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PAPER

Liquid crystalline PEDOT derivatives exhibiting reversible anisotropic electrochromism and linearly and circularly polarized dichroism[†]

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The multifunctional poly(3,4-ethylenedioxythiophene) [PEDOT] derivatives that exhibit liquid crystallinity, reversible anisotropic electrochromism, and linearly and circularly polarized dichroism are developed. A series of copolymer-type liquid-crystalline PEDOT (LC PEDOT) derivatives are synthesized and evaluated in terms of optical and electrochromic properties. Two of the polymers are monosubstituted LC PEDOT derivatives with phenylcyclohexyl (PCH) or cyanobiphenyl (CB) mesogenic side chain moieties linked to the main chain via an ester bond. Four are disubstituted polymers bearing PCH or CB side chain moieties linked to the main chain via an ester or an ether bond. All of the polymers showed thermotropically nematic LC (N-LC) phases of an enantiotropic nature. Macroscopically aligned LC PEDOT derivatives were prepared by rubbing the polymer films in their N-LC phases, yielding linearly polarized fluorescence and anisotropic electrochromism. The morphologies of the polymer films reversibly changed between the neutral and oxidized states through electrochemical dedoping and doping procedures. The electrochromism between the neutral and oxidized states occurred in the parallel and perpendicular directions of the aligned polymer film, affording a novel anisotropic electrochromism. The chiral nematic LC (N*-LC) phases were also induced in the polymers by adding chiral binaphthyl derivatives as chiral inducer into the LC PEDOT derivatives. The polymer films with the induced N*-LC phase exhibited circular dichroism, implying the formation of an interchain helically π -stacked structure or intrachain helically twisted structure.

1. Introduction

The optical and electrochemical properties of π -conjugated conducting polymers are intriguing. In organic electronics, conducting polymers have a number of advantages over small molecules, in particular, their stability, mechanical properties and ease of processing. Electrically conjugated polymers have been regarded as excellent materials to be applied to electronic devices, electrolytic capacitors, actuators, sensors, artificial muscles and light-emitting diodes (LEDs).¹⁻¹³ Among them, conjugated polymers with small band gaps have been drawing much attention because they potentially produce materials with high conductivities and desirable optical properties. The synthesis of π -conjugated polymers with small band gaps is one of the major focuses in the field of organic conductors.

Blocking the 3- and 4-positions of thiophene with an ethylenedioxy group yields a highly electron-rich fused heterocycle 3,4-ethylenedioxythiophene (EDOT), in which the ethylenedioxy bridge provides minimal steric repulsion between the rings. Poly

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto, 615-8510, Japan. E-mail: akagi@fps.polym.kyoto-u.ac.jp † Electronic supplementary information (ESI) available. See DOI: (3,4-ethylenedioxythiophene) (PEDOT) is a relatively new member in the family of conducting polymers.¹⁴⁻¹⁸ PEDOT has many interesting properties, including a low half-wave potential and a small band gap.^{19,20} This polymer is more electrochemically stable during cyclic voltammetry and has greater air and thermal stability in terms of electrical properties, compared with other kinds of polythiophene derivatives.^{21,22}

Liquid crystals are easily aligned by external forces, such as sheer stress and electric and magnetic fields. A π -conjugated polymer is insoluble and infusible because of the integrity of the main chain backbone. If a conjugated polymer is substituted with a liquid crystalline (LC) group, the polymer is soluble in organic solvents and it is aligned by the spontaneous orientation of the LC group. Besides, it can be macroscopically aligned by external perturbations, in a way similar to LC molecules. With the combination of liquid crystallinity and electrochromic functionality, we expect to prepare linearly dichroic electrochromic materials.²³⁻²⁶

Meanwhile, it is well known that when a small amount of chiral compound is added, as a chiral inducer, to a nematic LC (N-LC), a chiral nematic LC (N*-LC) phase is induced by virtue of chiral induction²⁷ that is also called sergeant-soldiers.²⁸ Although the chiral induction has been applied mainly to LC molecules, the application to LC polymers has been seldom

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achieved. If the even conjugate polymers bear an N-LC nature, they might exhibit an N*-LC phase by using the chiral inducer, giving rise to chirality and/or helicity.²⁹⁻³⁷ The LC PEDOT derivative with the induced chirality is expected to have circularly dichroic absorption and emission.

In this work, to cultivate multifunctional and high performance conjugated polymers useful for plastic electronics, we developed a series of copolymer-type LC PEDOT derivatives by chemical polymerizations. Macroscopically aligned polymer films were prepared by rubbing the films in the N-LC phase. The anisotropic electrochromism was observed in the aligned films. Subsequently, helical polymer films were prepared through a formation of the N*-LC phase constructed by adding the chiral inducer to the polymer in the N-LC phase. Circular dichroism was observed in absorption spectra of the LC PEDOT films with interchain helically π -stacked structure or intrachain helically twisted one.

2. Experimental

Techniques

All ¹H NMR and ¹³C NMR spectra were measured with an EX-270 spectrometer. CDCl₃ was used as the deuterated solvent, and trimethyl silane (TMS) was used as an internal standard. Infrared spectroscopic measurements were carried out with a Jasco FT-IR 550 spectrometer, using the KBr method. The phase transition temperatures were determined using a Perkin-Elmer differential scanning calorimeter (DSC) at a constant heating/cooling rate of 10 °C min⁻¹, and the first cooling and second heating processes were recorded. Optical texture observations were performed using a Carl Zeiss polarizing optical microscope (POM), equipped with a Linkam THMS 600 heating and cooling stage. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a Shodex A-80M column. X-Ray diffraction (XRD) measurements were performed with a Rigaku D-3F diffractometer in which the X-ray power and scanning rate were set to 1200 mW and 5 degrees per minute, respectively. Molecular mechanics (MM) calculations for the polymers were carried out with a Silicon Graphics Cerius2 system.

Materials

N,*N*-Dimethylformamide (DMF), tetrahydrofuran (THF), chloroform and toluene were distilled prior to use. EDOT was obtained from Aldrich Chemical. For purification, EDOT was distilled under vacuum (85 °C at 0.65 Torr). Diethyl azodicarboxylate (40 wt% in toluene; DEAD) and triphenylphosphine (TPP) were used as received from Tokyo Kasei (TCI). (*R*)- and (*S*)-2,2'-Dihydroxy-1,1'-binaphthyls (0.99 optical purity) were purchased from commercially available sources. The mesogenic compound 4-(*trans*-4-*n*-pentylcyclohexyl)phenol [PCH500] was purchased from Kanto Chemical Ltd.

2,5-Bis(tributylstannyl)-3,4-ethylenedioxythiophene

n-Butyl lithium (22.7 ml, 58 mol, 2.6 M in hexane) was slowly added to a stirred solution of 3,4-ethylenedioxythiophene (4.14 g, 29 mmol) and N, N, N', N'-tetramethylethylenediamine (TMEDA)

(11.96 g, 68 mmol) in anhydrous diethyl ether (70 ml) under argon atmosphere at room temperature. The mixture was stirred at room temperature for 10 min, and then refluxed for 30 min. The mixture was cooled to -78 °C, and tributylstannyl chloride (11.56 g, 58 mmol) was added slowly over 1 h. The reaction mixture was warmed up to room temperature and stirred for 3 h. The resulting solution was extracted three times with 300 ml of diethyl ether. The organic layer was then washed with an aqueous solution of saturated sodium chloride. After drying over Na2SO4 and filtration, diethyl ether was removed using a rotary evaporator. The residue was purified by column chromatography with hexane on pretreated silica gel which was washed with neat triethylamine, then hexane. The solvent was removed in vacuum and the residue was further purified through vacuum distillation to give 12.9 g of colourless liquid (yield: 73%). Anal. calcd for C₁₈H₃₂O₂SSn: C, 50.13; H, 7.48; O, 7.42; S, 7.44; Sn, 27.53. Found: C, 49.83; H, 7.53; S, 6.24; Sn, 27.73. ¹H NMR (270 MHz, CDCl₃, δ, from TMS): $\delta 6.57$ (s, 1H), 4.19 (m, 4H, -OCH₂), 0.24–0.44 (t, 9H, -CH₃) ppm. ¹³C NMR (270 MHz, CDCl₃, δ, from TMS): δ 141.8, 141.5, 107.1, 99.6, 77.5, 77.0, 3.1, 3.0, 2.8 ppm.

2,5-Dibromohydroquinone

A solution of 1,4-dibromo-2,5-dimethoxybenzene (14.2 g, 48 mmol) in dichloromethane (60 ml) was stirred for 30 min at room temperature. Then boron tribromide (25.0 g, 100 mmol) was slowly added to the solution and was refluxed for 24 h at 40 °C. The solution was allowed to cool to 0 °C. The precipitate was added to a large amount of water and stirred for 3 h at 0 °C. The solution was filtered to give 11.3 g as a white solid (yield: 89%). Anal. calcd for $C_8H_8Br_2O_2$: C, 26.90; H, 1.50; Br, 59.65; O, 11.95. Found: C, 26.7; H, 1.6; Br, 59.7. ¹H NMR (270 MHz, CDCl₃, δ , from TMS): δ 6.6 (d, 2H), 5.2 (d, 2H, –OH) ppm. ¹³C NMR (270 MHz, CDCl₃, δ , from TMS): δ 110.7, 122.5, 155.4, 110.7, 122.5, 155.4 ppm.

Pentylcyclohexylphenoxy-1-hexyl alcohol (PCH506OH)

Potassium carbonate (11.6 g, 84 mmol), potassium iodide (4.65 g, 28 mmol) and p-(trans-4-pentylcyclohexyl)phenol (6.8 g, 28 mmol) were added to 100 ml butanone in a three-neck roundbottom flask equipped with a magnetic stirrer and argon line at room temperature. Then 6-bromo-1-hexanol (5.07 g, 28 mmol) was very slowly added and the mixture was refluxed for 48 h at 60 °C. After evaporation, the solvent was extracted three times with 300 ml of diethyl ether. The organic layer was then washed with an aqueous solution of saturated sodium chloride. After drying over Na₂SO₄ and filtration, diethyl ether was removed using an evaporator. The crude product was passed through a column chromatograph (chloroform) and recrystallized from ethanol to give 8.11 g as a white solid (yield: 84%). ¹H NMR (270 MHz, CDCl₃, δ, from TMS): δ 7.4 (s, 2H), 6.9 (s, 2H), 4.2 (s, 1H), 3.9 (t, 2H), 3.7 (t, 2H), 1.8-1.0 (m, 29H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ, from TMS): δ 156.6, 138.6, 127.7, 114.9, 68.8, 62.0, 43.1, 37.9, 33.1, 31.4, 29.5, 25.3, 14.1 ppm.

6-(4-Cyano-4'-biphenyl)-oxy-1-hexyl alcohol (CB06OH)

Potassium carbonate (4.84 g, 35 mmol), potassium iodide (2.91 g, 18 mmol) and *p*-(*trans*-4-pentylcyclohexyl)phenol (3.60 g, 18

mmol) were added to 100 ml butanone in three-neck roundbottom flask equipped with a magnetic stirrer and argon line at room temperature. Then 6-bromo-1-hexanol (4.15 g, 18 mmol) was slowly added and the mixture was refluxed for 48 h at 80 °C. After evaporating, the solvent was extracted three times with 300 ml of diethyl ether. The organic layer was then washed with an aqueous solution of saturated sodium chloride. After drying over MgSO₄ and filtration, diethyl ether was removed using an evaporator. The crude product was passed through a column chromatograph (chloroform) and recrystallized from ethanol to give 6.37 g as a white solid (yield: 91%). ¹H NMR (270 MHz, CDCl₃, δ , from TMS): δ 7.7 (s, 2H), 7.6 (s, 2H), 7.5 (s, 2H), 6.9 (s, 2H), 3.9 (t, 2H), 3.7 (t, 2H), 1.8–1.3 (m, 8H) ppm. ¹³C NMR (CDCl₃, 270 MHz): δ 159.5, 145.2, 131.7, 127.9, 126.8, 119.0, 68.1, 62.9, 33.1, 29.4, 25.3 ppm.

6-(4-(4-Pentylcyclohexyl)phenoxy)hexyl 2,5-dibromobenzoate (M1)

A solution of triphenylphosphine (2.62 g, 10 mmol) and diethyl azodicarboxylate (DEAD) (4.31 g, 40 wt% in toluene, 10 mmol) in THF (10 ml) was stirred for 1 h at room temperature. Then, 2,5-dibromobenzoic acid (2.68 g, 10 mmol) and PCH506OH (3.46 g, 10 mmol) in THF (80 ml) were slowly added via pressure equalized dropping funnel. The reaction mixture was stirred at room temperature overnight under an argon atmosphere. TLC indicated completion of the reaction. The solution was extracted with dichloromethane, washed with water thoroughly, and dried over anhydrous sodium sulfate. The dichloromethane layer was removed by evaporation and was purified by column chromatography (silica gel, dichloromethane). The solvent was removed in vacuum and the residue was further purified through vacuum distillation to give 2.2 g as a white solid (yield: 57%). ¹H NMR (270 MHz, CDCl₃, δ, from TMS): δ 7.8 (s, 1H), 7.5 (s, 1H), 7.3 (s, 1H), 7.1 (d, 2H) 6.9 (d, 2H), 4.2 (t, 2H), 3.9 (t, 2H), 2.4 (m, 4H), 2.0-0.8 (m, 29H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ, from TMS): δ 166.3, 157.2, 140.2, 137.5, 137.1, 136.5, 128.2, 121.1, 118.8, 68.0, 43.7, 38.6, 35.5, 34.9, 32.6, 29.3, 29.0, 26.7, 25.3, 24.0, 15.5 ppm.

M2 to M6 were prepared using the methods similar to that described for M1. Details of the monomer synthesis are given in the ESI[†].

Poly[6-(4-(4-pentylcyclohexyl)phenoxy)hexyl-3,4ethylenedioxythiophene benzoate] (P1)

P1 was synthesized by Stille reaction between 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) and M1. A solution of M1 (596 mg, 1.0mmol), 2,5-bis(tributylstannyl-3,4-ethylenedioxythiophene) (720 mg, 1.0 mmol), dichlorobis(triphenylphosphine)palladium(II) (Pd(PPh₃)Cl₂) (15 mg, 0.02 mmol) in 5 ml of toluene was stirred under argon at 100 °C for 72 h. The reaction mixture was poured into a large amount of methanol (300 ml) containing hydrochloric acid (HCl) and vigorously stirred for 3 h. The resulting precipitate was collected by filtration and dissolved in the minimum amount of THF (5 ml) and stirred in methanol (300 ml) for 24 h. After filtration, the product was dried under vacuum to give 0.63 g as a yellow powder (yield: 48%). ¹H NMR (270 MHz, CDCl₃, δ, from TMS): δ 7.8 (s, 1H),

7.7 (s, 1H), 7.4 (s, 2H), 7.0 (s, 2H), 4.7 (t, 4H), 4.2 (t, 2H), 4.0 (t, 2H), 2.3 (t, 2H), 1.84–0.85 (m, 29H) ppm. ¹³C NMR (270 MHz, CDCl₃, δ , from TMS): δ 167.9, 156.6, 150.5, 147.6, 138.7, 138.2, 133.4, 133.1, 130.6, 130.1, 128.8, 128.2, 127.1, 114.1, 111.3, 111.0, 68.7, 65.3, 65.0, 43.7, 37.7, 29.6, 29.3, 27.1, 26.8, 22.7, 21.8, 14.1, 10.8 ppm.

P2 to **P6** were polymerized using the methods similar to that described for **P1**. Details of the polymerization are given in the ESI[†].

3. Results and discussion

3.1. Synthesis and structures of polymers

Fig. 1 shows the six kinds of LC PEDOT derivatives synthesized. Two of the polymers are monosubstituted LC PEDOT derivatives bearing phenylcyclohexyl (PCH) or cyanobiphenyl (CB) mesogenic side chain moieties that are linked to the main chain *via* an ester bond. Four of them are disubstituted LC PEDOT derivatives with PCH or CB mesogenic side chain moieties linked to the main chain *via* an ester or an ether bond. The liquid crystallinity of the polymers was examined in terms of the number of substitutions (one or two) and the linkage between the main and side chains (ester or ether).

The LC substitutions, PCH506OH and CB06OH, were synthesized through the Williamson etherification reaction, and the synthesis pathways are shown in Scheme 1. Hydroquinone and 2,5-bis(tributylstannyl)-3,4-ethylene dioxythiophene were prepared by a directed lithiation reaction, using twice the relative mole ratio of EDOT and followed by a reaction with tributylstannyl chloride. The LC-substituted dibromophenylene derivatives M1-M6) were prepared by the Mitsunobu reaction between the LC substituents (PCH506OH and CB06OH) and 2,5-dibromobenzoic acid for M1 and M2, 2,5-dibromoterephtalic acid for M3-M4, and 1,4-dibromohydroquinone for M5-M6. The polymerizations were carried out by Stille coupling reactions between 2,5-bis(tributylstannyl)-3,4-ethylenedioxythiophene (2) and the LC-substituted dibromophenylene derivatives M1-M6), as shown in Scheme 2.

P1 and **P2** are monosubstituted PEDOT derivatives in which the PCH and CB mesogens, combined with hexamethylene spacers, are linked to the main chains *via* ester bonds,



Fig. 1 Copolymer-type LC PEDOT derivatives with mono- and disubstituted side chains: PCH-LC polymers (P1, P3 and P5) and CB-LC polymers (P2, P4 and P6).



Scheme 1 Synthetic pathways of the liquid crystalline (LC) moieties.

respectively. **P3** and **P4** are disubstituted PEDOT derivatives in which two PCH and CB mesogens, combined with hexamethylene spacers, are linked to the main chains *via* ester bonds, respectively. The structures of **P5** and **P6** are the same as those of **P3** and **P4**, respectively, except that ether linkages replace the ester bonds.

3.2. Molecular weights and dispersion ratios

Table 1 shows the molecular weights and dispersion ratios of the polymers, evaluated by GPC measurements using standard

polystyrene (PS). The number-average molecular weights (M_n) of the polymers varied between 3300 and 6700. The dispersion ratios (M_w/M_n , M_w = weight-average molecular weights) of the polymers are 1.3–2.2, and the degrees of polymerizations (DPs) are 4–11, which correspond to 8–22 aromatic rings. The relatively low DPs of the polymers are due to the steric hindrance of the LC side chains during the polymerization. The effect of the steric hindrance is increased in the disubstituted PEDOT derivatives with LC mesogens on both side chains, especially in **P5** and **P6**. It was possible to prepare cast films to form the polymers for evaluating the chemical and optical properties of the films.



Scheme 2 Synthetic pathways of the copolymer-type LC PEDOT derivatives.

 Table 1
 The molecular weights, dispersion ratios and degrees of polymerization of the polymers, P1–P6, evaluated by GPC with a polystyrene standard

Polymer	$M_{\rm n}$	$M_{ m w}$	$M_{\rm w}/M_{\rm n}$	\mathbf{DP}^{a}	Number of aromatic ring
P1	3300	5500	1.7	6	12
P2	6700	14 900	2.2	11	22
P3	6300	9900	1.6	6	12
P4	5100	7800	1.5	6	12
P5	4100	5200	1.3	4	8
P6	4100	5200	1.3	5	10
^a Degree	of polyn	nerization			

3.3. Thermal properties

The thermal properties of the polymers were evaluated with the POM and DSC measurements. All the polymers showed thermotropic liquid crystallinity with an enantiotropic nature. Fig. 2 shows typical polarizing optical micrographs (POMs) of **P1** and **P2**. Schlieren textures were observed and are characteristic of nematic LC phases. The assignment of nematic LC phase is supported by X-ray diffraction (XRD) results; for instance, the polymers have only a broad peak in the wide angle region at 24.8° in 2θ (d = 3.6 Å) and a weaker overtone peak at 12.5° (d = 7.1 Å) for **P2**, a broad peak at 19.0° (d = 4.7 Å) for **P3**, and a broad peak at 19.9° (d = 4.5 Å) for **P5**. The peaks of 3.6–4.7 Å



Fig. 2 Polarizing optical micrographs (POMs) of polymers. (a) Schlieren texture of **P1** at 87 °C in the cooling process and (b) Schlieren texture of **P2** at 162 °C in the cooling process.

correspond to distances between main chains or LC side chains (see Fig. S5†).

Table 2 summarizes the phase transition temperatures determined from the DSC measurements. The conjugated polymers are highly viscous even in the isotropic phase because of their rigidity of main chains. In addition, the viscosity of the polymer increases as the temperature becomes close to the phase transition temperature from the isotropic to LC phase. This is because the polymers tend to be further associated with each other, which serves for a preparation of spontaneous alignment for the LC phase. These situations should give a supercooling of the isotropic phase. On the other hand, the primary and higher-order structures of the polymer formed in the N-LC phase remain unchanged in the glassy state. The polymers also exhibit the supercooling in the N-LC phase, where the phase transition temperature from the N-LC to the glassy state shifts to a lower temperature.

It is apparent from Table 2 that the polymers with CB side chains (P2 and P4) have higher and wider LC temperature regions than those with PCH side chains (P1 and P3). The polar cyanide (CN) group of the CB side chain enables interchain electrostatic interactions between the terminal sites of the side chains, which should stabilize the LC phase to yield a wider LC temperature region. The disubstituted polymers (P3 and P4) have higher and wider LC temperature regions than the corresponding monosubstituted polymers (P1 and P2). A notable difference in the LC temperature region can be seen between P4 and P6 in which the former and the latter have ester and ether bonds, respectively, to link the CB moieties with the main chains; P4 has a wider LC temperature region than P6. This implies that the ester bond is more rigid than the ether bond and can suppress the internal rotation of the side chains, leading to a more stable LC phase in P4.

Here it is of interest to note that the LC PEDOT derivatives have more stable LC phases, compared with LC poly(*p*-phenylene) [PPP] and other kinds of LC aromatic conjugated polymers.⁴¹ The high degree of stability of the LC phase can be related to the high planarity of the main chains of the PEDOT derivatives. When the π -conjugated polymer forms a LC phase,

 Table 2
 The phase transition temperatures and LC temperature regions of the polymers, determined from DSC measurements



it is necessary for the polymer to be aligned spontaneously in a domain. The spontaneous alignment of the conjugated polymer owes to a self-assembly of the polymers and also to an excluded volume effect. It is likely that a planar conjugated polymer is more preferable for the formation of the self-assembly because of its ability to have π -overlap interaction and/or van der Waals interaction between the polymer chains, than a less planar conjugated polymer such as poly-*p*-phenylene (PPP) derivatives. Actually, the dihedral angle between phenylene rings in PPP is estimated to be about 30° because of steric repulsions between neighboring hydrogen atoms belonging to the different phenylene rings. Thus, the planar conjugated polymer can form a stable self-assembly feasible for the spontaneous alignment, which leads to a stable LC phase.

3.4. Optical properties

Fig. 3 shows the UV-Vis and fluorescence spectra of **P1** and **P2** in chloroform and as cast films. The optical spectra of **P3–P6** are given in the ESI[†]. The optical properties of the polymers are summarized in Table 3. The polymers with PCH side chains dissolved in chloroform showed three absorption bands: < 250, 318 (shoulder) and 410 nm for **P1**; 280, 320 and 415 nm for **P3**; and 280, 350 (shoulder) and 426 nm for **P5**. The two bands at the shorter wavelength (250–280 nm) and the middle wavelength (318–350 nm) were assigned to the mesogenic core of the side chain. The band at the longer wavelength (410–426 nm) was assigned to the π - π * transition of the conjugated main chain.

The polymers with CB side chains in chloroform showed two absorption bands: 297 and 427 nm for **P2**; 296 and 412 nm for **P4**; and 296 and 415 nm for **P6**. The bands at the shorter (296– 297 nm) and longer (412–427 nm) wavelengths were assigned to the mesogenic core of the side chains and the conjugated main chains, respectively. It should be noted that the effective conjugation lengths of the polymers are not remarkably affected by the structural differences of the side chains (PCH and CB moieties), the number of substitution (mono- and di-substitutes) and the linkages between the main and side chains (ester and ether linkages) so far as the polymers in solution are concerned.



Fig. 3 UV-Vis absorption (upper) and fluorescence (lower) spectra of the polymers in chloroform and as cast films: (a) P1 and (b) P2. The insets contain photographs of the fluorescent colors of the polymers in chloroform and cast films.

The casting of the polymers gave rise to a broadening and a red shift of the absorption bands for the polymer main chain. As shown in Table 3, the polymers with ester bonds linking the side chains (**P1–P4**) exhibited small red shifts of 8–10 nm, and the polymers with the ether bonds linking the side chains (**P5** and **P6**) showed large red shifts of 33–34 nm. This means that the planarity of the conjugated main chain with the ether linkages is enhanced when the polymer is fabricated into the cast films. Hence, the flexible ether bond is more favorable to the formation of interchain π -stacking or interchain associations, leading to an increase in the effective conjugation length.

Fig. 3 shows the fluorescence spectra of the polymers in chloroform and as cast films. Polymers (P1 and P2) in chloroform showed blue fluorescence when they were excited by UV light at 365 nm from a 16 W lamp. The spectroscopic measurements indicate that the fluorescence bands of the polymers (P1–P6), attributed to the $\pi^*-\pi$ transition of the main chains, are located at the wavelength from 495 to 514 nm, which corresponds to blue emission. The Stokes shifts for the polymers in chloroform ranged from 73 to 90 nm. The quantum yields of the polymer fluorescence were also evaluated by dissolving quinine sulfate in 1 N sulfuric acid as the standard. As summarized in Table 3, the quantum yields ranged from 12 to 21%, depending on the number of the LC substitutions. The monosubstituted polymers (P1 and P2) appear to have higher quantum yields than the disubstituted polymers (P4–P6).

The fluorescence of the polymers in cast films was investigated. The films showed a green fluorescence at 515–534 nm for **P1–P4** and a greenish yellow one at 554–558 nm for **P5** and **P6**. The **P5** and **P6** films form more π -stacked structures between the polymer chains than the **P1–P4** films. This agrees with the results from the absorption spectra. The Stokes shifts for the films are in the range 92–106 nm, which is substantially larger than the range observed in the chloroform solution (73–90 nm).

3.5. Reversible electrochromism

It is useful to explain briefly the process of the electrochemical dedoping and doping. The polymer film cast on an ITO glass is immersed in an acetonitrile solution including 0.1 M

 Table 3
 The optical properties of the polymers in chloroform and cast films

	UV-vis (in	UV-vis (cast film)		Fluorescence (in CHCl ₃)				Fluorescence (cast film)		
Polymer	$\lambda_{max}/$ nm	λ _{max} / nm	⊿ª/ nm	$E_{\rm m}{}^b/$ nm	⊿ ^c / nm	Φ^d (%)	<i>E_x^e</i> / nm	$E_{\rm m}^{\ \ b}$ /nm	⊿ ^f / nm	<i>E</i> _x ^e / nm
P1	410	418	8	495	85	21	363	524	106	376
P2	427	435	8	500	73	21	362	534	99	381
P3	415	423	8	502	87	12	361	515	92	375
P4	412	422	10	502	90	12	371	528	106	397
P5	426	459	33	514	88	13	376	558	99	395
P6	415	449	34	502	87	14	418	554	105	371

^a Difference in wavelength of absorption band between solution and film.
 ^b Emission wavelength. ^c Stokes shift in solution. ^d Quantum yield (evaluated with quinine sulfate dissolved in 1 N sulfuric acid).
 ^e Wavelength of excitation light. ^f Stokes shift in film.



Fig. 4 (a) Optical photograph, (b) differential interference contrast (DIC) micrograph and (c and d) SEM images of the **P2** film in neutral and oxidized states.

tetra-n-butylammonium perchlorate used as a supporting electrolyte. The voltages of -0.8 V and +0.8 V vs. Ag/Ag⁺ are applied to the polymer film for the electrochemical dedoping and doping, respectively. The electrochemical dedoping and doping of the polymer produce the neutral and oxidized forms of the conjugated main chain, respectively. These forms are represented by benzonoid and guinoid structures, respectively (for instance, see Fig. 4c and d). In the doping state, the perchlorate anion is located as a dopant near the oxidized polymer bearing positive charges. Fig. 4 depicts an optical photograph, differential interference contrast (DIC) micrograph and scanning electron microscope (SEM) images of the P2 film in neutral and oxidized states. The P2 film exhibits electrochromism between the neutral and oxidized states, which is generated by electrochemical dedoping and doping. The yellow color of the P2 film in the neutral state becomes black in the oxidized state (Fig. 4a). The drastic change in color of the film is confirmed in the DIC micrographs of the neutral and oxidized P2 films (Fig. 4b). The SEM images show that the film surfaces in the neutral state are smooth and flat, while the oxidized states have rough globular morphologies. These morphologies reversibly change between the neutral and oxidized states, which is similar to the electrochromic changes that will be shown below.

Fig. 5 shows the UV-Vis absorption spectra of the **P2** film in the neutral and oxidized states. The neutral and oxidized states are reversibly generated through electrochemical dedoping and doping procedures, respectively. The absorption band at 420 nm in the neutral state and the broad band located from 500 to 800 nm in the oxidized state are responsible for the yellow and black colors in the dedoped and doped films, respectively. In other words, the reversible electrochromic change occurs through the electrochemical doping and dedoping.

3.6. Linearly polarized fluorescence (LPF)

We carried out the macroscopic alignment of the polymers by a rubbing technique. The polymers were heated to the LC temperature region on the quartz substrates and rubbed with a glass rod. Then the polymers were cooled to room temperature to yield macroscopically aligned films. Polarized optical



Fig. 5 UV-Vis absorption spectra of the **P2** film in neutral and oxidized states. The neutral and oxidized states are reversibly generated through electrochemical dedoping and doping procedures, respectively.

microscopic measurements of the aligned film showed that the LC texture was maintained even in the glassy state, and that the multidomain of the nematic LC phase was uniaxially aligned along the rubbing direction.

Fig. 6 shows the linearly polarized fluorescence (LPF) spectra of the aligned **P2** film on a quartz substrate in which the polarizer was placed parallel or perpendicular to the rubbing direction. The LPF intensity at 534 nm for unpolarized excitation light ($\lambda = 381$ nm) in the parallel (I_{\parallel}) direction was larger than that in the perpendicular one (I_{\perp}). The dichroic ratio (R) of the aligned film was evaluated to be 2.6, where R is defined as $R = I_{\parallel}/I_{\perp}$.³⁹⁻⁴¹ It is evident that the aligned **P2** film has an anisotropy in fluorescence, serving for a linearly polarized luminescent material.

Fig. 7 shows optical micrographs of the macroscopically aligned **P2** film in the neutral and oxidized states. Bright and dark optical textures are observed when the polarizer is set parallel and perpendicular to the aligned direction of the film, respectively. Such linearly polarized dichroism can be seen in both neutral (Fig. 7a and c) and oxidized states (Fig. 7b and d). The reversible electrochromism between the neutral and oxidized states occurs in the parallel and perpendicular directions of the aligned **P2** film. It can be remarked that this aligned film of the PEDOT derivative has linearly polarized electrochromism.



Fig. 6 Linearly polarized fluorescence (LPF) of aligned **P2** films. The dichroic ratio $(I_{\parallel}/I_{\perp})$ was 2.6. The aligned **P2** film on a quartz substrate (size: 10 × 50 mm) shows LPF upon excitation with UV light ($\lambda = 365$ nm, 16 W handy lamp).



Fig. 7 The reversible electrochromic behavior of a macroscopically aligned **P2** film between the neutral and oxidized states. The polarizer is set to (a and b) parallel and (c and d) perpendicular to the aligned directions of the film in the neutral and oxidized states. (e) A photo of the **P2** film with the neutral and oxidized states.

Interestingly, the electrochromism of the film occurs upon electrochemical doping and dedoping (Fig. 7e). The photo in this figure was acquired without a polarizer. The reversible electrochromism is confirmed in terms of the parallel direction (Fig. 7a and b) and the perpendicular one (Fig. 7c and d), although the differences between the brightness and contrast are diminished because of the polarizer in the measurement.

3.7. Chiral induction and circular dichroism (CD) spectra

Fig. 8 shows the POMs of P2 and P5 in the chiral nematic LC (N*-LC) phase. The N*-LC phase is induced by adding a chiral compound as a chiral inducer to the polymer in the N-LC phase. The chiral compound (R)-CB06-BINOL is an axially chiral binaphthyl derivative substituted with cyanobiphenyl and

hexamethylene moieties at the 2 and 2' positions of the binaphthyl ring.^{33,34,38-40} The mole ratio of the polymer to chiral inducer in the mixture was 100 : 5. The POMs show fingerprint textures with stripes (striae) of about 1 μ m that correspond to a half helical pitch of the N*-LC. This means that the helical pitches of **P2** and **P5** in N*-LC phases are 2 μ m, because the distance between the stripes (striae) of the N*-LC phase. It may be useful to note here that the helical pitch of the N*-LC pis and 360° in one-handed helical π -stacked structure. In other words, three stripes (striae) of the fingerprint texture observed in POM correspond to the helical structures with twisting angles of 0°, 180° and 360°, at which the birefringences are the same values, giving the stripes (striae) in the POM.

Fig. 9 shows the UV-Vis and CD spectra of the polymer films with N*-LC phases. The polymer films were prepared by adding the chiral compound, (R)- or (S)-CB06-BINOL to the PEDOT derivatives at room temperature and then annealing the polymer films at the N-LC temperature, followed by cooling them to room temperature to attain the glass state. The N*-LC structure and morphology of the LC conjugated polymer formed at high temperature for LC phase are well retained even after cooling to the temperature corresponding to the glass state.35,41,42 It is apparent that the P2, P4 and P5 films show bisignate Cotton effects in the absorption region of the π - π * transitions for the main chain. These results imply that the polymers form interchain helically π -stacked structures. In contrast, P1 and P3 give monosignate Cotton effects, suggesting the formations of intrachain helically twisted structures. These results are also observed in the case of the usage of PCH-substituted binaphthyl derivatives as chiral inducers.

P6 gives a much larger Cotton effect than the other polymers. **P6** shows a monosignate Cotton effect in the 400 to 550 nm region, corresponding to the absorption of the polymer chain. This implies that large chirality is induced in the polymer chain. At the same time, a bisignate Cotton effect with a high intensity



Fig. 8 POMs of P2 and P5 in the N*-LC phases. The N*-LC phase is induced by adding a chiral inducer, (*R*)-CB06-BINOL, to the polymer in the N-LC phase. The mole ratio of polymer to chiral induced was 100 : 5. The POMs show fingerprint textures with striae.



Fig. 9 UV-Vis and CD spectra of the polymer films on ITO glasses: (a) P1 and (b) P2. The polymer films were prepared by adding a chiral inducer, (R)- or (S)-CB06-BINOL, to the PEDOT derivatives at the N-LC temperature and cooling the mixtures to room temperature.

was observed in the region from 250 to 350 nm, which corresponds to the absorption of side chains with CB moieties. Note that the scale of the vertical axis in the CD spectra for Fig. S3-c† is nearly eight times larger than the others. It remains unclear why such a large Cotton effect is observed in this region, and this will require further investigation.

The polymers showed no notable shift in the absorption bands for the UV-Vis spectra before and after the addition of the chiral inducer. Meanwhile, the polymers showed Cotton effects in the CD spectra upon the addition of the chiral inducer. Thus, the positive or negative Cotton effect depends on the configuration (chirality) of the chiral inducer. Cotton effects for mirror images were observed, depending on the (R)- and (S)-configurations of the chiral inducer. The polymer film showed no Cotton effect in the CD spectra without the chiral inducer, even if the polymer was annealed at the N-LC temperature and followed by cooling to room temperature. As shown in Fig. S2-S4 (ESI[†]), there is essentially no difference between the phenylcyclohexyl (PCH)and cyanobiphenyl (CB)-substituted binaphthyl derivatives as chiral inducers, irrespective of whether the side chain substitution (PCH or CB) for the polymer is the same as the substituent of the binaphthyl derivative used as the chiral inducer. This is mainly due to the low concentration (5% mole ratio) of the chiral inducer, which cannot affect the miscibility of the chiral inducer with the polymer.

4. Conclusion

Copolymer-type LC PEDOT derivatives with PCH- and CB-type LC side chains were synthesized. All of the polymers showed

thermotropically nematic LC phases of an enantiotropic nature. Macroscopically aligned polymers, prepared by rubbing in their N-LC phases, exhibited linear dichroism in the absorption and fluorescence spectra. The morphologies of the polymer films are found to reversibly change between the neutral and oxidized states through electrochemical dedoping and doping procedures. The reversible electrochromism between the neutral and oxidized states also occurred in the parallel and perpendicular directions of the aligned film, producing anisotropic electrochromism. Chiral nematic LC (N*-LC) phases were induced in the polymers by the addition of the chiral binaphthyl compound as a chiral inducer into the LC PEDOT derivatives. The polymer films with the induced N*-LC phase exhibited circular dichroism in absorption, suggesting the formation of interchain helically π stacked structures or an intrachain helically twisted one, depending on the structures of the polymers. The present liquid crystalline PEDOT derivatives exhibiting reversible anisotropic electrochromism and linearly and circularly polarized dichroism could be used as multifunctional materials for advanced plastic electronics.

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