論文の内容の要旨

One-dimensional Azobenzene- and Bis(dipyrrinato)zinc(II)-linked Porphyrinic Wires − Synthesis and Photofunctionality

(アゾベンゼンおよびビス(ジピリナト)亜鉛(II)が架橋した一次元ポルフィリンワイヤー −合成と光機能)

ムスタファル　スザリザ
MUSTAFAR SUZALIZA

Introduction

The macrocyclic porphyrin framework is chemically composed of four pyrroles connected by methine bridges, providing high thermodynamic and chemical stability and unique photophysical properties. Porphyrins also possess the ability to form complexes with assorted metal ions. These characteristics of porphyrins are advantageous to be utilized in numerous application areas like electronics, medicine, and catalysis. In particular, porphyrins are exceptionally utilized in optoelectronics and photovoltaics applications due to their versatility in light absorptions and redox activities. Moreover, owing to the excellent electron transfer abilities and the capabilities to acquire light in a wide wavelength region, porphyrins become eminent in light-induced electron donating systems such as photonic molecular wires, dye-sensitized solar cells and so forth. In my study in the Ph.D course, I investigated two methodologies to form π-conjugated porphyrinic wires with photofunctionality. I achieved a formation of linear azobenzene-bridged porphyrin polymers by electrooxidation of [5,15-Di(4-aminophenyl)-10,20-diphenylporphyrinato]zinc(II) and bis(dipyrrinato)zinc(II) porphyrin wire by metal complexation of [5,15-bis(3,5-dioctyloxyphenyl)-10,20-diphenylbis(dipyyrrin)porphyrinato]zinc(II)

Results and Discussion

Synthesis of one-dimensional azobenzene-linked porphyrinic wires.

Monomer **1** was synthesized according to previous literature studies with a few modifications. Three different electrodes, glassy carbon (GC), indium-tin oxide (ITO) and tin oxide (SnO_2) were employed in this study in order to investigate the capability of monomer **1** to immobilized on different surface nature. The film was characterized by means of electrochemistry, Raman, UV/vis and XPS while the functionality of porphyrinic polymer wire, **P1** was determined by judging the photoelectric conversion ability thru light irradiation. **P1** was synthesized through electrochemical oxidation of **1** by means of radical coupling reactions. Raman spectroscopy confirmed the presence of the azobenzene linkage in **P1**, and UV/vis spectroscopy

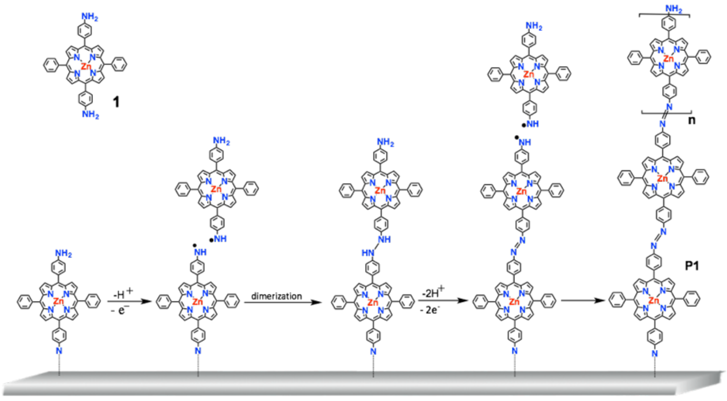

Figure 1. Plausible polymerization mechanism.

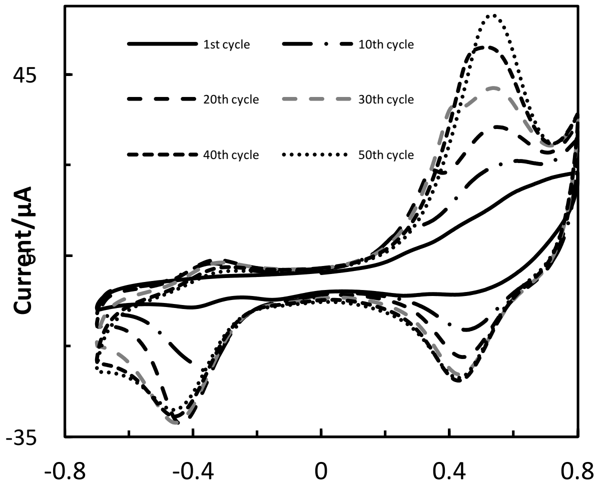

Figure 2. Cyclic voltammogram for **1** (2 mM) upon repetitive potential scans in 0.1 M Bu_4NClO_4-CH_2Cl_2 at GC

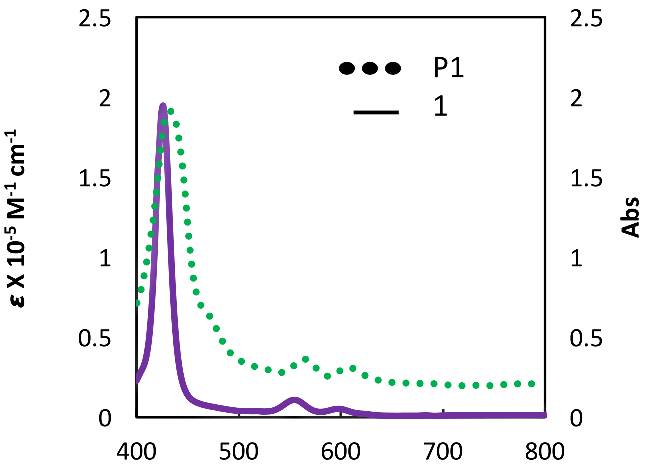

Figure 3. Absorption spectra of **1** in CH_2Cl_2 and **P1** on ITO.

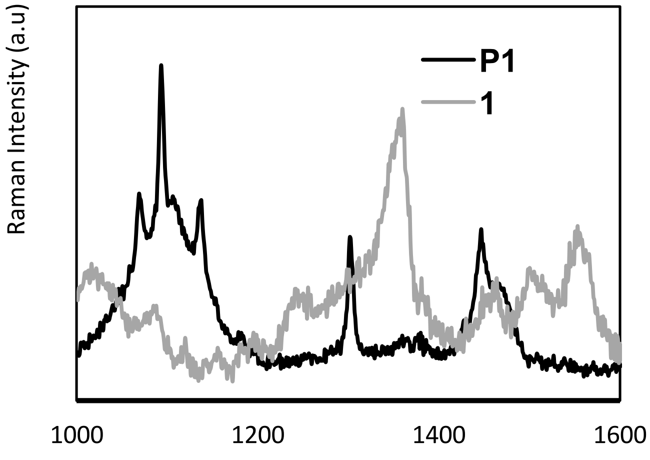

Figure 4: Raman spectra of **1** and **P1**

established no significant change of the porphyrinic moiety even after the electrooxidation. The polymerization mechanism is proposed to be started from the formation of a reactive anilino radical which generated by electrooxidation of monomer **1**. The growth of **P1** is enabled by the coupling between two anilino radical species (**Figure 1**). One of the anilino radicals is tethered on the electrode surface while the other will couple with another anilino radical in the solution phase. This coupling results in the formation of a hydrazine linkage, which further loses two protons to afford an azobenzene linkage.

In the cyclic voltammograms displayed in **Figure 2**, an anodic peak appeared at around 0.52 *vs.* Ag^+/Ag, indicating the oxidation of both amino group and porphyrin moiety. This interpretation is strongly supported by the disappearance of the shoulder peaks after the electropolymerization was completed. The current increases during electroplymerization demonstrate the formation and growth of an electroactive film on the GC surface. The **P1** practically displayed identical electrochemical behaviour to **P1** on GC when the electropolymerization was conducted on transparent electrodes such as ITO and SnO_2. The absoprtion spectra of **1** in dichloromethane and the **P1** film on ITO were measured and the results were carefully examined. Both spectra feature typical porphyrin absorption bands, whereas **P1** shows a slightly redshifted Soret band compared to **1** probably due to a longer π–conjugated chain in **P1** (**Figure 3**). From the absorption spectra, many information can be deduced such as the orientation of **P1** on ITO. **P1** is proposed to be perpendicular to electrode because the spectrum of **P1** does not show any characteristics derived from J- or H- conjugations. The presence of azobenzene linkage in **P1** was verified upon Raman spectoscopy (**Figure 4**). In addition to a common band at around 1460-1470 cm^{-1}, **P1** showed a characteristics band at 1446 cm^{-1}, whereas no band was detected in **1**. This band can be assigned to the strecthing vibration of the azo group. This finding strongly supports the hypothesis that the azobenzene linkage was generated upon the electrooxidative polymerization process.

By employing AFM and SEM, the morphology and thickness of **P1** were successfully figured out. The average thickness of **P1** was calculated to be 112 nm (**Figure 5**), while the surface coverage was 3.6×10^{-9} mol cm^{-2}, which was estimated from the average thickness and molecular size of **1**. In a SEM image, two distinguishable domains are clearly observed, indicating that the modification of ITO surface was successfully achieved.

As a functionality of **P1**, photoelectric conversion ability was examined by engaging the modified ITO as working electrode and triethanolamine as electron sacrificer. Upon irradiation with visible light to the working electrode applied with a bias potential (-0.22 V), the generation of an anodic current was detected as shown in **Figure 6**. The action spectrum of the photocurrent generation is coincident with the UV-vis absorption spectrum of **P1** thin films on an ITO modified electrode in the 400-500 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 0.04%.

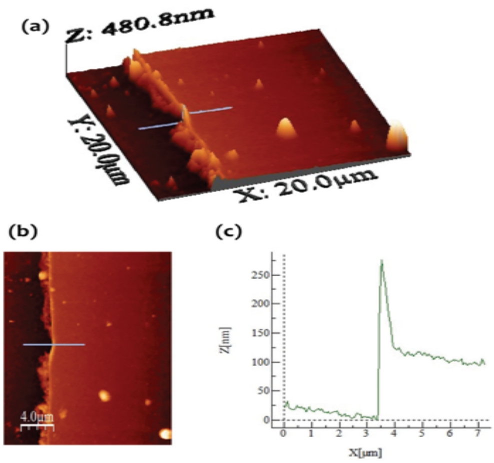

Figure 5: AFM height images.

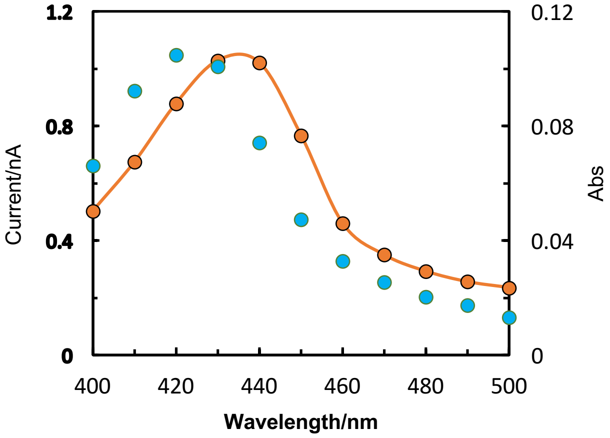

Figure 6: Action spectrum for photocurrent generation (green dots) and the absorption spectrum of P1 (orange solid line)

Synthesis of one-dimensional bis(dipyrrinato)zinc(II)-linked porphyrininc wires.

W2 was prepared by adding zinc(II) acetate solution in methanol to **M2** in chloroform. After that, the solution mixture was stirred for 30 hours at room temperature. The completion of the reaction was monitored by UV/vis spectroscopy.

The UV/vis absorption of **M2** and **W2** were measured and compared. In both spectra, typical porphyrin bands were recorded with Soret band maxima at ±428 nm. In **W2** spectrum, one additional absorption peak (493 nm) was observed which indicated the complexation between free base dipyrrin and zinc(II) ion. In fluorescence emission spectrum of **M2**, all the emission peaks were originally generated when poprhyrin moiety been excited. This happen because free dipyrrins generally emit very weak fluorescence. However, in **W2** spectrum, a

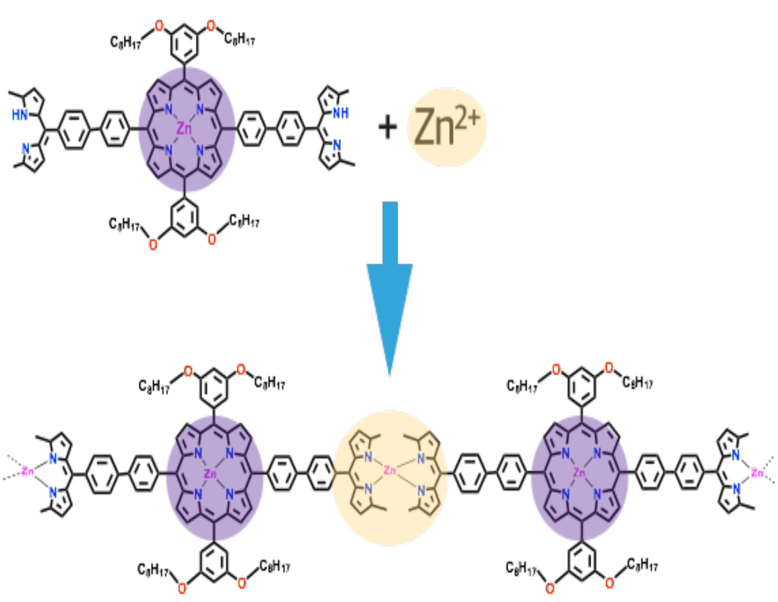

Figure 7: W2 preparing by complexation reaction

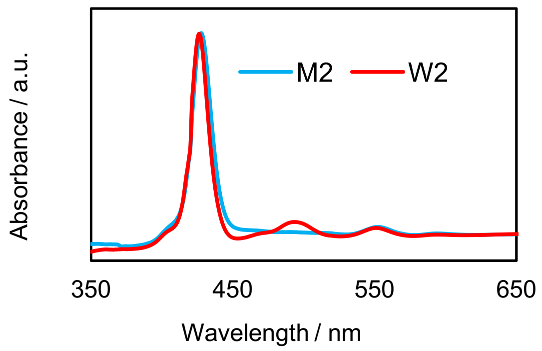

Figure 8: Absorption spectra of M2 and M2 in toluene

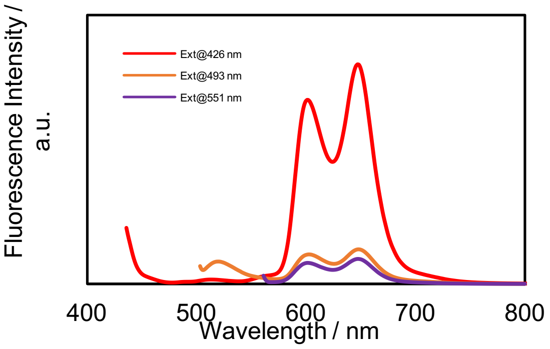

Figure 9: Fluorescence emission of W2 in toluene

fluorescence emission peak was recorded when **W2** solution was excited at 493 nm. Excited energy transfer had been observed from dipyrrin moiety to porphyrin moiety. This unique feature make **W2** as one of the possible candidates to be utilized in energy trasfer system such as in fabrication of photonic molecular wires.

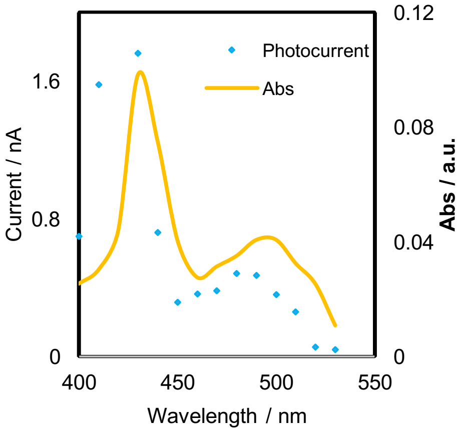

Figure 10: Action spectrum for photocurrent generation (blue dots) and the absorption spectrum of W2 (orange solid line)

The AFM measurement was conducted to study the physical properties such as height and length of **W2**. The topographic image of modified HOPG with dispersion of **W2**, displayed several white lines with the average height was 2.8 nm. This height was in good agreement with the size of **M2** estimated by DFT calculation.

The photofuctionality of **W2** was studied by engaging the modified SnO_2 with **W2** as photoanode. The measurement was conducted in aqueous solution due to good dispersibility of **W2** in many organic solvents. An anodic current was observed when the photoanode was irradiated by visible light. **Figure 10** shows an action spectrum for the photocurrent conversion, where the photoresponse spans were 400-550 nm. **W2** was found to exhibited better quantum yield, 0.19% which superior compared to **P1**(0.04%).

Conclusion

In summary, monomer **1** was succesfully electropolymerized on GC, ITO and SnO_2 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.On the other hand, another porphrinic wire was successfully prepared by complexation reaction between **M2** and metal cation. Both wires display photocurrent generation ability.

[Publication related to the thesis]

1. “Electrochemical fabrication of one-dimensional porphyrinic wires on electrodes” Suzaliza Mustafar, Kuo-Hui Wu, Ryojun Toyoda, Kenji Takada, Hiroaki Maeda, Mariko Miyachi, Ryota Sakamoto and Hiroshi Nishihara, *Inorg. Chem. Front.* **3**, 370-375 (2016).

[Publication not related to the thesis]

1. “Meso-N-arylamino- and N,N-diarylaminoporphyrinoids: Syntheses, properties and applications” Ryota Sakamoto, Suzaliza Mustafar and Hiroshi Nishihara, *J. Porphyr. Phthalocya.*, **19**, 1–11(2015).