Electrochromic Polymer Derived from Oxidized Tetrakis(2-hydroxyphenoxy) Phthalocyaninatocobalt(II) Complex

Mutsumi Kimura,* Takashi Horai, Kenji Hanabusa, and Hirofusa Shirai
Department of Functional Polymer Science, Faculty of Textile Science and Technology, Shinshu University, Ueda 386

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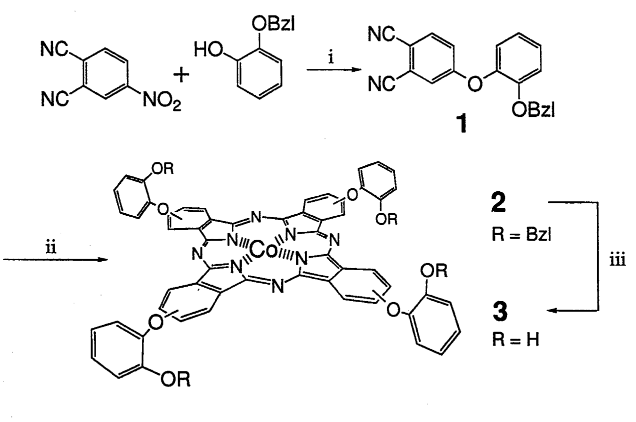
Tetrakis(2-hydroxyphenoxy)phthalocyaninatocobalt(II) complex **3** is synthesized and electrochemically polymerized to give polyphenyleneoxide films containing Co(II) phthalocyanine which exhibit an electrochromic behavior.

Metallophthalocyanines have been investigated in many fields including catalysts, liquid crystals, gas sensors, electronic conductivity, photosensitizers, nonlinear optics and electrochromic devices.[1] The preparation of the metallophthalocyanine thin film has also been investigated using several methods such as the Langmuir-Blodgget technique, vacuum sublimation, electrodeposition and electropolymerization.[2] The synthesis of low oxidation potential monomers containing metallophthalocyanine, which can undergo electropolymerization to obtain conducting and electroactive polymers, is expected to give new properties and new applications of metallophthalocyanine thin films. The faradic electrochromism in metallophthalocyanines has mainly been studied using the sandwich-type diphthalocyanine complexes of the lanthanide elements and cobalt phthalocyanine.[3] Herein, we report the synthesis of a new electroactive Co phthalocyanine with phenol groups together with the electropolymerization and an electrochromic property of the modified electrodes.

A new cobalt(II) phthalocyanine derivative **3** was synthesized as outlined in scheme 1. The reaction of 4-nitrophthalodinitrile with 2-benzyloxyphenol afforded **1** in 72% yield.[3] The complex **2** was prepared as follows; a mixture of anhydrous cobalt(II) chloride and **1** was heated in the presence of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) at 130 ℃ for 24 h (yield 46%). The purification of **2** was achieved by column chromatography. The cleavage of the benzyloxy group in **2** gave the complex **3** in 93% yield which was subsequently characterized by FT-IR, elemental analysis and UV-Vis spectroscopy.

The polymer film of **3** was electrochemically prepared on an indium tin oxide (ITO) coated glass upon repeated potential scans between -0.2 and +1.2 V *vs.* SCE at 100 mV s^{-1} in dry acetonitrile (MeCN) using tetrabutylammonium perchlorate (TBAP) as the electrolyte. Nitrogen was bubbled through the acetonitrile solution before electropolymerization. Figure 1 shows the polymer film growth multiple voltammograms obtained for **3**. The cyclic voltammogram shows an irreversible phenol oxidation peak at +0.58 V, a reversible phthalocyanine ring oxidation peak at +0.70 V, and a green fine polymer is deposited on the electrode's surface. In general, phenol and its derivatives can be oxidatively electropolymerized by scanning in the potential range between 0 and +1.2 V[4]. When the scan was limited to +1.0 V, a visibly rough and mechanically fragile film was deposited. Upon repeated scans, the relationship between peak currents and the number of scans in the cyclic voltammograms deviated from a straight line after 3 scans. This observation suggests an electron diffusion controlled process in the film due to the fast scan rate. Polymer film was washed with MeCN and placed in a monomer-free $NaBF_4$ aqueous solution for further investigation of their polymeric properties. The FT-IR spectrum polymer film containing Co phthalocyanine showed a strong signal at 1120 cm^{-1} corresponding to the formation of polyphenyleneoxide and disappearance of the peak at 3300 cm^{-1}, which is attributed to the phenol group in **3**. This change in the FT-IR spectra indicated that the phenol groups in **3** were polymerized onto the ITO glass by electrochemical oxidation.

The polymer exhibited two distinct redox processes with the first redox half wave potential of the polymer at -0.35 V and the second at -0.87 V *vs.* SCE (Figure 2). These two redox processes have a good reversibility, and the cyclic voltamogram was unchanged after 10 cycles. For the couple at -0.35 V, Co(II) phthalocyanine in the polymer undergoes a one-electron reduction



Scheme 1. Synthesis of phthalocyanine **3**. i)K_2CO_3, DMF, rt, 24 h. ii) DBU, $CoCl_2$, n-Pentanol, reflux,2 4 h. iii) HBr,CH_2Cl_2, rt,12 h.

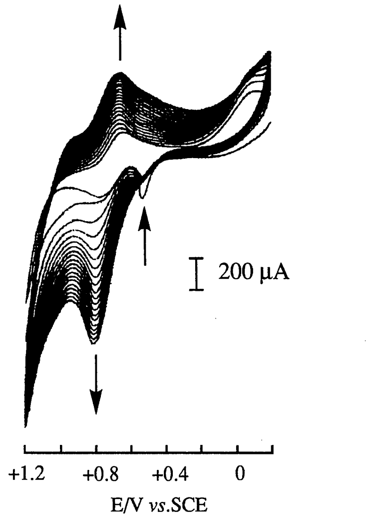


Figure 1. Repeated potential scanning electro-polymerization of **3** carried out 0.47 mmol dm^{-3} **3** in 0.1 mol dm^{-3} TBAP-MeCN.

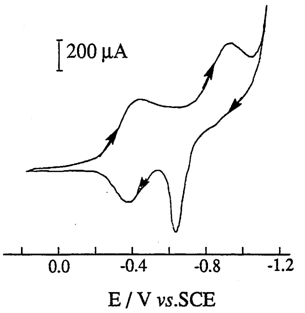


Figure 2. Cyclic voltammograms of **3** film on ITO glass (scan rate 100 mV s^{-1}, solvent 0.1 mol dm^{-3} $NaBF_4$ aqueous solution) .

to Co(I) phthalocyanine.[5] After the central metal reduction, the phthalocyanine ring was reduced at -0.87 V. The scan rate dependence of the peak current was probed and for each was found a linear relationship with the scan rate, indicative of an electrode supported electroactive film.

The optoelectrochemical properties of the polymer containing **3** were studied as a means of determining the condition of Co phthalocyanine in the thin film. The spectra of the film were recorded from 400 to 850 nm while incrementally stepping the potential to different redox states of the polymer as shown in Figure 3. The absorption spectra of **3** at 0 V gave a broad peak at 668 nm, which is attributed to Co(II) phthalocyanine.[6] Upon the decreasing of potential, a new absorption appears at 480 nm and the Q band is the red shifted form of Co(II) phthalocyanine. The increase in the absorption band around 480 nm and the red shift of the Q band suggests a one-electron reduction from Co(II) to Co(I), and the critical decreasing of the Q band above -0.8 V suggests a ring reduction of Co phthalocyanine in the film.[6] The polymer containing Co phthalocyanine is a transparent light green which gradually change to a yellowish green after the reduction of the central metal in Co phthalocyanine. At lower potentials, the polymer turns dark yellow due to the reduction of phthalocyanine ring. This color will remain until a potential change is induced, yielding an electrochromic memory.

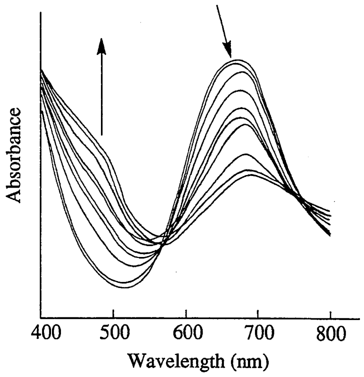


Figure 3. Optoelectrochemical analysis of **3** film in $NaBF_4$ aqueous solution; UV-vis spectra taken at 0, -0.1, -0.2, -0.3, -0.4, -0.5, -0.6, -0.7, -0.8, -0.9 and -1.0 V *vs*. SCE.
The arrows indicate the increase or decrease of the absorbance for the peaks during the coruse of the experiment.

In conclusion, a novel Co phthalocyanine with four phenol groups was synthesized and electrochemically polymerized to give polyphenyleneoxide films containing cobalt(II) phthalocyanine. The polymer film containing Co phthalocyanine showed an electrochromic behavior through two reduction processes of the central metal and phthalocyanine ring.

References

1 C. C. Lezmoff and A. B. P. Lever, Phthalocyanines, Properties and Applications, Vols. 1-3, VCH, New York (1989-1993).
2 M. T. Riou, M. Auregan, and C. Clarisse, *J. Electroanal. Chem.*,**187**, 349 (1985); A. W. Snow and N. L. Jarvis, *J. Am. Chem. Soc.*,**106**, 4706 (1984); T. Saji, K. Ebata, K. Sugawara, S. Liu, and K. Kobayashi, *J. Am. Chem. Soc.*, **116**, 6053 (1994); H. Li and T. F. Guarr, *J. Electroanal. Chem.*, **297**, 169 (1991); N. Kobayashi, H. Lam, W. A. Nevin, P. Janda, C. C. Leznoff, T. Koyama, A. Monden, and H. Shirai, *J. Am. Chem. Soc.*,**116**, 879 (1994).
3 F. Castaneda, C. Piechocki, V. Plichon, J. Simon, and J. Vaxiviere, *Electrochim. Acta*, **31**, 131 (1986); T. Fukuzawa, T. Koyama, G. Schneider, K. Hanabusa, and H. Shirai, *Inorg. Organomet. Polym.*, **4**, 261 (1994).
4 E. Tsuchida, H. Nishide, *Reactive Origomers*, ACS Symposium Series, (1985), *282*, chap. 8; K. Hanabusa, A. Nakamura, T. Koyama, and H. Shirai, *Polymer International*, **35**, 231 (1994).
5 M. J. Stillman and A. J. Thomson, *J. Chem. Soc., Faraday Trans., 2*, **70**, 790 (1974).
6 W. A. Nevin, W. Liu, and A. B. P. Lever, *Can. J. Chem.*, **65**, 855 (1986); W. A. Nevin, W. Liu, S. Greenberg, M. R. Hempstead, S. M. Maruccio, M. M. Melnik, C. C. Leznoff, and A. B. P. Lever, *Inorg. Chem.* **26**, 891 (1987).