

Electropolymerization of Bithienyl-appended Cerium(III) Triple Decker Porphyrin Complex

Kousei Yamashita, Masato Ikeda, Masayuki Takeuchi,* and Seiji Shinkai*

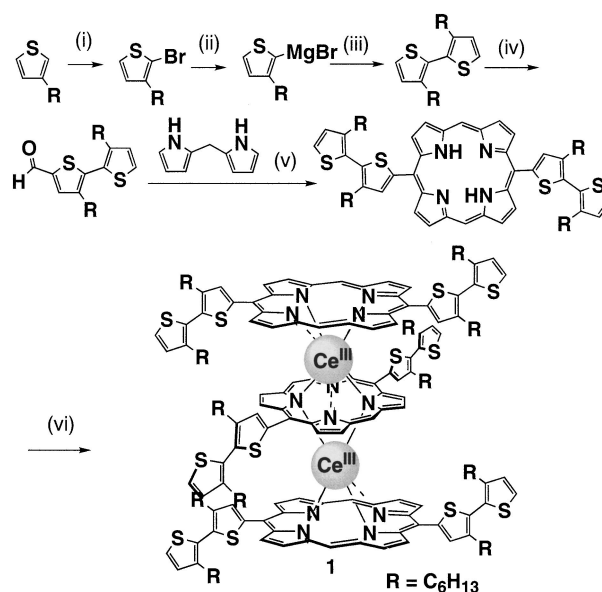
Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581

(Received December 16, 2002; CL-021065)

A cerium(III) triple decker porphyrin complex bearing bithienyl substituents (**1**) at the peripheral meso-positions was synthesized. Electrochemical polymerization of the triple decker porphyrin gave a unique polymer film on the ITO electrode surface without decomposition.

Electropolymerization of metal complexes has attracted much attention for applications to electroluminescent devices, sensors, and electrochromic coatings.¹ Since thiophene and oligothiophene derivatives can be easily oxidized because of their α, α' -coupling reactions, their electropolymerization has frequently been investigated.² Several groups have recently explored the electropolymerization of metal complexes incorporating oligothiophenyl substituents. Shimidzu et al. have investigated the electropolymerization of phosphorus(V) porphyrin bearing an axial oligothiophenylalkoxy ligand and metalloporphyrin bearing oligothiophenyl substituents at the meso-positions.³ Swager et al. have electropolymerized a number of metal-salen complexes bearing oligothiophenyl substituents.⁴ Shirai et al. and Swager et al. independently reported metalphthalocyanine bearing oligothiophenyl substituents.⁵ Our current interest is focused on the construction of supramolecular architectures based on lanthanoid metal double and triple decker porphyrin complexes, which are now considered to be a potential function unit for the construction of a multibit information storage system.^{6,7} Lanthanoid metal porphyrin complexes adopt double decker or triple decker type structures and possess multiple redox potentials.⁸⁻¹¹ Introduction of the lanthanoid metal porphyrin complexes to polymer architectures will, therefore, impart a variety of functions to the resultant polymers. Since these porphyrin units in the lanthanoid metal porphyrin complex would act as rotating pillars, one may expect that the resultant polymer matrixes should show the very unique superstructures as well as the redox potentials. Here we describe an electrochemical construction of a new triple decker porphyrin polymer film on the ITO glass electrode utilizing oxidative couplings between the bithienyl substituents, as a preliminary step toward constructing such a multibit information storage system.

The synthetic route of **1** is shown in Scheme 1. Bromination of 3-hexylthiophene using NBS in CHCl_3 -AcOH gave 2-bromo-3-hexylthiophene in 97% yield. The Grignard reagent prepared from 2-bromo-3-hexylthiophene was used for the subsequent coupling reaction with 2-bromo-3-hexylthiophene in the presence of Ni(dppp)Cl_2 as a catalyst to obtain 3,3'-dihexyl-2,2'-bithiophene (overall yield: 63%). Monoformylation of 3,3'-dihexyl-2,2'-bithiophene using POCl_3 /DMF (Vilsmeier reagent) gave 3,3'-dihexyl-5-formyl-2,2'-bithiophene in 71% yield.¹² 5,10-Bis(3,3'-dihexyl-2,2'-bithieno-5-yl)porphyrin was obtained from 3,3'-dihexyl-5-formylbithiophene and dipyrromethane using the method (TFA as an acid-catalyst and DDQ as an



Scheme 1. (i) NBS, CHCl_3 -AcOH, 97%, (ii) $\text{Mg/C}_2\text{H}_4\text{Br}_2$, Et_2O , (iii) 2-bromo-3-hexylthiophene, Ni(dppp)Cl_2 , Et_2O , 63%, (iv) POCl_3 /DMF, $\text{CH}_2\text{ClCH}_2\text{Cl}$, then NaHCO_3 , 71%, (v) TFA, CH_2Cl_2 , then DDQ, 28%, (vi) $\text{Ce(acac)}_3 \cdot 3\text{H}_2\text{O}$, 1,2,4-trichlorobenzene, 15%.

oxidant) described previously.¹³ Refluxing of the porphyrin ligand in 1,2,4-trichlorobenzene with $\text{Ce(acac)}_3 \cdot 3\text{H}_2\text{O}$ afforded a cerium(III) triple decker porphyrin **1** in 15% yield.^{8,11} Analytically pure **1** was obtained as a green solid by column chromatography (silica gel, eluent: chloroform and Bio-beads SX-3) and characterized by MALDI TOF MS, FAB-MS, and elemental analysis.¹⁴

The compound **1** was soluble in organic solvents such as CH_2Cl_2 , CHCl_3 , and hexane. The absorption spectrum of **1** in CH_2Cl_2 shows a π - π^* absorption band of bithienyl moieties at 334.0 nm, a Soret band at 405.0 nm, which was blue-shifted about 12.0 nm from that of free-base porphyrin (417.0 nm), and Q bands at 548.0 and 594.0 nm. The shape of the absorption spectrum was consistent with that of cerium(III) triple decker porphyrin reported previously.^{8,11} These spectral results indicate that there is no significant electronic interaction between porphyrin rings and bithienyl moieties in **1** at their ground states.

The cyclic voltammogram (CV) of **1** in CH_2Cl_2 revealed three separated redox waves (0.59, 0.89, and 1.20 V vs. Ag/Ag^+) in the first scan as shown in Figure 1 (bold line). The oxidation waves at 0.59 V and 1.20 V are assignable to the oxidation of cerium(III) triple decker porphyrin.⁸ The potential peak at 0.89 V is assigned to the oxidation of bithienyl moieties because this value is consistent with that for 5,10-bis(3,3'-dihexyl-2,2'-bithieno-5-yl)porphyrinato zinc(II) (0.82 V). Compound **1** was oxidatively polymerized (plain line in Figure 1) when the potential of the electrode was cycled between 0 and 1.4 V versus

the Ag/Ag⁺ couple at a scan rate of 50 mV/s (condition; working electrode: ITO glass electrode, counter electrode: Pt wire, reference electrode: Ag/Ag⁺, solvent: CH₂Cl₂, electrolyte: 0.1 mol dm⁻³ TBAPF₆). Poly(**1**) is highly crosslinked owing to the presence of the six unsubstituted sites on the terminal thiophenes that are active toward polymerization. Figure 1 shows a polymerization trace of **1**. The cycling of the electrode potentials results in the increase of electroactivity, indicating that insoluble polymer deposition on the electrode surface. Figure 1 (dashed line) shows the CV of the polymer film deposited on ITO glass electrode in TBAPF₆-CH₂Cl₂ in the absence of monomer **1**. Three characteristic redox waves (0.34, 0.79, and 1.20 V) were observed, which are attributed to cerium(III) triple decker porphyrin. These results demonstrate that the polymer film deposited on ITO glass electrode is comprised of cerium(III) triple decker porphyrins and has unique multiple redox potentials.

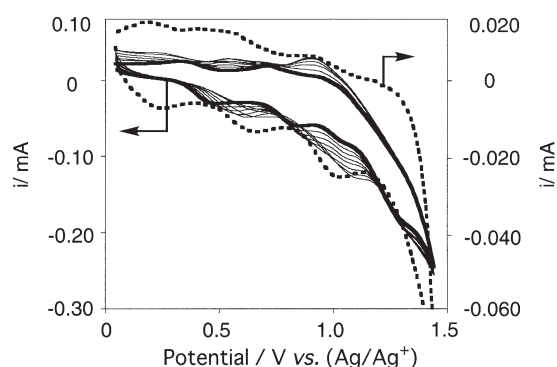


Figure 1. Cyclic voltammogram of **1** at the ITO electrode in 0.1 mol dm⁻³ TBAPF₆/CH₂Cl₂ solutions at a scan rate of 50 mV/s (plain line, the electroactivity of **1** increases during 15 cycles) and cyclic voltammogram of poly(**1**) (dashed line).

The absorption spectrum was measured for poly(**1**) film deposited on the ITO electrode (Figure 2). A sharp Soret band (409.0 nm) accompanied by a broad Q band (587.0 nm), which is characteristic for cerium (III) triple decker porphyrin, were observed.^{8,11} These spectral data firmly established that the polymer film of cerium(III) triple decker porphyrin (poly(**1**)) on ITO glass electrode has been obtained by the oxidative electropolymerization without decomposition.

In conclusion, we have demonstrated a new synthetic strategy for constructing a polymer film of cerium(III) triple decker porphyrin, which has multiple redox potentials, on the ITO

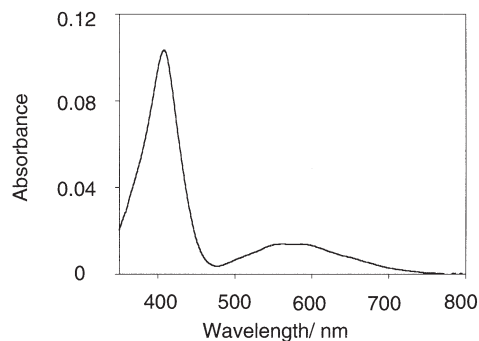


Figure 2. The absorption spectrum of poly(**1**) film deposited on the ITO electrode.

electrode utilizing electro-oxidative polymerization of dithienyl substituents in **1**. Further investigation into the redox or photophysical properties of the polymers will lead to more interesting applications.

References and Notes

- a) M. O. Wolf, *Adv. Mater.*, **13**, 545 (2001). b) M. O. Wolf and Y. Zhu, *Adv. Mater.*, **12**, 599 (2000). c) R. P. Kingsborough and T. M. Swager, *Prog. Inorg. Chem.*, **48**, 123 (1999). d) A. Deronzier and J. C. Moutet, *Coord. Chem. Rev.*, **147**, 339 (1996).
- a) "Handbook of Conducting Polymers," ed. by T. A. Skotheim, R. L. Elsenbaumer, and J. R. Reynolds, Marcel Dekker, New York (1998). b) R. D. McCullough, *Adv. Mater.*, **10**, 93 (1998). c) J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
- a) H. Segawa, N. Nakayama, and T. Shimidzu, *J. Chem. Soc., Chem. Commun.*, **1992**, 784. b) H. Segawa, F. P. Wu, N. Nakayama, H. Maruyama, S. Sagisaka, N. Higuchi, M. Fujitsuka, and T. Symidzu, *Synth. Met.*, **71**, 2151 (1995). c) T. Shimidzu, *Synth. Met.*, **81**, 235 (1996). d) T. Shimidzu, H. Segawa, F. Wu, and N. Nakayama, *J. Photochem. Photobiol., A*, **92**, 121 (1995).
- a) R. P. Kingsborough and T. M. Swager, *Adv. Mater.*, **10**, 1100 (1998). b) R. P. Kingsborough and T. M. Swager, *J. Am. Chem. Soc.*, **121**, 8825 (1999).
- a) T. Muto, T. Temma, M. Kimura, K. Hanabusa, and H. Shirai, *Chem. Commun.*, **2000**, 1649. b) T. Muto, T. Temma, M. Kimura, K. Hanabusa, and H. Shirai, *J. Org. Chem.*, **66**, 6109 (2001). c) R. P. Kingsborough and T. M. Swager, *Angew. Chem., Int. Ed.*, **39**, 2897 (2000).
- M. Ikeda, A. Sugasaki, Y. Kubo, K. Sugiyasu, M. Takeuchi, and S. Shinkai, *Chem. Lett.*, **2001**, 1266.
- a) S. Shinkai, M. Ikeda, A. Sugasaki, and M. Takeuchi, *Acc. Chem. Res.*, **34**, 494 (2001). b) M. Takeuchi, M. Ikeda, A. Sugasaki, and S. Shinkai, *Acc. Chem. Res.*, **34**, 865 (2001). c) M. Takeuchi, T. Imada, and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, **37**, 2096 (1998). d) M. Takeuchi, T. Imada, and S. Shinkai, *Tetrahedron Lett.*, **39**, 7897 (1998). e) M. Ikeda, M. Takeuchi, A. Sugasaki, A. Robertson, T. Imada, and S. Shinkai, *Supramol. Chem.*, **12**, 321 (2000). f) M. Ikeda, T. Tanida, M. Takeuchi, and S. Shinkai, *Org. Lett.*, **2**, 1803 (2000). g) A. Sugasaki, M. Ikeda, M. Takeuchi, and S. Shinkai, *Angew. Chem., Int. Ed. Engl.*, **39**, 3839 (2000). h) A. Sugasaki, K. Sugiyasu, M. Ikeda, M. Takeuchi, and S. Shinkai, *J. Am. Chem. Soc.*, **123**, 10239 (2001). i) M. Ikeda, M. Takeuchi, S. Shinkai, F. Tani, Y. Naruta, S. Sakamoto, and K. Yamaguchi, *Chem.—Eur. J.*, **8**, 5541 (2002).
- a) J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus, and R. Weiss, *J. Am. Chem. Soc.*, **108**, 3652 (1986). b) D. K. P. Ng and J. Jiang, *Chem. Soc. Rev.*, **26**, 433 (1997). c) J. W. Buchler and D. K. P. Ng, in "The Porphyrin Handbook," ed. by K. M. Kadish, K. M. Smith, and R. Guilard, Academic Press, San Diego (2000), Vol. 3, Chap. 20 and references cited therein.
- Photo- and redox-driven ligand rotational activities of cerium(IV) double decker porphyrin complexes have been investigated by Aida et al.; a) K. Tashiro, K. Konishi, and T. Aida, *Angew. Chem., Int. Ed. Engl.*, **36**, 856 (1997). b) K. Tashiro, T. Fujiwara, K. Konishi, and T. Aida, *Chem. Commun.*, **1998**, 1121. c) K. Tashiro, K. Konishi, and T. Aida, *J. Am. Chem. Soc.*, **122**, 7921 (2000).
- a) T. Gross, F. Chevalier, and J. S. Lindsey, *Inorg. Chem.*, **40**, 4762 (2001). b) D. Gryko, J. Li, J. R. Diers, K. M. Roth, D. F. Bocian, W. G. Kuhr, and J. S. Lindsey, *J. Mater. Chem.*, **11**, 1162 (2001). c) T. F. Magnera, L. M. Peslherbe, E. Körblóvá, and J. Michl, *J. Organomet. Chem.*, **548**, 83 (1997).
- H. Miwa, N. Kobayashi, K. Ban, and K. Ohta, *Bull. Chem. Soc. Jpn.*, **72**, 2719 (1999).
- a) F. Würthner, M. S. Vollmer, F. Effenberger, P. Emele, D. U. Meyer, H. Port, and H. C. Wolf, *J. Am. Chem. Soc.*, **117**, 8090 (1995). b) M. S. Vollmer, F. Würthner, F. Effenberger, P. Emele, D. U. Meyer, T. Stümpfig, H. Port, and H. C. Wolf, *Chem.—Eur. J.*, **4**, 260 (1998).
- Q. M. Wang and D. W. Bruce, *Synlett*, **1995**, 1267.
- 1**: Mp; 144.2–148.6 °C, GPC (TSKgel G3000H-TSKgel G4000H, CHCl₃, 0.50 mL/min, monitored at 400 nm) retention time 34.7 min, MALDI TOF MS (CHCA) *m/z* 3198.58 ([M+H]⁺ = 3198.12), FAB MS *m/z* 3198.12 ([M+H]⁺ = 3198.1167), UV-vis (CH₂Cl₂): λ_{max} (log ε) 334.0 (4.80), 405.0 (5.48), 548.0 (0.91), 594.0 (0.91), Calcd. for Ce₂C₁₈₀H₂₀₄N₁₂S₁₂·0.5CHCl₃: C, 66.49; H, 6.33; N, 5.16%; Found: C, 66.61; H, 6.63; N, 4.83%.