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Benzo[*b*]trithiophene Polymer Network Prepared by Electrochemical Polymerization with a Combination of Thermal Conversion

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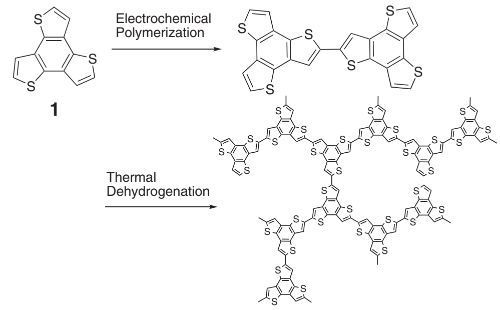
A two-step procedure of two-dimensional polymer constructed from benzo[*b*]trithiophene (BTT) was proposed by electrochemical polymerization and thermal conversion. Electropolymerized BTT oligomer on an electrode was thermally converted to conjugated polymer. Obtained conductive material is found to retain BTT structure by Raman spectra and to extend π conjugation by absorption spectra.

Organic semiconductors are key materials for future electronic devices.[1,2] Conjugated polymers which are one-dimensional π-conjugated materials have many advantages offering light, thin, and flexible devices with low cost compared with inorganic semiconductors. Extension of π conjugation in these materials from one dimension (1D) to two dimensions (2D) might provide high carrier mobility. Construction of 2D molecular networks has been extensively investigated in recent years.[3] Examples are self-organization of benzo[*b*]trithiophene–tricarboxylic acid,[4] condensation of 1,4-phenylenediboronic acid,[5] metal-surface-catalyzed homocoupling of diiodobenzene[6] and hexaiodocyclohexa-*m*-phenylene.[7] These examples utilize the reactions of assembled precursor molecules on a surface to form a 2D system. Although these examples provide well-organized structure on surfaces, π conjugation of these examples is not fully developed.

Polythiophenes are known to have a well-established 1D π-conjugated system.[8] We previously reported electrochemical epitaxial polymerization, which is the molecular-scale polymerization of monomers along the atom-lattice of substrate, to produce highly ordered polythiophene wires with a length of 100 nm on iodine-modified Au(111).[9,10] 2D materials are desired to be fabricated on electrode using this electrochemical technique. Thiophene-based molecules, which possesses C_3 symmetry such as benzo[*b*]trithiophene (BTT **1**)[11–13] are candidates as a precursor to form a well-developed 2D π-conjugated thiophene network by the polymerization reaction. There is only a report with regard to the electropolymerization of BTT using cyclic voltammetry on a Pt disc or ITO electrode, showing instability of electropolymerized BTT from the results of oxidation potential varied with repeated scans.[13] However, the detailed features of these compounds are unknown.

In this letter, a two-step method to produce 2D conjugated polymer network on substrate, electropolymerization of BTT to form oligomers with combination of thermal conversion into 2D polymers is reported (Scheme 1). An advantage of electropolymerization is to form BTT oligomers adsorbed onto electrode surface. Formed BTT oligomers have a higher sublimation temperature than that of monomer because the monomer sublimates at temperature of 200 °C with an atmospheric pressure of nitrogen (Supporting Information[14]). Therefore, thermal treatment around 500 °C in order to develop further conjugation by a dehydrogenation reaction can be applied to BTT oligomers as a second step. Heating at near 400–500 °C is reported to be suitable for dehydrogenation to produce graphene nanoribbon in ultrahigh vacuum conditions.[15]



Scheme 1. Preparation of 2D-network benzo[*b*]trithiophene polymer by electropolymerization with a combination of thermal conversion.

BTT (**1**) monomer was synthesized according to the literature.[12,13] Raman spectrum of BTT and its simulation are shown in Figures 1a and 1b. Electrochemical polymerization of BTT was performed on a Au surface in order to form oligomers in an electrolyte solution of tetrabutylammonium hexafluorophosphate–dichloromethane by applying voltage pulses under ambient conditions. Application of 1.3 V pulses into a Au(111) electrode produced yellow films. The Raman spectrum after electropolymerization is shown in Figure 1c. New peaks at 1135, 1250, 1350, and 1530 cm^{-1} appear turning from the BTT monomer spectrum. These spectra are different from amorphous carbon, which usually displays two peaks at 1350 and 1590 cm^{-1}. The Raman spectrum after electropolymerization is in a good agreement with that of calculations for BTT oligomers (12mer) as shown in Figure 1e. From these results, yellow films produced on Au(111) electrodes after electropolymerizarion are deduced to be the BTT oligomers. Electropolymerized BTT oligomers on a Au(111) electrode were followed by a heat treatment at 500 °C under a high vacuum of 1×10^{-5} Pa for 30 min. Electropolymerized yellow films turned black after heat treatment. The Raman spectrum after heat treatment is similar to that of electropolymerized BTT oligomers as shown in Figure 1d. This indicates that the thiophene rings remain without degradation after the heat treatment. Raman spectrum

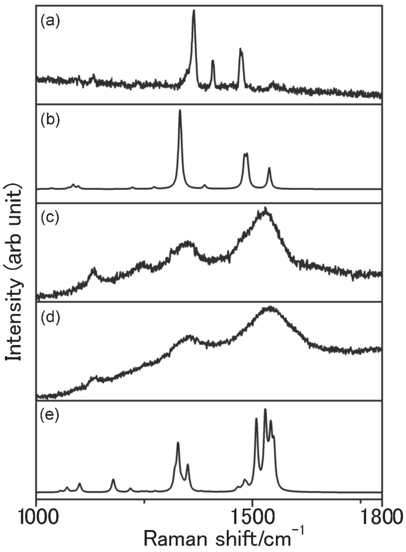


Figure 1. Raman spectra of BTT-derived materials and simulation. (a) BTT (**1**) cast on Au(111). (b) Simulation of BTT (**1**).[18] (c) Electropolymerized BTT oligomers on Au(111) electrode with 200 pulses at 1.3 V. (d) After thermal treatment of (c) at 500 °C, 30 min under 10^{-5} Pa. (e) Simulation of BTT 12mer.[18]

simulation as a function of conjugation length of BTT (2, 3, 4, 6, and 12mers) is shown in Supporting Information.[14] Calculation shows the independence of conjugation length of BTT on Raman spectra because these oligomers exhibit almost the same peak positions.

π conjugation of obtained materials at each step was investigated by optical absorption spectrum. Obtained films by electropolymerization on Au(111) and those after heat treatment under high vacuum were transferred from Au(111) to the transparent glass substrates with adhesive for the optical measurements. Electropolymerized BTT oligomers exhibit absorption spectrum with a maximum wavelength at 420 nm (Figure 2a). Chemical synthesis of dendritic oligo-BTTs up to 10mer was reported and BTT unit number dependence on absorption spectrum was investigated.[17] Reported BTT oligomers show bathochromic shifts in the order of the number of BTT units, 2, 4, 6, and 10mers, respectively. Our absorption spectrum of electropolymerized BTT oligomers is almost in good agreement with their spectrum of the high conjugation length of 10mer. In contrast to the absorption spectrum of electropolymerized BTT oligomers, those after heat treatment show extremely broad spectrum in the visible region (Figure 2b). This indicates the heat treatment might make BTT oligomers to form well-developed conjugated polymer by a cyclodehydrogenation reaction. Whereas the yellow films of electropolymerized BTT oligomers are insulators showing less than 10^{-9} S cm^{-1} by four-probe conductivity measurement, black films after heat treatment showed electrical conductivity of 6.7×10^{-2} S cm^{-1}. These data also show that heating under high vacuum after electropolymerization develops well-conjugated samples. Other properties of these materials are under investigation.

In conclusion, we proposed the method combined electropolymerization and thermal treatment applied for C_3 symmetric BTT molecule to produce the conjugated-polymer network. Thermally treated electropolymerized BTT film at 500 °C shows 10^7 times higher conductivity than before. It retains thiophene structure in spite of heating by Raman spectra. Absorption spectra of heat-treated electropolymerized BTT film suggests extended π conjugation. These results indicate the production of 2D network polymer consisted from C_3 symmetric BTT.

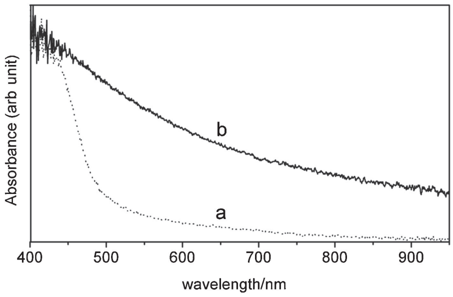


Figure 2. Optical absorption spectra of BTT-derived materials on glass substrate transferred from Au(111). These are subtracted by the background spectrum of glass and adhesive. (a) Electropolymerized BTT film (electropolymerization: 1.3 V, 200 pulses on Au(111)). (b) After thermal treatment of (a) (electropolymerization: 1.3 V, 200 pulses on Au(111), thermal treatment: 500 °C, 1 h under 10^{-5} Pa).

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