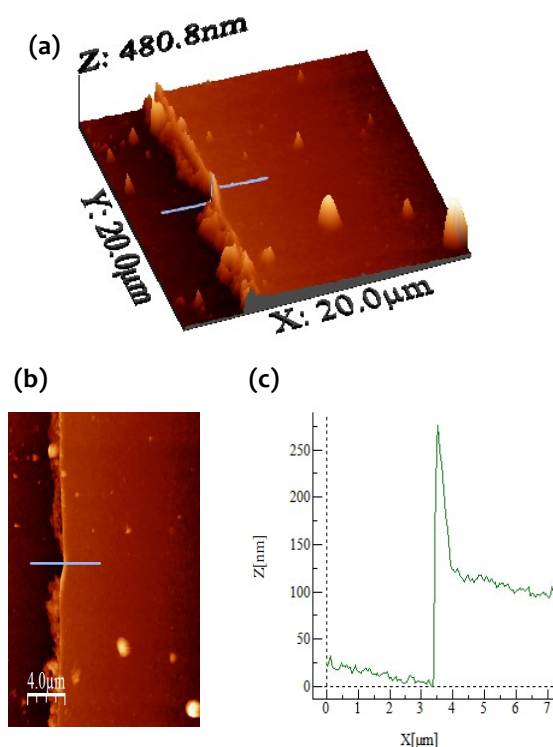


Fig. 5 (a,b) AFM height (3D and normal) images of an ITO electrode modified with the porphyrin polymer. (c) AFM cross-sectional profile along the blue line.

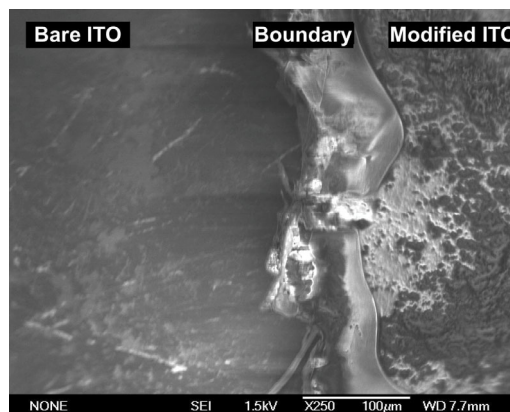


Fig. 6 SEM image an ITO electrode modified with the porphyrin polymer.

Figure 7 shows the absorption spectra of **1** in dichloromethane and the **P1** film on ITO. Note that **P1** deposited on ITO exhibited a greenish yellow color (Figure 8). The spectrum of the **P1** film features absorption bands typical of porphyrin;³⁴ the Soret band (435 nm) and Q-bands (563 and 607 nm). Moreover, the spectrum of **P1** (The Soret band at 424 nm and Q-bands at 554 and 588 nm) is quite similar to that of **1**. This series of facts indicates that the porphyrinic skeleton was maintained in **P1** in the course of the electropolymerization process.

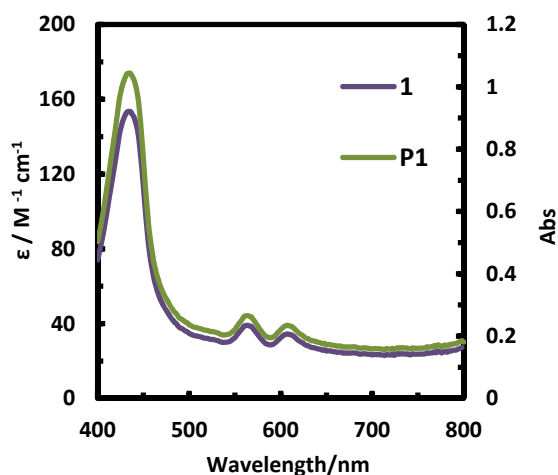


Fig. 7 Absorption spectra of **1** in dichloromethane and **P1** on ITO.

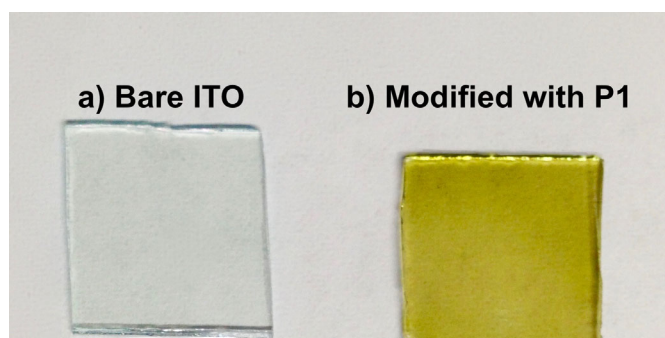


Fig. 8 Photographs of an ITO electrode before and after the modification with **P1**.

The raman spectra of **1** and **P1** were measured using probe light at 532 nm, and the result is depicted in Fig. 9. In addition to a common band at around $1460\text{--}1470\text{ cm}^{-1}$, **P1** showed a characteristic band at 1446 cm^{-1} , whereas no band was detected in **1**. This band can be assigned to the stretching vibration of the azo group.³⁵⁻³⁷ This result supports our claim that the azobenzene linkage was generated upon the electrooxidative polymerization process.

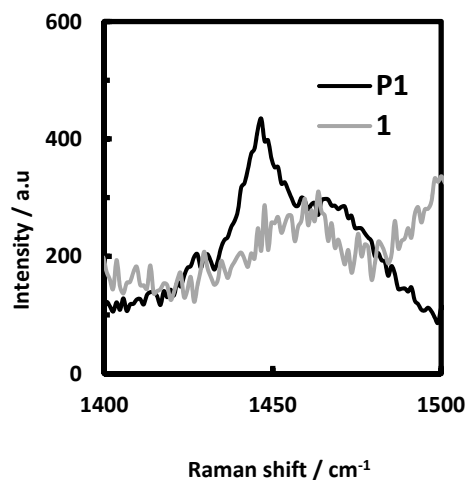


Fig. 9 Raman spectra of **1** and **P1**.

As a functionality of **P1**, photoelectric conversion ability was examined. **P1** on an ITO electrode was employed as a working electrode, and the whole setup of the photoelectric conversion system is described in the experimental section. Upon irradiation with visible light to the working electrode applied with a bias potential (-0.22 V) led to generate an anodic current as shown in Fig. 8. The action spectrum of the photocurrent generation was coincident with the UV-vis absorption spectrum of **P1** thin films on an ITO modified electrode in the $400\text{--}500\text{ nm}$ range. This indicates that light absorption by the porphyrinic moiety is responsible for the photocurrent generation. The quantum efficiency of the system was calculated to be 0.005% .³⁸

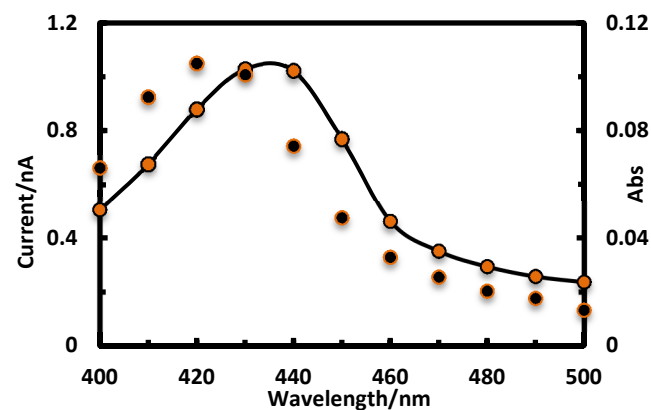


Fig. 10 Action spectrum for the photocurrent generation (black dots) and the absorption spectrum of **P1** on an ITO substrate (black solid line with orange dots)

Proposed polymerization mechanism

Cyclic voltammetry disclosed that **P1** is attached on electrode surfaces, Raman spectroscopy confirmed the presence of the azobenzene linkage in **P1**, and UV/vis absorption spectroscopy indicates that the porphyrinic moiety was preserved. These studies help us propose a possible polymerization mechanism (Scheme 1). The electrooxidation of **P1** leads to the formation of a reactive anilino radical form,³⁹ which can be applied for the modification of glassy carbon surface. In the case of ITO and SnO_2 , although the detail chemical structure is unclear, an electron pathway is formed via the possible interaction such as coordination bond and hydrogen bond. On the other hand, the growth of **P1** is provided by the coupling between two anilino radical species: One is tethered on the electrode surface, and the other is in the solution phase. The coupling results in the formation of a hydrazine linkage, which undergoes electrochemical oxidation to the azobenzene linkage. In fact, the repetitive cyclic voltammetry scan in Fig. 2 shows that the anodic peak current for the oxidation process is greater than the cathodic one. The additional anodic current corresponds the irreversible oxidation of the hydrazine linkage.

Conclusion

In summary, 5,15-di(4-aminophenyl)-10,20-diphenylporphyrinatozinc(II) monomer **1** was successfully electropolymerized on GC, ITO and SnO₂ electrodes to give porphyrin polymer **P1** tethered with azobenzene linkages. A possible oxidative polymerization mechanism involves the dimerization of **1** through the formation of an anilino radical form. The presence of azobenzene linkage in **P1** was confirmed by a series of electrochemical and spectroscopic studies. The polymer displays photocurrent generation ability.

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