

**Unusual electrochemical response of oligoalkylthiophene films:
involvement of bipolarons**

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Abstract

Cyclic voltammograms of π -conjugated oligoalkylthiophene (13T) films are found to show two oxidation peaks during the 1st potential cycling up to 0.8 V. In the subsequent cycles, however, the 2nd oxidation peak disappears completely and the 1st peak shifts by ca. 0.1 V to the cathodic direction. This finding along with spectroscopic measurements of 13T film before and after electrochemical stimulus suggest first that two different phases to be oxidized at separate potentials coexist in a pristine 13T film and second that one phase can be switched to the other by being oxidized to generate bipolarons.

Introduction

Recently, π -conjugated oligothiophenes have received much attention because of not only useful model compounds for better understandings of electric and optical properties of the corresponding conducting polymers, but also their possible applications in the optoelectronics such as light emitting diode and photoelectric conversion, and field effect transistor [1-5]. A number of physicochemical studies have been conducted on oligothiophenes and oligoalkylthiophenes in solution. However, very little is known about electrochemical properties in their solid-state [6-10]. In the present study, electrochemical and optical properties of thin films of oligoalkylthiophene consisting of 13 thienylene units are investigated to clarify the solid-state natures of the π -conjugated oligomer. It is revealed that a change in conformation of the oligomer chain is induced by electrochemical generation of bipolarons and this conformational change governs electrochemical and optical properties of the 13T films.

Results and discussion

Thin films of oligoalkylthiophene (13T), shown in Fig. 1, were prepared by a spin coating at 3000 rpm on Au-coated glasses or ITO electrodes using different concentrations of 13T in chloroform. Fig. 2 shows CV curves of a pristine 13T film obtained during the 1st and 2nd potential cyclings between -0.1 and 0.8 V. A pristine 13T film clearly shows two oxidation peaks of similar heights at 0.4 and 0.73 V, being accompanied with one broad reduction peak at 0.52 V and almost combined two reduction peaks (curve a). In the 2nd and subsequent potential cyclings, the 2nd

oxidation peak disappears completely, and the 1st peak gains its height and shifts to the cathodic direction (curve b). It is worthy to note here that the 1st redox wave for the pristine film was quite stable during many cycles so far as the potential was cycled in the range up to 0.6 V. By comparing these redox potentials with those for a series of monosilanylene-oligothienylene copolymers [11], it is inferred that the 2nd oxidation step is ascribable to the generation of bipolarons on oligoethienylene units whose effective π -conjugation length is much shorter than a full conjugation unit of 13T, or rather close to a half of 13T. Furthermore, the negative shift of the redox potential suggests that the 13T film after bipolaron generation consists of more extensively conjugated oligoethienylene units than the one before bipolaron formation.

Absorption and fluorescence spectra of the 13T film measured before and after electrochemical stimulus beyond ca. 0.7 V are depicted in Fig. 3. A pristine 13T film exhibits a broad absorption band at 450 nm (2.78 eV) with two side peaks at 550 and 600 nm (curve a). The energy difference of the two peaks is 0.19 eV, in good agreement with those for equally-spaced three side peaks observed with polycrystalline thin films of quaterthiophene, sexithiophene, and octithiophene [12]. Correspondingly, a fluorescence spectrum of the pristine films shows a main peak at 620 nm and a few satellite peaks on the long wavelength side (curve a'). After the 13T film experiences the potential stimulus at 0.7 V, the absorption spectrum changes its feature completely (curve b) like the change in shape of CV curves: two side peaks disappear and a single broad absorption band at 475 nm (2.63 eV) similar in shape to the one for 13T in chloroform (curve c) gains its height. Likewise, the fluorescence spectrum shows a broad band at 610 nm with a slight structure on the low energy side (curve b'). Fichou et al. have concluded that 1) the absorption side peaks are ascribable to a coupling of

the π - π^* transition with vibrational levels of the excited state, 2) the vibronic contributions are characteristic of the quasi-planar and rigid-rod conformation of α -oligothiophenes in the solid state, and 3) the conformation is determined by intermolecular interactions. On these bases together with electrochemical data, one can presume that the extension of the π -conjugation length induced by bipolaron formation accompanies a change from a quasi-planar to a non-planar conformation of the 13T oligomer.

By summarizing the above discussions, a tentative structure model is proposed for 13T oligomers in the solid state before and after bipolaron formation (Scheme 1). In the pristine 13T film, the 13T oligomer in the neutral state is twisted along the main chain at the center of the oligomer and the half of the nearby 13T oligomer is stacked by ring-ring interactions to give a somewhat planar conformation (Scheme 1a). In this quasi-planar conformation, the 13T film has a redox nature similar to the one for the 6T film and exhibits side peaks in the absorption spectrum due to intrachain vibronic contribution. When the 13T film is oxidized at potentials beyond 0.7 V, bipolarons are generated on the 6T units of the 13T oligomers. When bipolarons having planar quinoid structures are formed on the 6T units, the quinoid structure tends to extend over the full unit of the 13T oligomer and consequently the twisted conformation breaking π -conjugation at the center of 13T is dissolved. As a result, the resulting 13T oligomers would have full conjugation lengths. This conformational change is irreversible, so that the 2nd oxidation peak observed with the pristine film disappears in the subsequent cycles. The 13T oligomers in the resulting films interact to a lesser extent with each other and show optical features characteristic of non-planar oligomers (Scheme 1b). In addition, the neutral 13T film is subject to a redox reaction at less

positive potentials than the pristine film because of the extension of the π -conjugation length from 6T to 13T.

Experimental

All electrochemical measurements were performed with a three-electrode system consisting of Ag/Ag⁺ and Pt wire as the reference and counter electrode, respectively. Cyclic voltammograms were recorded in MeCN/Et₄NClO₄ (0.1M) solutions using a Hokuto Denko HAB-151 potentiostat equipped with a function generator. In-situ absorption spectra were recorded on a Shimadzu UV-3101PC spectrophotometer, and fluorescence and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer.

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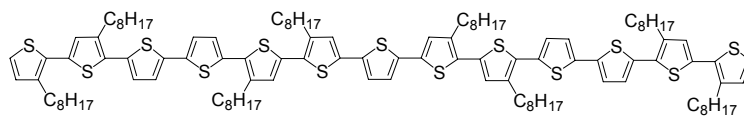


Fig. 1 Molecular structure of oligoalkylthiophene (13T).

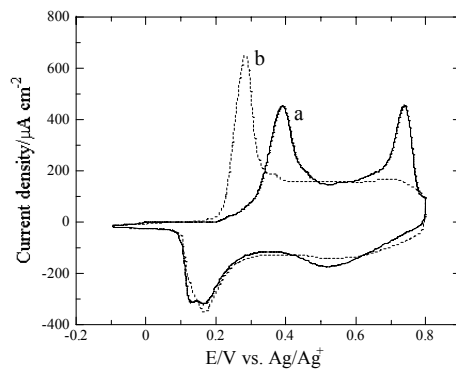


Fig. 2 Cyclic voltammograms of a 13T film. Curves a) and b) are obtained during the 1st and 2nd cycles, respectively.

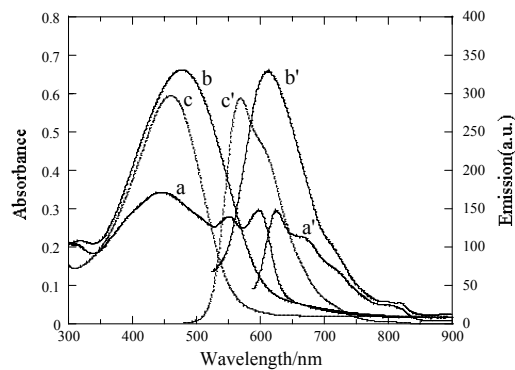
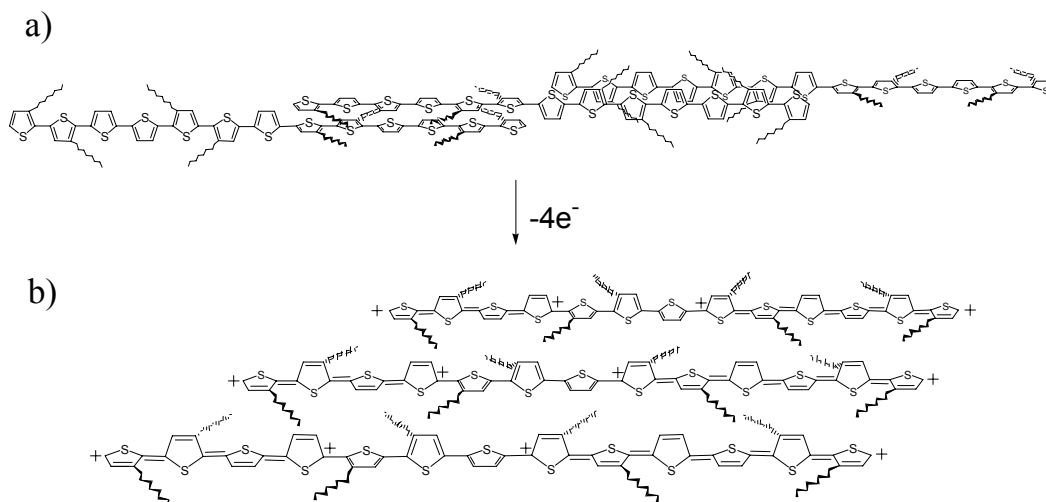


Fig. 3 a), b) Absorption and a'), b') emission spectra of a 13T film on ITO substrate a), a') before and b), b') after application of potential. c) Absorption and c') emission spectra of 13T in chloroform.



Scheme 1 Conformational models proposed for 13T oligomers in a) phase I and b) phase II.