

Communication

## Synthesis of a Terpene-Based New Chiral Inducer and Preparation of an Asymmetric Polymer

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**Abstract:** A new chiral compound was synthesized based on *L*-borneol. A cholesteric liquid crystal (LC) electrolyte solution was prepared by adding it as a chiral inducer to a nematic LC. A chiral poly(3,4-ethylenedioxythiophene) (PEDOT\*, \* = asymmetry) film was prepared by electrochemical polymerization in the induced cholesteric LC. The PEDOT\* film showed a maximum absorption band due to a  $\pi$ – $\pi^*$  transition in the UV-Vis absorption and bisignate Cotton effect in the reduced state in circular dichroism (CD). The CD spectrum indicates that PEDOT\* backbones form right-handed helical aggregation. However, the maximum optical absorption band due to  $\pi$ – $\pi^*$  transition of the PEDOT\* decreases and a new absorption band appears at long wavelengths upon oxidation due to generation of polarons as charge carriers. Bisignate Cotton effect disappears and broadly negative CD signal appears at long wavelengths in the oxidized state.

**Keywords:** electrochemical polymerization; poly(3,4-ethylenedioxythiophene); bornyl group; chiral inducer; cholesteric liquid crystal; optical activity

### 1. Introduction

Chiral conjugated polymers have seen much attention for their properties and have been applied in optoelectronic devices [1]. Many reports have discussed study chiral induction of conjugated skeletons [2–9].

Application of liquid crystalline compounds is effective method for ordered conjugated polymers [10–13]. Since asymmetric electrochemical polymerization has been found, electrochemical polymerizations of achiral monomers in cholesteric liquid crystal (LC) (chiral nematic LC) have been performed [14]. Key points of this polymerization are “sandwich-cell electrochemical polymerization method and electrochemical polymerization in LC electrolyte solution”, which has been originally developed by Goto [15]. Vortex poly(3,4-ethylenedioxythiophene) (PEDOT) films synthesized by electrochemical polymerization in chiral nematic LC was firstly carried out in 2009 [16]. This polymer film shows electrochemically driven change in optical rotation and circular dichroism. This polymer can be expected for application of structural color indicators, and gratings. Also, chiral 2,2'-bis(3,4-ethylenedioxythiophene) (BEDOT)-based copolymer was prepared by chemical and electrochemical polymerization [17]. Electrochemical polymerization [18], polycondensation [19], and polymerization by a Ni-based catalyst [20] have been carried out in cholesteric LC solution. Furthermore, binaphthyl molecules were synthesized in a chiral LC medium [21]. Liquid crystal molecules form one-handed helical structure in cholesteric LC phase, which induces one-handed helical aggregation of polymer backbone during the polymerization process in the cholesteric LC [16].

Cholesterol oleyl carbonate has been used as a chiral inducer (chiral dopant) [22,23]. However, twisting power of pure aliphatic chiral compounds tend to be weak due to flexibility of alkyl chain [24]. Bornyl group has some advantageous properties to application for chiral inducers. Stereogenic center at bornyl group bonding OH group have rigid structure [25]. Conformational flexibility of molecules can weaken twisting power of chiral inducers [24]. The structural property of bornyl group is desirable for chiral inducers.

In this study, we performed synthesis of a new chiral inducer containing a bornyl group. In order to increasing twisting power of the chiral inducer, we used 4-iodo benzoic acid. The introduction of 4-iodo benzoic acid is expected to improve twisting power of the chiral inducer by three aspect: (1) benzene ring of 4-iodo benzenecarboxylic acid improves  $\pi$ - $\pi$  interaction between the chiral inducer and LC molecules; (2) the iodine atom provides intra-molecular polarization of the chiral inducer; and (3) the iodine atom can induce inter-molecular CN-I interaction between the chiral inducer and LC molecules. Polarization of chiral inducers can affect twisting power of the chiral inducers [26]. Also, CN-I interaction between the solute and solvent is significant because it is the strongest interaction in CN-X interaction (X: halogen atom) [27]. For example, in tetrathiafulvalene (TTF) derivatives, the distance of CN-I is approximately 0.3 nm and CI-N and I-NC angle are close to 180° [28]. These experimental results suggest that the long axis of the chiral inducer is parallel to orientation direction of 4-cyano-4'-hexylbiphenyl (6CB). Therefore, CN-I interaction may enhance helical twisting power of the chiral inducer because the chiral inducer cannot induce large-scaled disarrangement of LC structure. Furthermore, we prepared a cholesteric LC electrolyte solution by using the bornyl-group-based chiral inducer. Next, chiral poly(3,4-ethylenedioxythiophene) (PEDOT\*, \* = asymmetry) film was prepared by the asymmetric electrochemical polymerization in the cholesteric LC electrolyte solution.

## 2. Experimental Section

### 2.1. Instruments

<sup>1</sup>H Nuclear Magnetic Resonance (NMR) spectroscopies were carried out with an AVANCE-400 (Bruker, Billerica, MA, USA). <sup>13</sup>C NMR spectroscopies were carried out with a JNM-ECS 400 (JEOL, Tokyo, Japan). The chemical shifts in deuterated chloroform (CDCl<sub>3</sub>) were determined against tetramethylsilane (TMS) as an internal standard. UV-Vis optical absorption spectra were taken with a UV-3100PC (Shimadzu, Kyoto, Japan). Circular dichroism (CD) spectra were measured with a J-720 (JASCO, Tokyo, Japan). Helical twisting powers of the chiral inducers were obtained with the Cano-wedge cell (KCRK-03, tanθ = 0.0083) (E.H.C., Tokyo, Japan). Optical texture observations were carried out using a Nikon ECLIPS LV 100 high-resolution polarizing optical microscope (POM) with a Nikon LU Plan Fluor lens and a Nikon CFIUW lens (Tokyo, Japan). Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) analysis was conducted using UltrafleXtreme-TN MALDI-TOF/TOF (Bruker). The chiral inducer was mixed with alpha-cyano-4-hydroxycinnamic acid used as a matrix in tetrahydrofuran (THF) solution.

### 2.2. Materials

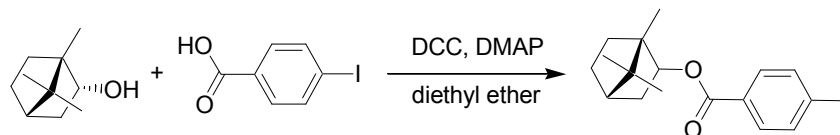
All of the reagents were used without further purification. *L*-Borneol and 4-iodobenzoic acid were purchased from ACROS ORGANICS (Antwerp, Belgium). Tetrabutyl ammonium perchlorate and *N,N*-dimethyl-4-aminopyridine were purchased from Tokyo Chemical Industry (TCI, Tokyo, Japan). *N,N*-Dicyclohexyl carbodiimide was obtained from Wako Pure Chemical Industries (Osaka, Japan). 6CB was purchased from Merck (Darmstadt, Germany). Diethyl ether, chloroform, dichloromethane and *n*-hexane were obtained from Nacalai Tesque (Kyoto, Japan). Silica gel (60 N) was purchased from Kanto Chemical (Tokyo, Japan). 2,3,2',3',2'',3''-Hexahydro-[5,5':7',5'']*ter*(thieno[3,4-*b*][1,4]-dioxine) (*ter*EDOT) [29] was used as a monomer for the electrochemical polymerization in cholesteric LC electrolyte. *ter*EDOT was prepared by previously reported method via Grignard coupling reaction in this study [16].

## 3. Results and Discussion

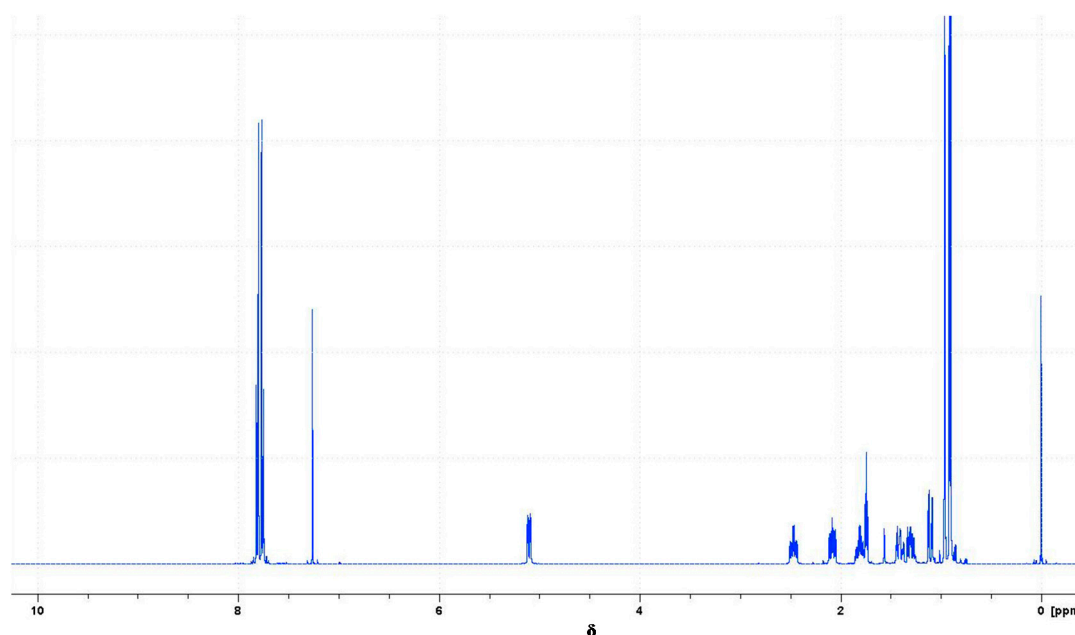
### 3.1. Synthesis and Twisting Power of a Chiral Inducer

A chiral inducer was synthesized from 4-iodobenzoic acid and *L*-borneol by Steglich esterification (Scheme 1). 4-Iodobenzoic acid (1.2446 g, 5.0 mmol), *L*-borneol (0.9289 g, 6.0 mmol), *N,N*-dicyclohexyl carbodiimide (1.0367 g, 5.0 mmol), *N,N*-dimethyl-4-aminopyridine (0.1257 g, 1.0 mmol) were mixed in 10 mL of diethyl ether at room temperature for 19 h. The mixture was extracted with dichloromethane and NaOH, and dried over magnesium sulfate, then purified by silica gel column chromatography (eluent: hexane/chloroform = 1/1) to afford a pale yellow solid (0.6610 g, 1.72 mmol, 34.4%). Figure 1 shows <sup>1</sup>H NMR spectrum of the chiral inducer. The chiral inducer shows multiplet signal at 5.082–5.121 due to protons at the ester-linked stereogenic center of the bornyl group. Furthermore, the chiral inducer shows no signal derived from the hydroxy group of *L*-borneol. The result indicates that we successfully synthesized the desired compound. <sup>1</sup>H NMR (400 MHz;

$\text{CDCl}_3$ ; TMS)  $\delta$  0.902 (s, 3H), 0.915 (s, 3H), 0.963 (s, 3H) 1.082–1.125 (dd, 1H,  $J = 3.4, 13.8$  Hz), 1.268–1.437 (m, 2H), 1.729–1.824 (m, 2H), 2.048–2.115 (m, 1H), 2.440–2.473 (m, 1H), 5.082–5.121 (m, 1H), 7.740–7.771 (m, 2H), 7.793–7.823 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ; tetramethylsilane, TMS) 13.61, 18.91, 19.72, 27.39, 28.08, 36.86, 44.97, 47.91, 49.11, 80.89, 100.43, 130.37, 130.98, 137.69, 166.31.  $m/z = 385.06$ .



**Scheme 1.** Synthesis of a chiral inducer. DCC: *N,N'*-dicyclohexylcarbodiimide; DMAP: *N,N'*-dimethyl-4-aminopyridine.



**Figure 1.**  $^1\text{H}$  NMR spectrum of the chiral inducer.

Twisting power of the chiral inducer was measured by the Grandjean–Cano wedge method in 6CB. We calculated helical twisting power (HTP), molar helical twisting power (MHTP) and macroscopic helical twisting power ( $\beta_M$ ) by:

$$\text{HTP} = (p \cdot c)^{-1} \quad (1)$$

$$\text{MHTP} = \text{HTP} \cdot M_d \times 10^{-3} \quad (2)$$

$$\beta_M = (p \cdot c \cdot M_h / M_d)^{-1} \quad (3)$$

Here,  $p$  and  $c$  are the helical pitch of the cholesteric LC and the weight concentration of the chiral inducer, respectively.  $M_d$  and  $M_h$  are the molecular weight of the chiral inducer and the solvent, respectively. The results are summarized in Table 1. These results confirm the chiral induction function of the terpene-base chiral inducer. Visual inspection with a polarizing optical microscope (POM) demonstrated that addition of the chiral inducer produces cholesteric LC as a chiral nematics. In twisting power, CN–I interaction can affect the results because it is the strongest interaction in CN–X

interaction (X: halogen atom) [27]. 6CB molecules have head-to-head CN–CN interaction [30,31]. Hence, the small twisting power of the chiral inducer may be because CN–I interaction can break ordered structure of LC matrix. However, experimental and theoretical results indicate that a predominant factor affecting a magnitude of HTP is conformation and molecular geometry of chiral inducers [32–35].

**Table 1.** Twisting power of the chiral inducer.

HTP <sup>a</sup> ( $\mu\text{m}^{-1}$ )	MHTP <sup>b</sup> ( $\mu\text{m}^{-1}\cdot\text{mol}^{-1}\cdot\text{kg}$ )	$\beta_{\text{M}}$ <sup>c</sup> ( $\mu\text{m}^{-1}$ )
4.07	1.56	5.93

<sup>a</sup> Helical twisting power (HTP) is defined by Equation (1); <sup>b</sup> Molar helical twisting power (MHTP) is defined by Equation (2); <sup>c</sup> Macroscopic helical twisting power is defined by Equation (3).

### 3.2. Synthesis and Properties of an Optically Active PEDOT\* Film

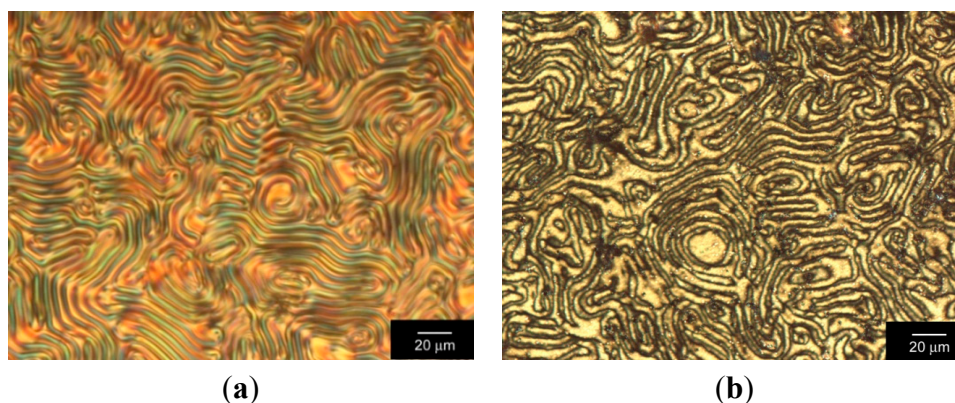
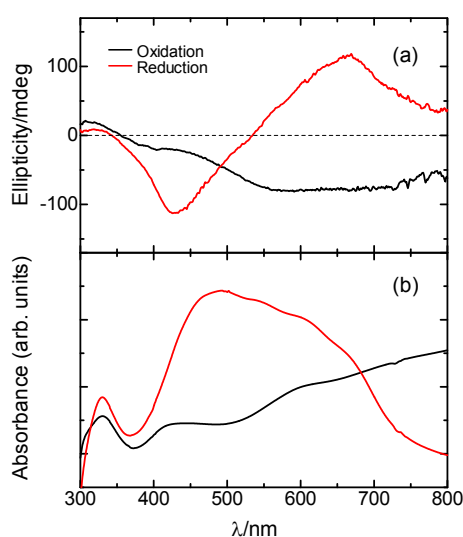
As a first attempt at application, we conducted a polymerization in cholesteric LC prepared by using the terpene-based chiral inducer. The constituents of the cholesteric LC electrolyte solution are summarized in Table 2. Figure 2a shows a polarizing optical microscopy (POM) image of the cholesteric LC electrolyte solution at 19 °C revealing the fingerprint texture generally observable for cholesteric liquid crystals. The cholesteric LC electrolyte solution was injected between two indium-tin-oxide (ITO) glass electrodes separated by a Teflon sheet (thickness = 0.2 mm) as a spacer. Electrochemical polymerization was carried out by applying 4 V direct current (DC) at 15 °C. A thin polymer film was deposited on the anode side of the ITO glass electrode after 5 min. The cholesteric LC electrolyte solution was washed off with *n*-hexane and then dried.

Figure 2b shows the POM image of the polymer film prepared by electrochemical polymerization in cholesteric LC electrolyte, revealing a fingerprint texture similar to that of the cholesteric LC electrolyte. Figure 3 displays circular dichroism (CD) and ultraviolet (UV)-Vis absorption spectra. The pristine, oxidized, polymer film was electrochemically reduced by applying −1.1 V against an Ag/Ag<sup>+</sup> reference electrode in 0.1 M tetrabutyl ammonium perchlorate (TBAP)/acetonitrile solution.

The film shows its maximum optical absorption due to  $\pi$ – $\pi^*$  transitions of the main-chain at ~500 nm, and shows first-positive and second-negative Cotton effect. The bisignate Cotton effect, exhibiting positive to negative signals at long wavelength can be due to Davydov splitting, indicate that the PEDOT\* backbones form right-handed helical aggregation, likely produced by transcription from the asymmetric helical form of the matrix cholesteric LC prepared with the chiral inducer. However, the film in the oxidized state shows a different spectral form. The maximum optical absorption band at ~500 nm is decreased, while a new absorption band appears at long wavelengths (Figure 3b). The change of absorption spectra suggests generation of polarons (radical cationic states) by the electrochemical oxidation (Figure 3a). In the CD spectrum, bisignate Cotton effect disappears while broadly negative CD signals appear at long wavelengths in the oxidized state. In other chiral PEDOT derivatives in film state, a broadly negative CD signal appears and a chiral orientation of the polymer backbones retains in iodine doped state [36]. Besides, such broadly CD signal in oxidation state can be observable in other conjugated polymers such as TTF derivatives [37]. These accumulated experimental results suggest that, in this study, broadly negative CD signal derived from polarons band in doped state.

**Table 2.** Constituents of cholesteric liquid crystal electrolyte solution.

Material	Role	Chemical Structure	Quantity (mg, $\mu\text{mol}$ )
4-Cyano-4'-hexylbiphenyl (6CB)	Matrix		98.55, 374.19
Chiral inducer	Induction of chirality		3.11, 8.08
<i>ter</i> EDOT	Monomer		1.95, 4.62
Tetrabutyl ammonium perchlorate (TBAP)	Supporting salt		0.19, 0.54

**Figure 2.** (a) Polarizing optical microscopy (POM) image of cholesteric liquid crystal electrolyte solution containing monomer at 19 °C. (b) POM image of the polymer film prepared in a cholesteric liquid crystal electrolyte induced by the terpene-based chiral inducer.**Figure 3.** (a) Circular dichroism (CD) and (b) UV-Vis absorption spectra of the polymer film.

#### 4. Conclusions

The chiral inducer containing bornyl group was successfully synthesized. The iodine atom in the inducer provides intra-molecular asymmetric polarization of the chiral inducer, and may improve the chiral

induction function. PEDOT\* films were synthesized by electrochemical polymerization in the induced cholesteric LC electrolyte. The PEDOT\* films showed an absorption band due to  $\pi$ - $\pi^*$  transitions at  $\sim 500$  nm and the bisignate Cotton effect in the reduced state. The CD spectrum indicates formation of right-handed helical aggregation of the PEDOT\* backbones. On the other hand, the maximum optical absorption band due to  $\pi$ - $\pi^*$  transitions decreases and an absorption band appears at long wavelengths in the oxidized state due to generation of polarons. In the CD spectra, bisignate Cotton effect disappears and a broadly negative CD signal appears at long wavelengths due to CD-active polarons band.

The results demonstrate that natural terpene compounds can be applied as chiral induction agents for chiral reactions.

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## Author Contributions

Atsushi Matsumura performed synthesis and characterization of the polymer. Hiromasa Goto and Fan Yang synthesized of the monomer. Hiromasa Goto conceived and directed the research.

## Conflicts of Interest

The authors declare no conflict of interest.

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