



Improvements of morphologies and emission characteristics of highly purified organic oligomer semiconductors

Takeshi Yamao^{a,*}, Takuya Sakaguchi^a, Keiichiro Juri^a, Hiroko Doi^a, Akira Kamoi^{a,1}, Naotoshi Suganuma^b, Shu Hotta^a

^a Department of Macromolecular Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

^b Photonics Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba Central 5-1, 1-1-1, Higashi, Tsukuba 305-8565, Japan

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ABSTRACT

We have purified oligomer semiconductors through vacuum sublimation and compared the film morphologies and the device performance of the purified materials with those of unpurified ones. We fabricated melt-molding films and thin film organic field-effect transistors (OFETs) using both the purified and unpurified oligomers. Comparing morphologies of the molten films we found regular arrangements of the crystal domains for the purified oligomers. Furthermore, the purified materials show definite light emission from the OFET devices.

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1. Introduction

A variety of organic semiconductors comprising conjugated molecules and polymers have been used for optical and electronic devices e.g. organic light emitting diodes (OLEDs) [1–3], organic field-effect transistors (OFETs) [4,5], and organic light-emitting field-effect transistors (OLEFETs) [6,7]. The purity of organic semiconductors is one of the critical factors that determine the device performance.

Amongst the organic semiconductors, thiophene/phenylene co-oligomers (henceforth abbreviated as TPCOs) [8,9] consist of in-line thiophene and benzene rings and have been regarded as one of the best candidates for high-performance electronic devices. Their crystals grown by a vapor phase method [10] and by a liquid phase method [11] have shown high mobilities on OFET devices [10,11]. These crystals exhibit not only photopumped spectrally narrowed emissions (SNEs) [12] and laser oscillations [13] but light emissions on OLEFETs [14]. Use of both purified TPCO materials and their crystals is therefore expected to improve the electrical and optical properties.

We have purified TPCO materials by vacuum sublimation. Using the purified materials we made melt-molding films to investigate their morphologies and emission characteristics. We also made OFET devices with the purified materials. In this article we present improved film morphology of the melt-molding films of the purified TPCOs. We also compare the device characteristics of the OFETs made

of the materials after and before being purified. The light emission is definitely observed from the OFETs based on the purified TPCO.

2. Experimental details

We used in the present studies 5,5'-diphenyl-2,2':5',2'':5'',2''':5''':5''''-quinoxethiophene (P5T) [8] and 5,5'-bis(4-biphenyl)-2,2'-bithiophene (BP2T) [9]. Their structural formulae are shown in Fig. 1(a) and (b). These were synthesized and recrystallized according to literature methods [8,9]. Here we refer to the recrystallized TPCOs as “unpurified” materials. These were further purified by the train sublimation technique [15,16]. A major part of a sublimation purification apparatus is schematically shown in Fig. 1(c). A band type heater (76.2 mm in width), wound around a stainless steel pipe (38 mm in outside diameter and 600 mm in length), generates a temperature gradient along the pipe. The temperature decreases toward the left side of the pipe [Fig. 1(c)]. Powder TPCO materials were sublimed on a quartz boat set under the heater.

The heater temperatures were decided according to the melting points of TPCO materials; the temperature was regulated to be 325–370 °C for P5T (the melting point is 350 °C [8]), and 350–380 °C for BP2T (358 °C [9]). The boat and several quartz cylinders (16 mm in diameter and 100 mm in length) were closely aligned in a quartz tube (22 mm in diameter and 1000 mm in length) that was sealed at the right-hand end with a stainless steel flange. The purification was carried out for 2–3 h under vacuum ($\sim 10^{-4}$ Pa). Purified powder materials were deposited on the inside wall of the quartz cylinder aligned next to the boat. After carrying out this purification processes twice, 36.1 (77.5) wt.% out of the starting material of P5T (BP2T) was collected as purified. These purified TPCO materials show bright

* Corresponding author. Tel.: +81 75 724 7780; fax: +81 75 724 7800.

E-mail address: yamao@kit.ac.jp (T. Yamao).

¹ Present address: Technical Development Group Specialty Polymer Business Unit, Nippon Carbide Industries Co., Inc., 17-3 Sakae-cho, Sano, Tochigi 327-0816, Japan.

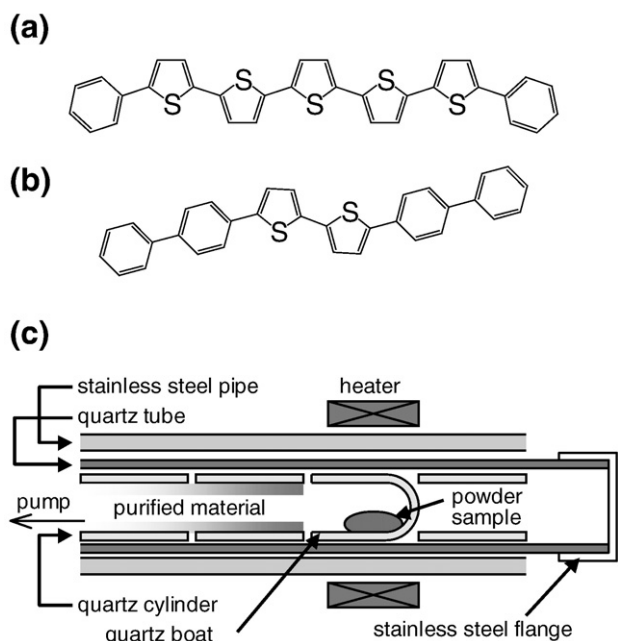


Fig. 1. Structural formulae of (a) 5,5''-diphenyl-2,2':5';2'':5'',2''':5''',2''''-quinquethiophene (P5T) and (b) 5,5'-bis(4-biphenyl)-2,2'-bithiophene (BP2T). (c) Schematic diagram of a major part of a sublimation purification apparatus.

emissions under fluorescent lights. We remark that after the first purification dark brown nonvolatile impurities remained in the quartz boat with pale volatile impurities left inside the quartz cylinders away from the boat.

Melt-molding films were fabricated using a slightly modified method described previously [17]. An appropriate amount ($\sim 1\text{--}3$ mg) of each of the purified and unpurified TPCO powders was placed on an 18-mm square glass substrate, and covered with another glass substrate. These substrates were preliminarily cleaned with an aqueous solution of sulfuric acid and hydrogen peroxide. The TPCO materials between the substrates were carefully heated on a hot plate having a slight temperature gradient along the lateral direction, until the molten TPCOs spread across the substrates. The materials were then cooled such that the temperature of the hot plate was decreased by 10°C for 45 min and by another 10°C for 30 min. The TPCO materials were further cooled with the hot plate switched off. These processes were carried out under the flowing nitrogen gas (30–35 ml/min) in order to avoid material degradation. The resulting films (formed between the glass substrates) were observed with a polarizing microscope (Nikon, ELIPSE LV100POL) both in the presence and absence of fluorescence. When we measured the emission spectra from the films, the emissions were introduced to a photonic multichannel analyzer (Hamamatsu, PMA11/C7473-36) via an optical fiber. In this configuration we were able to record the emission spectra of the films of $\sim 20\ \mu\text{m}$ in size [18].

For OFET fabrication we used premade device substrates on which comb-shaped interdigitated electrodes were formed by successively depositing Cr and Au. The channel lengths of the devices were 0.4, 0.6, 1.0, and $10\ \mu\text{m}$ with the fixed channel width of 8 μm . These substrates were cleaned with organic solvents in an ultrasonic bath. Thin films of both the purified and unpurified TPCO materials were deposited onto the device substrates under vacuum in order to complete bottom contact OFET devices. In the case of the BP2T devices the substrates were exposed to hexamethyldisilazane vapor before the BP2T deposition. The current-voltage characteristics of the devices were measured in vacuum ($\sim 10^{-3}$ Pa) with either an Advantest R6245 two-channel voltage current source/monitor or a Keithley Model 4200 semiconductor characterization system. The emission measurements

were solely carried out using the latter apparatus in combination with a silicon photodiode detector (Newport, Low-Power Detector 818-UV).

3. Results and discussions

We show the improved morphologies of the melt-molding films. Fig. 2(a) and (b) indicates polarizing micrographs of the melt-molding film of the purified P5T taken under the diagonal and extinction positions of the crossed Nicols, respectively. Of these, Fig. 2(b) indicates that in the wide black matrix of the photograph the two principal axes of refractive indices coincide with the direction of either the polarizer or analyzer. This black matrix covers more than $7.5\ \text{mm} \times 10.5\ \text{mm}$. On the other hand, in the unpurified P5T film the corresponding matrix covered an area of at most 2 mm in size. Besides, some voids and degraded materials were observed (unshown).

We closely observed the black matrix of the purified P5T melt-molding film. Fig. 2(c) shows an enlarged fluorescence micrograph (unpolarized) of a part of the matrix in Fig. 2(b). In Fig. 2(c), dark rectangles indicate the crystal domains separated by cracks observed as bright lines. Note that in TPCO crystals the edges and cracks exhibit by far stronger emissions than other parts [18]. These cracks were

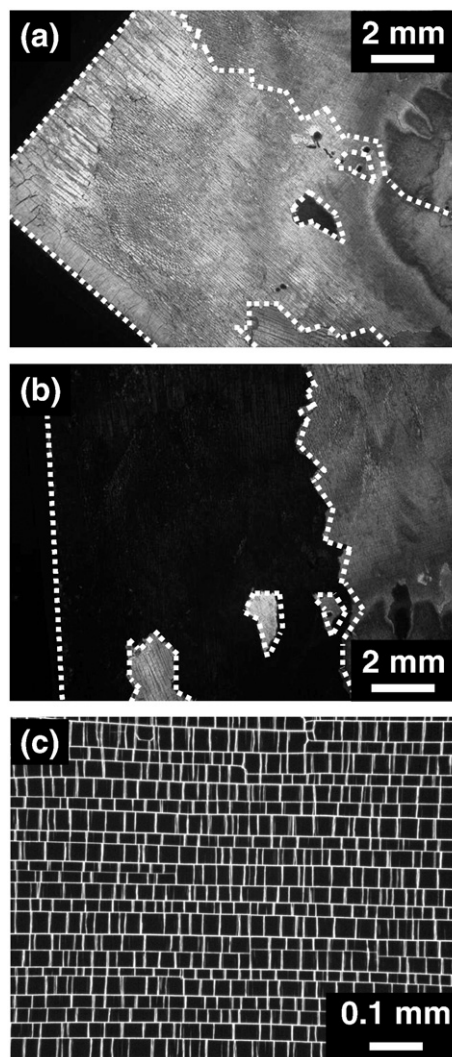


Fig. 2. Micrographs of a melt-molding film of purified P5T. The micrographs (a) and (b) are polarizing micrographs taken under the diagonal and the extinction positions of the crossed Nicols, respectively. (c) A fluorescence micrograph at the black matrix shown in (b).

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