Electrochemical Synthesis of One-dimensional Donor–Acceptor Polymers containing Oligothiophenes and Phosphorus Porphyrins

Hiroshi Segawa, Norihiro Nakayama and Takeo Shimidzu*

Division of Molecular Engineering, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

Novel porphyrin polymers linked in the axial direction, which have an alternating one-dimensional structure of oligothiophene (electron donor) and P^V porphyrin (electron acceptor), have been synthesized by the electrochemical polymerization of symmetrical P^V porphyrin triads with two oligothiophene moieties.

The construction of molecular systems containing multiple redox centres has been an important subject in the realization of molecular electronic devices.[1] With such objectives in mind, several donor–photosensitizer–acceptor triad molecules, have been synthesized and investigated in photoinduced electron transfer reactions.[2] In order to construct such molecules as large molecular systems, one feasible approach is based on the appropriate incorporation of the photosensitizer and a suitable electron donor and/or acceptor into a polymeric chain.[3] However, the production of such types of polymers containing a number of large aromatic moieties or metal complexes is difficult because of their intractable solubility and flexibility properties, limiting the possibilities for controlled fabrication on terminal electrodes. In order to overcome these difficulties, electrochemical polymerization is considered to be useful, since the polymer will be directly deposited on the terminal electrode. With this in mind, we have synthesized symmetrical donor–acceptor–donor triad molecules which can be polymerized by the normal electrochemical oxidation to form novel one-dimensional donor–acceptor polymers.

In our study, oligothiophenes, which can be easily dimerized by electrochemical oxidation, were used as electron donors and coupling elements.[4] For the efficient photoinduced electron transfer from the oligothiophene donors, the photosensitizer should have strong electron accepting properties. Additionally, in order to inhibit defects in the polymer chain, the photosensitizer should be stable to the electrochemical oxidation conditions. For these reasons, P^V porphyrins, which have strong oxidizing powers and are stable to oxidation, were used as the photosensitizer.[5] P^V porphyrins can form two stable axial bonds on the central phosphorus atom.[6] As a consequence of this stable bond formation, P^V porphyrin derivatives having two axial oligothiophene moieties can be synthesized easily. After their polymerization, novel face-to-face porphyrin polymers separated by ordered oligothiophene units should be obtained. This led us to synthesise the three triad molecules **1**, **2** and **3**.

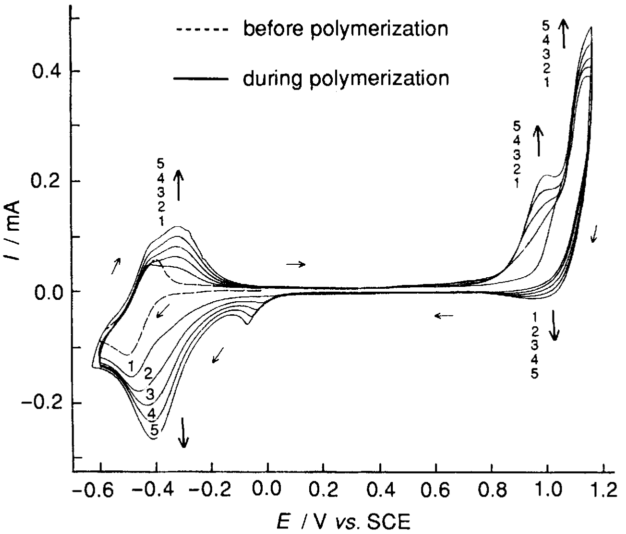


Fig. 1 Cyclic voltammogram for the electrochemical polymerization of **3**. Broken line: before polymerization; full lines: during polymerization. Numbers on curves are scan numbers.

Oligothiophenemethanols were synthesized *via* formylation by Vilsmeier reaction of corresponding oligothiophenes and followed by chemical reduction using $NaBH_4$ by a literature method.[7] Thiophene-2-methanol (Wako) was used as received. The P^V porphyrin derivatives **1**, **2** and **3** containing two thienylalkoxy or oligothienylalkoxy groups at the axial positions of the central phosphorus atom were synthesized by the reaction of the dichloro P^V tetraphenylporphyrin[5d] and the corresponding thienyl or oligothienyl alcohols at 90 °C for 3 h.

The ^1H NMR, ^{31}P NMR, IR and mass spectra of **1**, **2** and **3** confirmed that the two equivalent alkoxy groups are attached to the central phosphorus atom at its fifth and sixth coordination positions.† The triad molecules **1**, **2** and **3** have normal P^V porphyrin absorption spectra together with thienyl or oligothienyl absorptions (Table 1). Although all the derivatives have similar fluorescence originating from the P^V porphyrin, the life-time and the relative quantum yield of the fluorescence depended on the axial substituents (Table 1); the fluorescence was strongly quenched in **2** and **3** compared with diethoxy P^V tetraphenylporphyrin (τ = 4.4 ns) without the thienyl moieties.[6] The fluorescence quenching shows the occurrence of photoinduced electron transfer from the oligothienyl moieties to the P^V porphyrin unit of **2** and **3**.

The P^V porphyrin derivatives **2** and **3** were polymerized by electrochemical oxidation [working electrode, indium–tin oxide (ITO); counter electrode, platinum; reference, standard calomel electrode (SCE); solvent, 0.1 mol dm^{-3} $Bu^n{}_4NBF_4$ in MeCN], whereas **1** was scarcely polymerized. Fig. 1 shows the cyclic voltammogram for the electrochemical polymerization of **3**. As the results for the electrochemical oxidation of **2** and **3**, poly-**2** and poly-**3** were deposited on the ITO electrode at potentials > 1.2 and 0.9 V *vs.* SCE, respectively. At the same time, the peak currents around −0.4 V *vs.* SCE assigned to the redox reaction of the P^V porphyrin moieties were increased, indicating the deposition of the porphyrin polymer on the

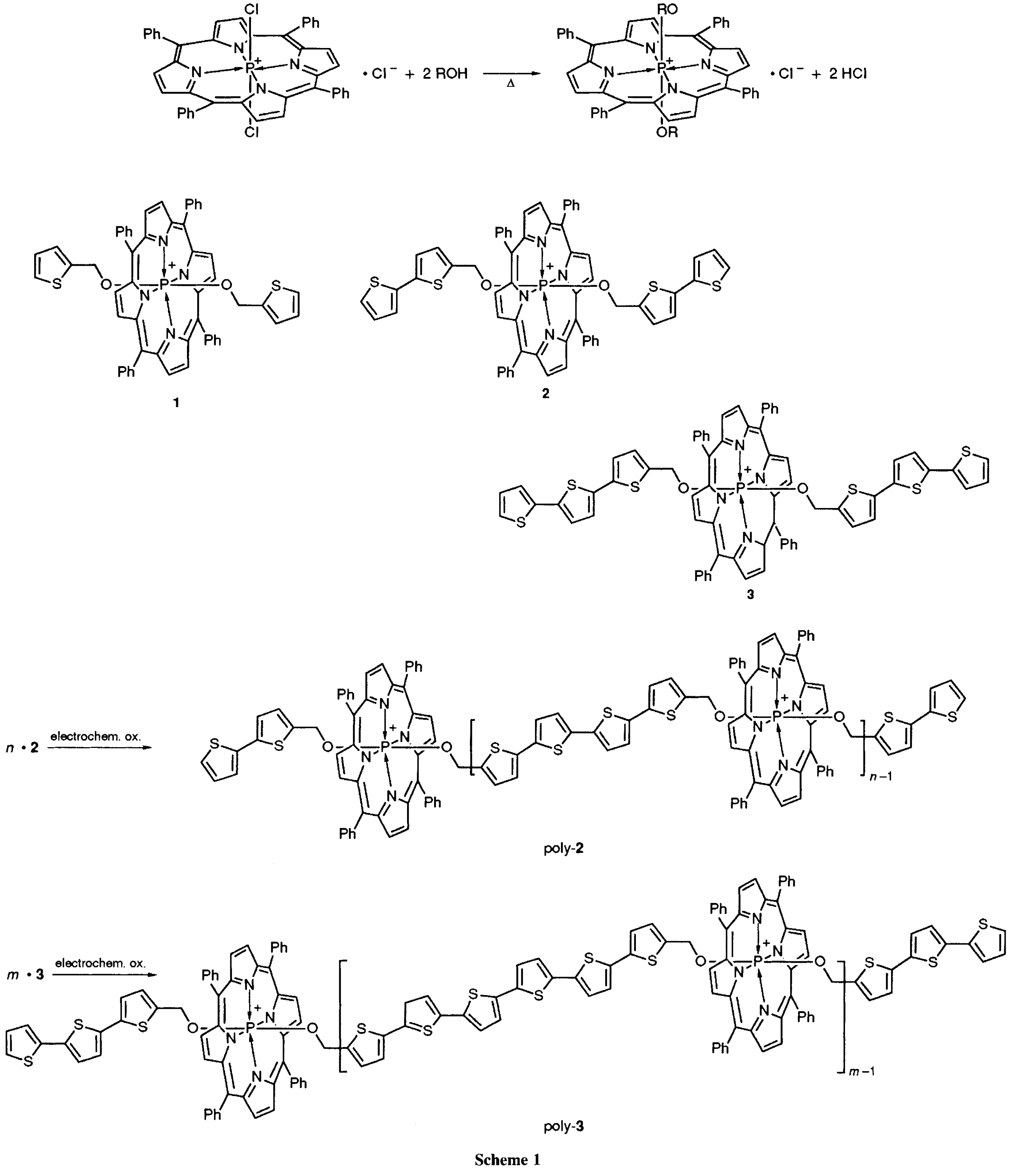
---

† ^1H NMR ($SiMe_4$), ^{31}P NMR (85% H_3PO_4, external), IR (ν/cm^{-1}) and mass (parent peak) data of the obtained derivatives are as follows. **1**: ^1H NMR, δ 9.08 (d, 8H, pyrrole-β), 7.77 (m, 20H, phenyl), 6.45 (dd, 2H, thienyl), 6.09 (dd, 2H, thienyl), 4.81 (dd, 2H, thienyl), −1.13 (d, 4H, CH_2); ^{31}P NMR, δ −182.5; IR, 1021 (P=O), 840 and 853 (C–H out-of-plane, thienyl-α); MS, *m/z* (M^+) 869. **2**: ^1H NMR, δ 9.10 (d, 8H, pyrrole-β), 7.75 (m, 20H, phenyl), 7.04 (dd, 2H, bithienyl), 6.78 (dd, 2H, bithienyl), 6.56 (dd, 2H, bithienyl), 6.15 (d, 2H, bithienyl), 4.69 (d, 2H, bithienyl), −1.15 (d, 4H, CH_2); ^{31}P NMR, δ −182.1; IR, 1021 (P=O), 840 (C–H out-of-plane, terminal thienyl-α); MS *m/z* (M^+) 1033. **3**: ^1H NMR, δ 9.11 (d, 8H, pyrrole-β), 7.77 (m, 20H, phenyl), 6.90–7.26 (m, 6H, terthienyl), 6.85 (d, 2H, terthienyl), 6.47 (d, 2H, terthienyl), 6.15 (d, 2H, terthienyl), 4.70 (d, 2H, terthienyl), −1.17 (d, 4H, CH_2); ^{31}P NMR, δ −182.1; IR, 1023 (P=O), 856 (C–H out-of-plane, terminal thienyl-α); MS *m/z* (M^+) 1197. The phosphorus–proton couplings, the strong ring current shifts and the integrated intensities of the ^1H NMR spectral data of axial substituents imply that the two equivalant (oligo)thienyl groups are attached to the central phosphorus atom at the fifth and sixth coordination positions. The ^{31}P NMR data of **1**–**3**, which are in the range typical of six-coordinate phosphorus compounds,[8] also supports such structures. The parent mass spectral peaks coincided with the expected molecular mass of the derivatives without counter ion.

Table 1 Absorption and emission properties of bis(thienylalkoxy)- and bis(oligothienylalkoxy)-phosphorus(v) porphyrin triad molecules in MeCN

	Absorption λ_{max}/nm				Fluorescence			
	Axial group	Soret	Q(1,0)	Q(0,0)	λ_{max}/nm		τ/ns[a]	Φ_f
1	232	430	559	599	613	668	4.1	2.7×10^{-2}
2	310	428	558	600	615	668	<0.5	5.1×10^{-4}
3	357	431	561	604	622	673	0.8	3.9×10^{-3}

[a] The life-time of the fluorescence of diethoxy P^V tetraphenylporphyrin which has no thienyl group is 4.4 ns in MeCN.



Scheme 1

electrode. In the case of poly-**3**, a new anode peak (1.0 V *vs.* SCE) assigned to the oxidation of sexithiophene formed by the coupling reaction of the axial substituents was generated. In the absorption spectra of the polymer obtained, the UV absorptions assigned to the bithiophene (310 nm) and terthiophene (357 nm) moieties of the starting monomers completely disappeared. Additionally, the IR absorption spectra of C–H out-of-plane vibrations at α-positions of the terminal thiophene units of the axial substituents (**2**: 840, **3**: 856 cm^{-1}) disappeared on polymerization at the α-position. Consequently, it was concluded that the polymers obtained are one-dimensional polymers with an alternating structure of the P^V porphyrin and oligothiophene moieties as shown in Scheme 1.

Interestingly, the conductivity of poly-**2** and poly-**3** was strongly enhanced by the photoirradiation.‡ It is suggested that photoinduced carrier formation occurs efficiently in the donor–acceptor polymers. In the present preliminary study, we have found not only appreciable photoconductivity but also nonlinear optical properties of the polymers obtained.

This work was partially supported by a Grant-in-Aid for Scientific research on New Programme (03NP0301) from the Ministry of Education, Science, and Culture of Japan. This work was also funded in part by photo science and technology foundation.

Received, 9th March 1992; Com. 2/01259F

References

1 J. Simon, F. Tournilhac and J.-J. Andrè, *New J. Chem.*, 1987, **11**, 383; C. E. D. Chidsey and R. W. Murray, *Science*, 1986, **231**, 25; M. S. Wrighton, *Science*, 1986, **231**, 32.

2 M. R. Wasielewski, *Photoinduced Electron Transfer*, ed. by M. A. Fox and M. Chanon, Elsevier, 1988, part A, p. 161 and references cited therein; T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth and A. L. Moore, *Nature*, 1984, **307**, 630.

3 J. J. Hopfield, J. N. Onuchic, and D. N. Beratan, *Science*, 1988, **241**, 817.

4 G. Tourillon, *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, 1986, vol. 1, 293 and references cited therein.

5 (*a*) P. Sayer, M. Gouterman and C. R. Connell, *J. Am. Chem. Soc.*, 1977, **99**, 1082; (*b*) C. J. Carrano and M. Tsutsui, *J. Coord. Chem.* 1977, **7**, 79; (*c*) C. A. Marrese and C. J. Carrano, *J. Chem. Soc., Chem. Commun.*, 1982, 1279; (*d*) C. A. Marrese and C. J. Carrano, *Inorg. Chem.*, 1983, **22**, 1858; (*e*) C. A. Marrese and C. J. Carrano, *Inorg. Chem.*, 1984, **23**, 3961.

6 H. Segawa, K. Kunimoto, A. Nakamoto and T. Shimidzu, *J. Chem. Soc., Perkin Trans. 1*, in the press.

7 A. M. Eachern, C. Soucy, L. C. Leitch, J. T. Arnason and P. Morand, *Tetrahedron*, 1988, **44**, 2403; T. B. Patrick, and J. L. Honegger, *J. Org. Chem.*, 1974, **39**, 3791.

8 *Multinuclear NMR*, ed. by J. Mason, Plenum Press, 1987, 369.

---

‡ The conductivity of the polymers in the dark was 1.2×10^{-9} S cm^{-1} for poly-**2** and 5.1 ^{1} 10^{-8} S cm^{-1} for poly-**3**. In both polymers, the conductivity was strongly enhanced by the photoirradiation. In the case of photoirradiation by 500 W Xe lamp through UV and IR cut-off filters (Toshiba, L39 and IR25S) with a water jacket, the enhancement was greater than threefold. Of course, the enhancement depends on the light intensity, and becomes larger by irradiation with a strong light source.