Futurum
Tsukuba Science Journal

Conductive Polymer

Electrochemical preparation of poly(1,3-dinaphthyl isothianaphthene)

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ABSTRACT

Isothianaphthene is one of the promising monomer units of conjugated polymers because of isothianaphthene based polymers show small bandgap. In this research, isothianaphthene based new monomer unit was synthesized. Theoretical discussion of the monomer unit with density functional theory was carried out. Electrochemical polymerization of the monomer yielded electroactive polymer thin films. UV-vis optical absorption spectra and electron spin resonance evaluated optical bandgap and magnetic property of the resultant piolymer. Bandgap of the polymer was to be 1.58 eV.

Keywords: bandgap, isothianaphthene, electrosynthesis.

Introduction

Recently, researches on low-bandgap polymers and applications have been carried out [1,2]. Thiophene based conjugated polymers have been received much attention for applications possibility. Polythiophene have bandgap to be 2.0-2.2 eV [3]. Conjugated polymer materials based organic electric luminescence devices (OEL) emit light in visible range.

Polyisothianaphthene (Figure 1) is a unique conjugated polymer because the dedoped form has small bandgap of 1.0 eV [4,5], and the doped form shows doping band at infrared region, resulting colorless. Film forming property and stability against oxidation of oxygen in the air are important issue to overcome for applications [6,7].

In this study, new monomer based on isothianaphthene is synthesized, and polymerized with electrochemical method [8-10]. Sandwich cell electropolymerization method which we developed allows liquid crystal electrochemical polymerization and liquid crystal magnetic electrochemical polymerization [11-13]. Isothianaphthene was prepared with previous reported method [14].

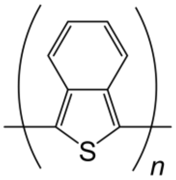

Figure 1. Chemical structure of polyisothianaphthene.

Experimental

Material

Tetrabutylammonium perchlorate (TBAP), 1-bromonaphthol, hydrazine anhydrous, tetrakis(triphenylphosphine)palladium(0), propylene carbonate, trimethylstannyl chloride and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine were purchased from Tokyo Chemical Industry, Toyo, Japan, and used as received.
Ethanol, dichloromethane, hexane, ethyl acetate, tetrahydrofuran, *n*-butyllithium in hexane and diethyl ether were purchased from Nacalai Tesque, Kyoto, Japan, and used as received. Toluene was

purchased from Nacalai tesque, Kyoto, Japan, and purified by distillation.
1,2-Bischloromethylbenzene and sodium periodate were purchased from Aldrich, United States, and used as received. Sodium sulfide nonahydrate, magnesium sulfate, sodium hydrogen carbonate and aluminum oxide powder were purchased from Wako Chemical, Tokyo, Japan, and used as received.

Monomer synthesis

1,3-Dihydro-benzo[*c*]thiophene (1).

Sodium sulfide nonahydride (26.14 g, 109 mmol) was added in ethanol (250 mL)/distilled water (50 mL) and dissolved with stirring. 1,2-Bischloromethylbenzene (12.31 g, 70.3 mmol) was added through a soxhlet extractor and the mixture was refluxed at 110 °C. After evaporation of the solvent, the residual tan-colored oil was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate. Evaporation of the solvent *in vacuo* gave a yellow solid (8.55 g, 62.7 mmol, yield = 89.7 %). ^{1}H-NMR (TMS (ppm), CDCl3): δ 4.27 (s, 4H, $-CH_2-$), 7.18–7.27 (m, 4H, 3,4,5,6-*H*).

1,3-Dihydro-benzo[*c*]thiophene 2-oxide (2).

Sodium periodate (13.7 g, 64.0 mmol) was dissolved in distilled water (177 mL). Compound 1 (8.55 g, 62.7 mmol) was dissolved in ethanol (213 mL). The ethanol solution was dropping into water solution at 0 °C with vigorous stirring. After stirring for 3 h at room temperature, a white inorganic salt in the solution was filtered off. After evaporation of the solvent, the residual oil was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate. Recrystallization with hexane and diethyl ether afforded colorless crystal (4.23 g, 28.2 mmol, yield = 45.0 %). ^{1}H-NMR (TMS (ppm), CDCl3): δ 4.16 (d, 2H, C–*H*), 4.30 (d, 2H, C–*H*), 7.31–7.34 (m, 2H, 4,5-*H*), 7.38 (dd, 2H, 3,6-*H*).

1,3-Di(trimethylstannyl)isothianaphthene (3).

Compound 2 (1.51 g, 9.90 mmol) and aluminum oxide powder (2.41 g, 23.6 mmol) were mixed and finely crushed in a mortar. Sublimation of the mixture under reduced pressure and gradually heating at 110 °C gave isothianaphthene (**4**) as a white solid (0.302 g, 2.25 mmol). Freshly sublimated compound 4 (0.302g, 2.25 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (0.660 g, 5.68 mmol) were dissolved in THF (6.6 mL) under an argon atmosphere.
15 % *n*-butyllithium in hexane (3.4 mL, 5.70 mmol) was added slowly to the mixture at −78 °C. the mixture was stirred vigorously at room temperature for 1 h. The mixture was cooled to −78 °C again, and a solution of trimethylstannyl chloride (1.15 g, 5.77 mmol) in THF (6.6 mL) was added to the mixture. The mixture was slowly warmed up to room temperature and stirred for 12 h. The mixture was poured into a saturated sodium hydrogen carbonate aqueous solution and separated. The aqueous layer was extracted with ether twice and the combined organic layer was dried over magnesium sulfate. After evaporation of the solvent, recrystallization from petroleum ether (30–70 °C) gave a pale yellow solid (0.667 g, 1.45 mmol, yield = 14.6 %). ^{1}H-NMR (TMS (ppm), CDCl3): δ 0.49 (s, 18H, $-CH_3$), 7.07 (dd, 2H, 5,6-*H*), 7.67 (dd, 2H, 4,7-*H*).

1,3-Dinaphthyl isothianaphthene (5, DN-ITN)

Compound 4 (115.0 mg, 0.25 mmol), 1-bromonaphthol (231.3 mg, 1.12 mmol) and tetrakis(triphenylphosphine) palladium (0) ($Pd(PPh_3)_4$) (0.023 g) were added to toluene (2 mL), and the mixture was refluxed at 90 °C under an argon. After 24 h, the solution was extracted with dichloromethane and water. The organic layer was dried over magnesium sulfate. Evaporation of the solvent *in vacuo* afforded a crude product. The crude product was purified by silica gel column chromatography (eluent: hexane/ethyl acetate = 1/1) to afford a reddish brown solid (23.4 mg, 0.061 mmol, yield = 24.2 %). ^{1}H-NMR (TMS (ppm), CDCl3): δ 7.17 (t, 2H), 7.25 (t, 2H), 7.33 (t, 2H), 7.53–7.60 (m, 4H), 7.76–7.83 (m, 4H), 7.93 (dd, 2H), 8.22 (dd, 2H).

Electropolymerization

DN-ITN as a monomer and TBAP as a supporting salt were dissolved in propylene carbonate. The electrolyte solution was injected into sandwiched cell consisting with indium tin oxide glass electrode and Teflon spacer [12]. Direct current of 4.0 V was applied to the electrolyte for 10 min. After electropolymerization, the cell was disassembled and washed with THF and hexane. The polymer film poly(DN-ITN) has been prepared on ITO glass.

Result and discussion

DFT calculation

Electronic and conformational details of the DN-ITN were obtained with density functional theory (DFT) calculations. Electric charge distribution model is shown Figure 2(a). This result indicates propagation positions of the monomer in the electropolymerization. Possible polymer structure according to the charge distribution was shown in Figure 2(b). Figure 2(c,d) revealed highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) models of the DN-ITN monomer from the DFT calculation.

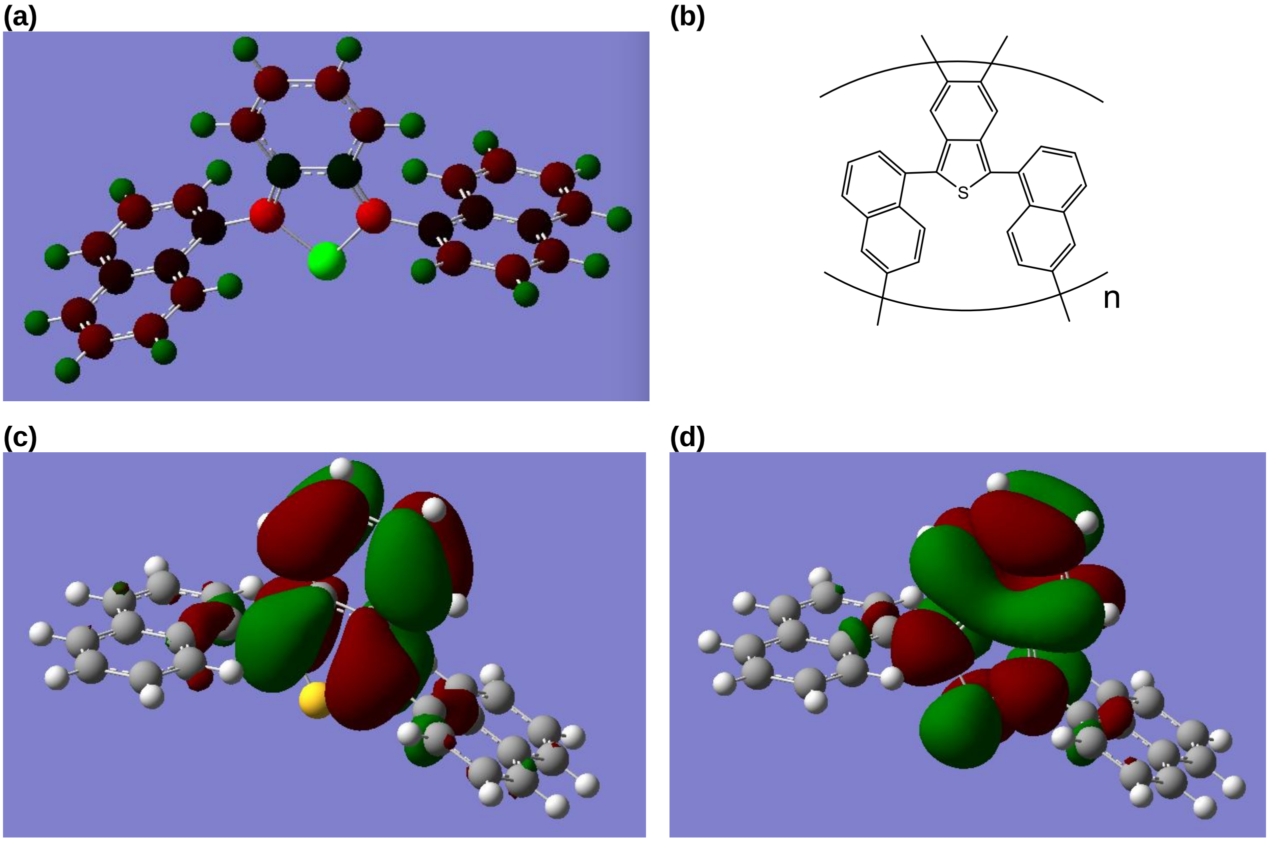

Figure 2. Density functional theory (DFT) calculations of DN-ITN: (a) electronic and conformational model, (b) possible polymer structure, (c) HOMO, (d) LUMO.

UV-vis absorption spectra

Optical bandgap can be obtained by UV-vis absorption spectra [4]. UV-vis optical absorption spectra of poly(DN-ITN) were measured, Figure 3. As prepared polymer film was oxidized in the electro-chemical process. The broad absorption bands derived from polarons and bipolarons in the oxidized polymer were observed at >900 nm. Reduced state poly(DN-ITN) film was obtained by treatment with hydrazine vapor. The reduced state film shows no absorption band at long wavelengths because the polarons and bipolarons bands were disappeared by the hydrazine reduction. Both the oxidized and the reduced forms show $\pi-\pi^*$ transition of the main chain. The polymer shows characteristic absorption bands at 400 nm and 450 nm. Bandgap energy of polymer can be calculated from band edge of the $\pi-\pi^*$ transition of the main chain in the reduced state [4]. Figure 4 shows absorbance as a function of photon energy (eV), indicating bandgap of the polymer is to be 1.58 eV. This bandgap value can be improved compared with 2.0 eV of polythiophenes reported in the previous research [15].

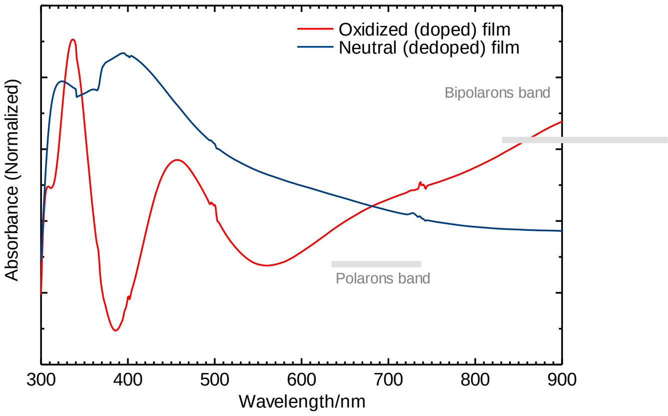

Figure 3. UV-vis absorption spectra of poly(DN-ITN).

Low-bandgap copolymer

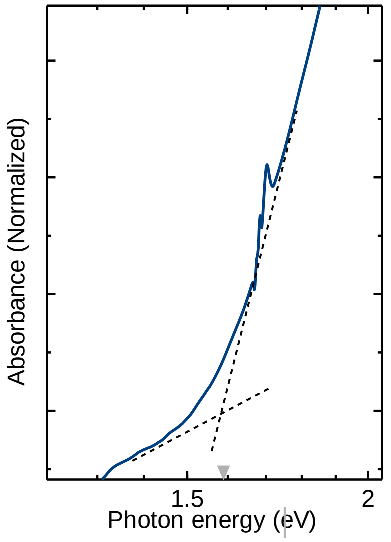

Figure 4. Band-gap energy of poly(DN-ITN).

Electron spin resonance

Magnetic property of poly(DN-ITN) is obtained with electron spin resonance (ESR) spectroscopy measurement. The ESR observes unpaired electron as a radical of polarons.

Reduced state of poly(DN-ITN) was peeled off from the ITO glass and set in the ESR tube. The samples were measured every 5 min after iodine addiion to carrie out in-situ ESR measurements with iodine vapor doping. No ESR signal was observed at 0 min because of undoped, indicating the polymer is conmpletely dedoped by the hydrazine vapor before the iodine doping, Figure 5. After the doping (> 5 min), unpaired electron density was rapidly increased due to progress of the doping for poly(DN-ITN), which generated polarons as radical cations in the main chain. Subsequently, the ESR intensity was slowly decreasing. This is because occurance of transition of polarons to bipolarons (dications) by the heavy doping.

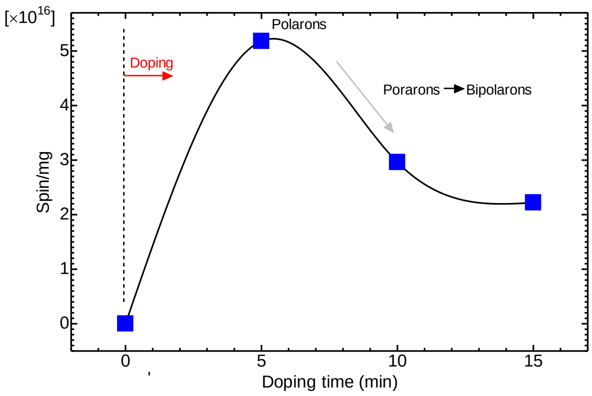

Figure 5. In-situ electron spin resonance (ESR) spectroscopy measurements of the polymer with iodine vapor doping.

Conclusions

Isothianaphthene combined with naphthyl unit was synthesized. DN-ITN as a monomer was polymerized with electrochemical method. Resultant polymer thin film was obtained on ITO glass. Optical absorption and electron spin resonance measurements reveal the oxidation (doping) process. Bandgap energy of poly (DN-ITN) in the neutral state is to be 1.58 eV.

Acknowledgments

This research was supported by Chemical Analysis Division Research Facility Centre for Science and Technology of University of Tsukuba.

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Received: 6 January, 2018.
Accepted: 12 January, 2018.

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