

Synthesis of Covalently-linked Linear Donor-Acceptor Copolymers Containing Porphyrins and Oligothiophenes

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A series of monomers of 5,15-dithienyl porphyrin, 5,15-di-bithienyl porphyrin and their metal complexes were synthesized in high yields. 5,15-Di-bithienyl porphyrin and its metal complexes were polymerized by chemical oxidation using FeCl_3 as oxidant (>90%) for making organic conductor and the linear porphyrin-thiophene copolymers were obtained. The structures of the copolymers were identified by elemental analysis and IR spectra. The conductivity of poly 5,15-di-bithienyl porphyrin was measured to reach over 10^{-6} S/cm. 5,15-Dithienyl porphyrins and its metal complexes could not be polymerized under the similar conditions, but could be polymerized by electrochemical oxidation on the gold-plate electrode.

Keywords organic conductor, thienylporphyrin, porphyrin-thiophene copolymer, electropoly merization, chemical oxidation

The construction of macro-molecular system containing multiple redox centers or photosensitizers is an important subject in the design of molecular electronic devices.^{1,2} For such objectives, systematization of donor-redox center-acceptor triad molecules into large molecular systems is one of the most feasible approaches, because the exquisite incorporation of the photosensitizers and suitable electron donors and/or acceptors into a polymeric chain is useful for various molecular electronic systems.³⁻⁵ Thiophenes and oligothiophenes, which can be easily dimerized by chemical and electrochemical oxidation, are both electron donors and coupling elements.⁶ Porphyrins are stable enough to not only the chemical and electrochemical oxidation but also redox centers and photo-sensitizers. Some net-like porphyrin-thiophene copolymers and linear ones in which porphyrins are connected with axial oligothieryl substituents have been prepared,^{7,8} but their conductivities are not very good. This led us to synthesize the symmetrical donor-acceptor-donor triads (thienylporphyrins and their metal complexes), and further to polymerize them to form the novel linear donor-acceptor copolymers by chemical and electrochemical oxidation. The synthetic processes are summarized in Scheme 1.

Dipyrrylmethane (**1**) and bithienylaldehyde (**3**) were synthesized according to the method we previously described.⁹ The free base porphyrins (**6** and **7**, yield: 45.1% and 61.2%, respectively) were obtained by oxidation of the corresponding porphyrinogens (**4** and **5**), which were prepared from the reaction of **1** with thienylaldehyde (**2**) or **3** catalysed by trichloroacetic

acid or trifluoroacetic acid, respectively in dry acetonitrile under Argon atmosphere with 2,5-dichloro-3,6-dicyano-1,4-benzoquinone (DDQ) in THF. Their metal complexes were prepared by heating the free base porphyrins with the corresponding metal acetates in chloroform at reflux and the yields of them were very high (>90%).

The copolymers of **12**, **13** and **14** were synthesized by chemical polymerization using FeCl_3 as oxidant from corresponding monomers **7**, **10** and **11** in high yields (>90%). The elemental analysis results of the copolymers were similar to their monomers, showing that the polymers and the monomers have the similar structures. In their IR spectra, the vibration absorptions of saturated C—H (about 290 cm^{-1}), porphyrin ring (about 1050 cm^{-1}), N-metal (about 1005 cm^{-1}) and thienyl ring (about 690 cm^{-1}) were visible, indicating that the thienyl porphyrins were the basic units of the polymers. Additionally, the absorption bands of C—H out-of-plane vibrations at α -position of the terminal thiophene group (**7**: 845 cm^{-1} , **10**: 848 cm^{-1} , **11**: 840 cm^{-1}) disappeared after the monomers were polymerized, indicating that the thienyl groups were oxidized to link each other to form the linear covalently-linked porphyrin-thiophene copolymers.¹⁰

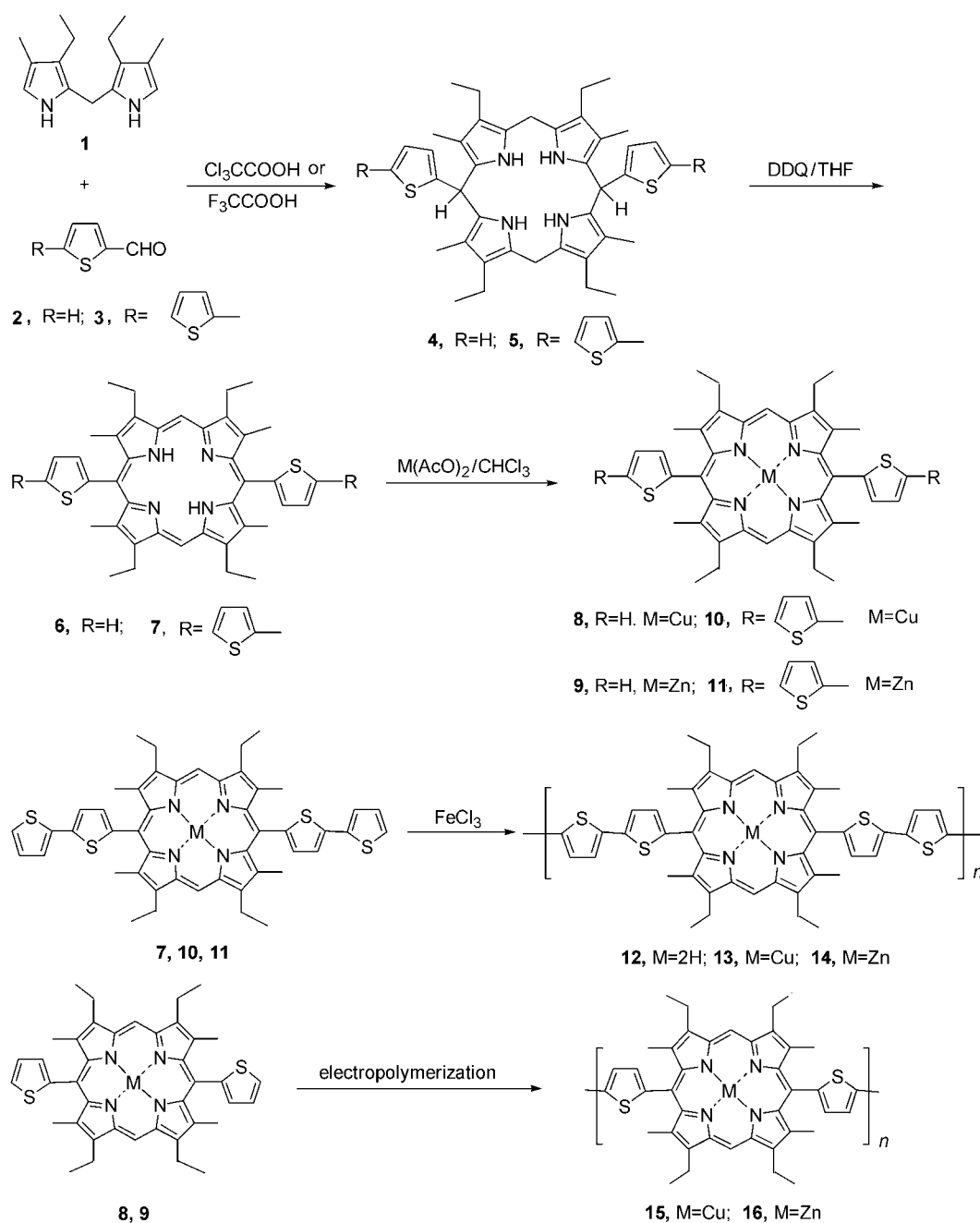
As the copolymers **12**, **13** and **14** were prepared, they were doped with FeCl_3 directly. The conductivity of copolymer **12** doped with FeCl_3 was over 10^{-6} S/cm, which was higher than that of other porphyrin-thiophene copolymers prepared by Shimidzu.^{6,7,10} The higher conductivity may be due to the better conjugation

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Scheme 1



between the thienyl group and the porphyrin ring. Compared to the octaethylporphyrin, the big red-shift of the solet absorption (30 nm) of the thienylporphyrins indicated that the conjugation system of the porphyrins was expanded largely by the thienyl and bithienyl substituents. And this expansion accelerated the energy and electron transfer between the porphyrin and oligothiophene units.

The thienylporphyrins (**6**, **8** and **9**) could not be polymerized by chemical oxidation due to the effect of the steric hindrance. Compounds **8** and **9** were polymerized by the electrochemical oxidation (working electrode: gold-plate electrode; counter electrode: platinum; reference: standard calomel electrode SEC; solvent: 0.1

$\text{mol}\cdot\text{dm}^{-3}$ $n\text{-Bu}_4\text{NClO}_4$ in dry MeCN), whereas **6** could not be polymerized for its very low solubility in common organic solvents. Figures 1 and 2 show the cyclic voltammograms for the electro-polymerization of **8** and **9**, respectively. After the electrochemical oxidation of **8** and **9**, their polymers **15** and **16** were deposited on the surface of the gold-plate electrode at the potentials >1.1 and 0.9 V vs. SCE, respectively. At the same time, the peak currents around 1.1 and 0.9 V, assigned to the coupling reaction of the thienyl groups at the meso-position of the porphyrins, were increased with the increase of the scan number, indicating that the deposition of the porphyrin-thiophene copolymers on the electrode formed the conductive film. In addition, in the case of

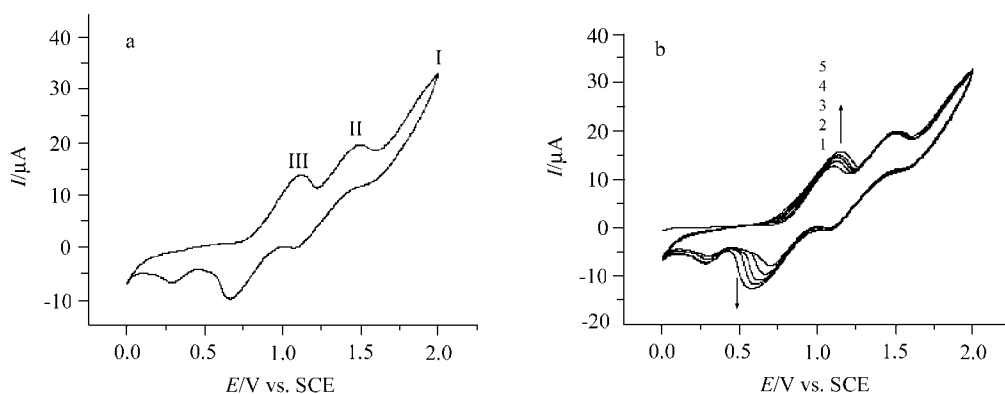


Figure 1 Cyclic voltammogram of **8** (numbers on curves are scan numbers, a: before polymerization; b: during polymerization).

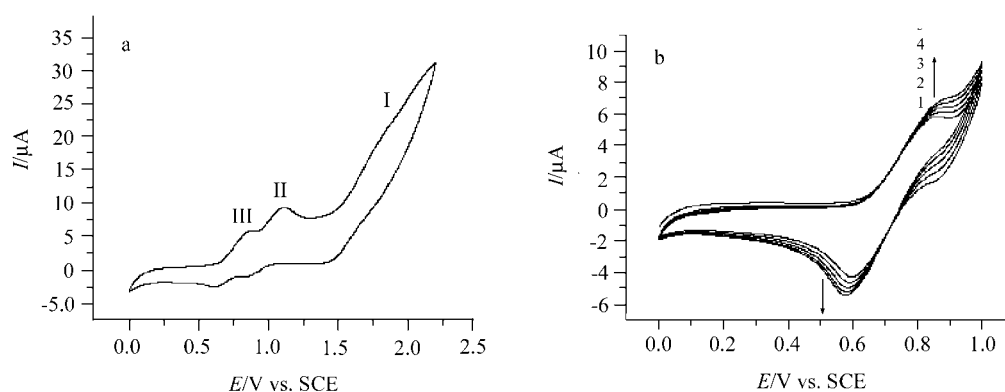


Figure 2 Cyclic voltammogram of **9** (numbers on curves are scan numbers, a: before polymerization; b: during polymerization).

15, the peak currents assigned to the oxidation of the porphyrin (peaks I and II) formed by losing one and two electrons of the porphyrin ring were not increased, which meant that the porphyrin ring was stable when the thienyl groups were oxidized to link each other. Consequently, it was concluded that the polymers obtained on the electrode were one-dimensional polymers with an alternating structure of the porphyrin and bithiophene moieties shown in Scheme 1.

In summary, 5,15-di-bithienyl porphyrin and its metal complexes can be polymerized to give the linear porphyrin-tetrathiophene copolymers by chemical oxidation using FeCl_3 as oxidant. Although 5,15-dithienyl porphyrin and its metal complexes could not be polymerized by the chemical oxidation, the metal complexes were polymerized by electrochemical oxidation on the gold-plate electrode to offer the porphyrin-bithiophene copolymers. The conductivity of poly 5,15-di-bithienyl-2,8,12,18-tetraethyl-3,7,13,17-tetramethyl porphyrin doped with FeCl_3 was over 10^{-6} S/cm which was in the range of semiconductor.

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