Synthesis of liquid crystalline compounds containing thiol groups at both ends as reactive substituents and their immobilization on a gold substrate

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ABSTRACT

In this study, we synthesized four bifunctional compounds containing two alkoxy groups, at which reactive thiol groups were introduced. Among these compounds, a compound with four and five methylene units in each alkyl chain did not exhibit a liquid crystalline phase. The other three compounds exhibit one or two liquid crystalline phases, and the number of liquid crystalline phases depends on the number of methylene units in their alkyl chains. These liquid crystalline compounds were oriented in one direction using a rubbed alignment film, and the oriented compounds were transferred onto a gold substrate. Using these gold substrates as working electrodes, cyclic voltammetry (CV) was performed with potassium ferricyanide as the redox probe. As the deposition time increased, the current intensities of a pair of redox waves gradually decreased. This trend suggests that with longer deposition times, a larger amount of the liquid crystalline compound was transferred to the gold substrate surface. These findings shed light on the relationship among the structures of bifunctional compounds, their liquid crystalline behavior, and their alignment properties on gold substrates, thereby offering valuable insights for potential applications in nanotechnology and materials science.

Introduction

Electronic devices using organic compounds are attracting significant interest for application

in wearable and flexible devices because of their low cost, light weight, flexibility, and

printability [1]. In organic electronic devices, organic photo- and electroactive materials are

sandwiched between electrodes made of inorganic compounds or coated onto their surfaces.

Therefore, the compatibility between inorganic electrodes and organic materials is expected to

have a significant impact on device performance. From this perspective, a technique for

introducing organic self-assembled monolayers (SAMs) onto the surface of inorganic

electrodes has been used to control the performance of organic optoelectronic devices. For

example, in OFETs, a silicon (Si) substrate coated with silicon dioxide (SiO_2) is used as the

gate electrode (Si) and insulating layer (SiO_2), and a charge-transporting organic compound is

applied to the SiO_2 surface [2,3]. In this case, it has been reported that the treatment of the SiO_2

surface with a silane coupling agent, such as octadecyltrichlorosilane (ODTS), can form a SAM

film through the formation of covalent bonds through a condensation reaction between the

chlorosilyl (Si-Cl) group of ODTS and the silanol (Si-OH) group on the surface of SiO_2 to introduce hydrophobic organic groups on the hydrophilic SiO_2 surface, resulting in a significant change in wettability and improvement of the crystallinity of the organic film, which can improve the device performance. Although this technique can control the morphology of an organic semiconductor thin film, it cannot control the orientation of the molecules in the film. If the orientation of organic semiconductor molecules can also be controlled, it is expected to improve the performance of devices and create new functions, such as enhanced charge-carrier mobility in OFETs and the realization of anisotropic displays in OECDs.

From this viewpoint, we conceived the idea that by introducing SAMs in which liquid crystalline (LC) molecules are aligned in one direction in the in-plane direction of the substrates, the orientation of organic functional molecules fabricated on top of the SAM film can be controlled. LC compounds are unique materials with both anisotropic orientation like crystals and fluidity like liquids, and the direction of their orientation can be controlled by a rubbing treatment or the application of an electric field [4]. Generally, LC molecules contain both rigid mesogens for anisotropic orientation and flexible alkyl spacers for fluidity. The fluidity of LC compounds can effectively make contact with the substrate surface. However, even if the LC compounds are simply transferred to the substrate surface, their orientation can be easily perturbed by thermal and/or mechanical energy. The introduction of anchoring groups that can react with inorganic electrodes, such as the chlorosilyl group, maintains the orientation of the

LC molecules on the electrodes. Although previous studies introduced LC compounds as SAM films, they were immobilized on the substrate surface at only one end of the molecule, and the mesogenic moiety of the LC compound was oriented in the out-of-plane direction of the substrate surface [5]. Therefore, no orientation-ordered structure was introduced on the plane parallel to the substrate surface, as was the case for ODTS. In contrast, the authors previously introduced anchoring groups (trichlorosilyl groups) at both ends of an LC compound (**SiCl-10BP10**, Figure 1 (a)) and succeeded in developing a SAM film in which the mesogen moieties were aligned in the in-plane direction of the substrate surface [6]. However, the immobilization of LC molecules using a trichlorosilyl group as an anchoring group is limited because they can be introduced to metal oxide substrates such as SiO_2, titanium oxide (TiO_2), and indium tin oxide (ITO), but they cannot be introduced on metal electrode materials such as gold and platinum. In addition, the chlorosilyl group is thermally and chemically unstable; therefore, when the sample is heated to induce a liquid crystalline state, part of the sample is thermally decomposed, and when the sample is left in air without dry treatment, the chlorosilyl groups are easily hydrolyzed.

In this study, novel LC compounds with thiol groups at both ends (**SH-*m*BP*n***; Figure 1 (b)) were synthesized. Thiol groups can be anchored on metal surfaces such as gold and platinum [7-9]. In addition, because the thiol group is more thermally stable than the chlorosilyl group, the reactive substituent does not decompose even when the LC compound is heated to

form an LC state. The chlorosilyl group also reacts with atmospheric moisture, whereas the

thiol group has excellent chemical stability, allowing the LC phase to be identified using

polarized light microscopy and X-ray diffraction (XRD). Furthermore, it allows for

immobilization on gold substrates, thus enabling the evaluation of SAM film immobilization

using conductivity. The phase structures of the four novel compounds with thiol groups at both

ends were identified using differential scanning calorimetry (DSC), polarized optical

microscopy (POM), and XRD. The LC compounds were then aligned on the rubbed film and

immobilized on the gold substrate surface by transferring them to the gold substrate surface
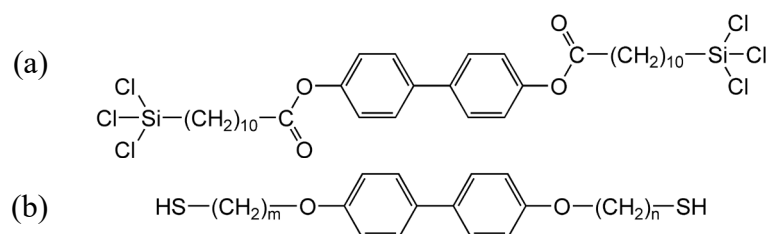
while maintaining their alignment.

Figure 1. Chemical structures of (a) **SiCl-10BP10** and (b) **SH-*m*BP*n*** (*m* = 4, *n* = 5: **SH-4BP5**; *m* = *n* = 5: **SH-5BP5**; *m* = 3, *n* = 11: **SH-3BP11**, *m* = 5, *n* = 11: **SH-5BP11**).
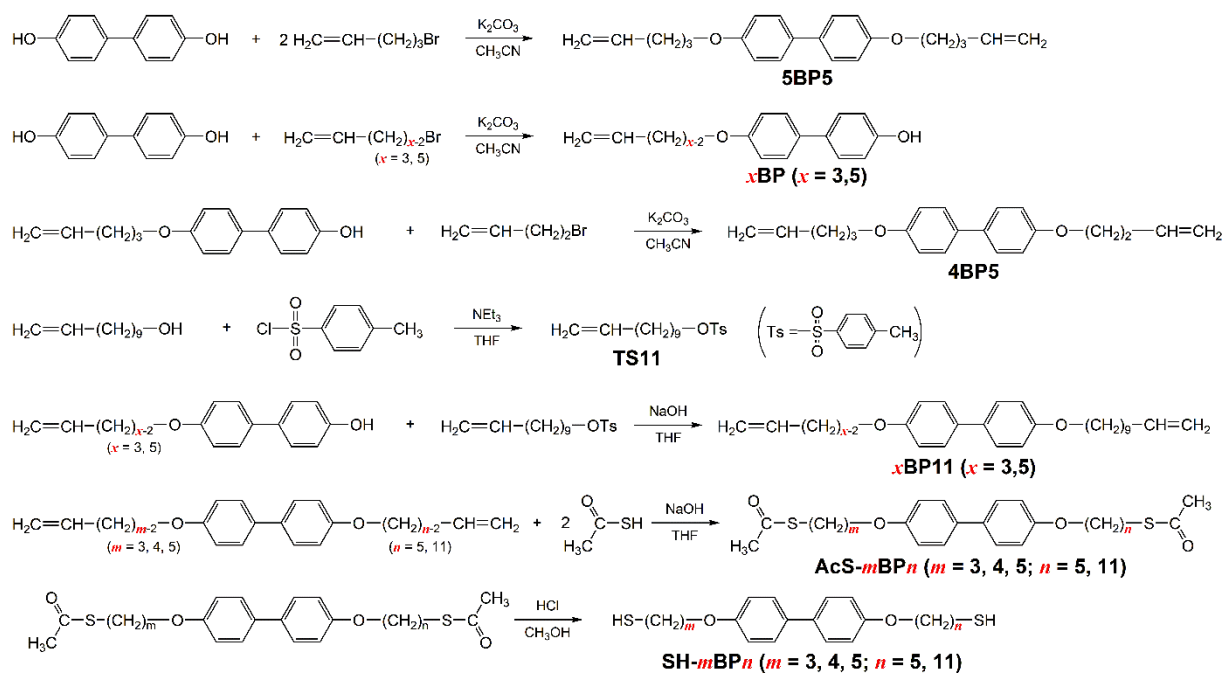
Experimental

Materials

Acetonitrile, tetrahydrofuran (THF), methanol, dichloromethane, and *n*-hexane were purified

using standard methods and used immediately after purification. 1,1′-Biphenyl-4,4′-diol, 5-

bromo-1-pentene, 4-bromo-1-butene, 3-bromo-1-propene, 11-undecen-1-ol, 2,2'-azobis(isobutyronitrile), and thioacetic acid were purchased from Tokyo Chemical Industry and used without further purification. Hydrochloric acid, potassium carbonate, and tosyl chloride were purchased from Nacalai tesque. Silica (60N, irregular, neutral, and particle size 63-200μm) was purchased from Kanto Chemical. 10-Undecen-1-yl tosylate (**Ts11**) was synthesized from 10-undecen-1-ol and tosyl chloride, according to a previous report [10].

Synthesis of SH-mBPn

A typical synthetic procedure for **SH-*m*BP*n*** is shown in Scheme 1. The detailed synthetic procedure for **SH-5BP5** is presented below. Because the synthetic methods for the other compounds are similar to those of **SH-5BP5**, their synthetic methods are briefly described, and their spectral data are summarized in the supporting information.

Scheme 1.

4,4'-Bis(4-penten-1-yloxy)-1,1'-biphenyl (5BP5)

To an acetonitrile (180 mL) solution of 1,1′-biphenyl-4,4′-diol (10.0 g, 53.7 mmol) and an excess amount of potassium carbonate, 5-bromo-1-pentene (11.4 g, 132 mmol) was slowly added at room temperature. The reaction mixture was refluxed for 12 h. The reaction mixture was poured into 1N hydrochloric acid and extracted twice with dichloromethane (100 mL each). The combined organic extracts were washed with an aqueous solution of sodium hydrogen carbonate and water and then dried over anhydrous sodium sulfate. The solvent was removed using a rotary evaporator. Chloroform (200 mL) was added to the residue, and the solution was refluxed for one hour. After cooling to room temperature, the resulting solution was subjected to suction filtration. The solvent was removed from the filtrate, and the residue was purified by

silica gel column chromatography (eluent: dichloromethane). White solid, 7.73 g (24.0 mmol), yield: 45 %.

^{1}H NMR (500 MHz, CDCl$_3$, δ, ppm): 7.46 (d, 4H, C$_6$**H**$_4$, J = 8.80 Hz), 6.94 (d, 4H, C$_6$**H**$_4$, J = 8.80 Hz), 5.87 (ddt, 2H, CH$_2$=C**H**-CH$_2$-, J = 6.66, 10.21, 17.12 Hz), 5.08 (ddt, 2H, C**H**$_2$=CH-, J = 1.65, 1.84, 17.12 Hz), 5.01 (ddt, 2H, C**H**$_2$=CH-, J = 1.22, 1.84, 10.21 Hz), 4.00 (t, 4H, -CH$_2$C**H**$_2$O-, J = 6.48 Hz), 2.26 (dddt, 4H, CH$_2$=CH-C**H**$_2$-, J = 1.22, 1.65, 6.60, 6.66 Hz), 1.90 (tt, 4H, -CH$_2$C**H**$_2$CH$_2$O-, J = 6.42, 6.60 Hz). HRMS (APCI) m/z calcd for C$_{22}$H$_{27}$O$_2$ 323.20056 ([M+H]$^+$), found 323.20068 ([M+H]$^+$).

4,4'-Bis(5-acetylsulfanyl-pent-1-yloxy)-1,1'-biphenyl (AcS-5BP5)

To a toluene (50 mL) solution of **5BP5** (2.30 g, 7.14 mmol) and 2,2'-azobis(isobutyronitrile) (AIBN) (0.71 g, 4.35 mmol), thioacetic acid (5 mL, 1.08 g/mL, 70.9 mmol) was slowly added at room temperature. The reaction mixture was heated at 70 °C for 12 h. After confirming by NMR that the signals originating from the starting material disappeared, the reaction solution was cooled to room temperature and added to a saturated aqueous sodium carbonate solution to quench the reaction. Dichloromethane was added to the solution, which was washed with water and dried over anhydrous sodium sulfate. The solvent was removed using a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: dichlorometane/*n*-hexane=2/1 by volume). Yellow solid, 2.85 g (6.01 mmol), yield: 84 %.

¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.46 (d, 4H, C₆*H*₄, *J* = 8.80 Hz), 6.93 (d, 4H, C₆*H*₄, *J* = 8.80 Hz), 3.98 (t, 4H, -CH₂C*H*₂O-, *J* = 6.42 Hz), 2.91 (t, ,4H, -CH₂C*H*₂S-, *J* = 7.28 Hz), 2.33 (s, 6H, -S(CO)C*H*₃), 1.82 (tt, 4H, -CH₂C*H*₂CH₂O-, *J* = 6.42, 7.28 Hz), 1.66 (tt, 4H, -CH₂C*H*₂CH₂S-, *J* = 7.22, 728 Hz), 1.55-1.60 (m, 4H, -O(CH₂)₂C*H*₂(CH₂)₂S-). HRMS (ESI) *m/z* calcd for C₂₆H₃₄O₄NaS₂ 497.17907 ([M+Na]⁺), found 497.17850 ([M+Na]⁺).

4,4'-Bis(5-mercapto-pentan-1-yloxy)-1,1'-biphenyl (SH-5BP5)

AcS-5BP5 (2.29 g, 4.83 mmol) was added to a 300 mL two-neck round-bottom flask filled with argon. Methanol (180 mL) with argon bubbled through it for 20 minutes was added to the flask, followed by 1M hydrochloric acid (HCl) in methanol (40 mL) and heated at 80 °C. After confirming that the signal originating from the starting material had completely disappeared from the NMR spectrum, the reaction solution was cooled to room temperature and filtered with suction. The solvent was removed from the filtrate using a rotary evaporator, and the residue was recrystallized from *n*-hexane to obtain white crystals. White solid, 1.53 g (3.92 mmol), yield: 81 %.

¹H NMR (500 MHz, CDCl₃, δ, ppm): 7.45 (d, 4H, C₆*H*₄, *J* = 8.81 Hz), 6.94 (d, 4H, C₆*H*₄, *J* = 8.81 Hz), 3.99 (t, 4H, -CH₂C*H*₂O-, *J* = 6.42 Hz), 2.57 (dt, 4H, -CH₂C*H*₂SH, *J* = 7.27, 7.82 Hz), 1.80 (tt, 4H, -CH₂C*H*₂CH₂O-, *J* = 6.42, 7.15 Hz), 1.71 (tt, 4H, -CH₂C*H*₂CH₂SH, *J* = 7.22, 7.27 Hz), 1.59 (tt, 4H, -O(CH₂)₂C*H*₂(CH₂)₂SH, *J* = 7.15, 7.22), 1.37 (t, 2H, -CH₂S*H*, *J* = 7.82

Hz). ^{13}C NMR (125 MHz, CDCl$_3$, δ, ppm): 158.23, 133.52, 127.81, 114.84, 67.86, 33.88, 28.91, 25.07, 24.68. HRMS (APCI) m/z calcd for C$_{22}$H$_{30}$O$_2$S$_2$ 390.16817 (M$^+$), found 390.16815 (M$^+$).

4'-(2-Propen-1-yloxy)-1,1'-biphenyl-4-ol (3BP) and 4'-(4-penten-1-yloxy)-1,1'-biphenyl-4-ol (5BP)

3BP and **5BP** were synthesized in the similar manner to the synthesis of **5BP5**, by changing the feed ratio of starting materials of biphenol and alkenylbromide. White solid, yield: 58 % (**3BP**). White solid, yield: 49 % (**5BP**).

4-(3-Buten-1-yloxy)-4'-(4-penten-1-yloxy)-1,1'-biphenyl (4BP5)

4BP5 was synthesized similarly to **5BP5** by changing the feed ratio of the starting materials of 5BP instead of biphenol and alkenylbromide. White solid; yield: 49 %.

4-(2-Propen-1-yloxy)-4'-(10-undecen-1-yloxy)-1,1'-biphenyl (3BP11) and 4-(4-penten-1-yloxy)-4'-(10-undecen-1-yloxy)-1,1'-biphenyl (5BP11)

3BP11 and **5BP11** were synthesized from the reaction of *x*BP (*x* = 3, 5) and 10-undecen-1-yl tosylate (**Ts11**) via a condensation reaction between 10-undecen-1-ol and tosyl chloride. White solid, yield: 91 % (**3BP11**). White solid, yield: 90 % (**5BP11**).

4-(4-Acetylsulfanyl-butan-1-yloxy)-4'-(5-acetylsulfanyl-pent-1-yloxy)-1,1'-biphenyl (AcS-4BP5), 4-(3-acetylsulfanyl-propan-1-yloxy)-4'-(11-acetylsulfanyl-undecan-1-yloxy)-1,1'-biphenyl (AcS-3BP11), and 4-(5-acetylsulfanyl-pent-1-yloxy)-4'-(11-acetylsulfanyl-undecan-1-yloxy)-1,1'-biphenyl (AcS-5BP11)

AcS-4BP5, **AcS-3BP11** and **AcS-5BP11** were synthesized in a manner similar to that for **AcS-5BP5** using the corresponding bis(alkenyloxy)biphenyl compounds, ***m*BP*n*** (***m*** = 3, 4, 5; ***n*** = 5, 11). White solid, yield: 57 % (**AcS-4BP5**). White solid, yield: 57 % (**AcS-3BP11**).-White solid, yield: 96 % (**AcS-5BP11**).

4-(4-Mercapto-butan-1-yloxy)-4'-(5-mercapto-pent-1-yloxy)-1,1'-biphenyl (SH-4BP5), 4-(3-mercapto-propan-1-yloxy)-4'-(11-mercapto-undecan-1-yloxy)-1,1'-biphenyl (SH-3BP11), and 4-(5-mercapto-pent-1-yloxy)-4'-(11-mercapto-undecan-1-yloxy)-1,1'-biphenyl (SH-5BP11)

SH-4BP5, **SH-3BP11** and **SH-5BP11** were synthesized in a similar manner as **SH-5BP5** using the corresponding bis(acetylsulfanylalkoxy)biphenyl compound, **AcS-*m*BP*n*** (***m*** = 3, 4, 5; ***n*** = 5, 11). White solid, yield: 88 % (**SH-4BP5**). White solid, yield: 46 % (**SH-3BP11**). White solid, yield: 37 % (**SH-5BP11**).

Preparation of LC-SAMs on gold substrates.

LC-SAMs were prepared on inorganic substrates as previously described [6]. Briefly, a

precursor of polyimide resin (Nissan Chemical Industries, SUNEVER) for the alignment of liquid crystalline molecules was spin-coated on a slide glass and heated at 80 °C for 5 min, then 250 °C for 1 h to give a polyimide film. The film was rubbed using a rubbing cloth (Yoshikawa Chemical, YA-20-R) and washed via sonication in water/isopropanol (1/1) for 1 min. A dichloromethane solution of **SH-*m*BP*n*** was drop-casted onto the rubbed polyimide film, heated at 100 °C to evaporate the solvent. Thereafter, the sample surface was flattened by melting, and then cooled to 89 °C to obtain the liquid crystalline phase. The gold substrate (thickness:10 nm) was prepared by vacuum-depositing onto a mica substrate (Okenshoji Co., Ltd.) that had been freshly cleaved to a thickness of approximately 50 μm. The obtained gold substrate was annealed at 500 °C for 6 h in air in an electric furnace. The gold substrate was placed on **SH-*m*BP*n*** in the liquid crystalline phase for 6 – 24 h. Finally, the substrate was rinsed with dichloromethane to remove unreacted **SH-*m*BP*n*** and dried overnight in a dry chamber. The introduction of **SH-*m*BP*n*** onto the gold substrate was confirmed by cyclic voltammetry (CV) measurements of potassium ferricyanide.

Instruments

^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer (Varian Inc., NMR System 500). Mass spectrometry measurements were performed using a mass spectrometer (Thermo Fisher Scientific, LTQ Orbitrap XL). The transition temperatures of the compounds were

determined using a differential scanning calorimeter (Shimadzu, DSC-60) operating at a scanning rate of ± 5 °C/min for both heating and cooling cycles under nitrogen flow (50 mL/min). Polarized optical microscopy (POM) measurements were performed using a Nikon HFX-DX microscope. To identify each phase of the compounds, X-ray diffraction (XRD) was performed at various temperatures using a Bruker AXS D8 ADVANCE. A gold electrode was fabricated using a vacuum evaporation device equipped with an electron gun (SANVAC ED-1500R) and annealed in a small programmable electronic furnace (AZ ONE, MMF). Cyclic voltammetry (CV) was performed using a potentiostat/galvanostat (Hokuto Denko HZ-3000) with a three-electrode system.

Results and Discussion

Because the viscosity of **SiCl-10BP10** with polar ester groups was high in the LC phase, it was less efficient in transferring LC compounds to the substrate. Therefore, in this study, we synthesized four compounds without ester groups, with alkyl spacers and different carbon chain numbers (Scheme 1).

In all compounds, 4,4'-biphenol is used as the starting material, and two alkenyl groups are introduced by the Williamson coupling reaction [11]. The bromoalkenes ($CH_2=CH-(CH_2)_{x-2}-Br$, x = 3, 4, 5) have been reacted with potassium phenolate derivatives prepared from potassium carbonate and biphenol or alkenyloxybiphenol in acetonitrile to give alkenylphenyl ethers (**3BP**,

5BP, **4BP5**, and **5BP5**), which were isolated after chromatographic purification in approximately 50 % yield. 11-Bomo-1-undecene is also commercially available but is expensive to purchase on a laboratory scale. Therefore, we synthesized 10-undecen-1-yl tosylate (**Ts11**) by a condensation reaction between 10-undecen-1-ol and tosyl chloride [10]. **3BP11** and **5BP11** were synthesized by the reaction of **TS11** and **3BP** or **5BP** in an aqueous solution of sodium hydroxide in a reasonable yield.

Thioacetate groups at both terminal alkyl chains were introduced by the addition of thioacetic acid to ***m*BP*n*** using 2,2'-azobis(isobutyronitrile) (AIBN) as radical initiator at 70 °C [12]. Thethioacetates, **AcS-*m*BP*n***, were obtained in 57-91 % yield after chromatography on silica gel. The desired bis-thiol groups were introduced by heating in a mixed solution of methanol and hydrochloric acid. The resulting compounds were identified using nuclear magnetic resonance and mass spectroscopy.

The DSC measurements of the obtained compounds were performed (Figure 2), and their phase transition temperatures are summarized in Table 1. The DSC curve of the heating process of **SH-4BP5** shows only one endothermic peak, whereas that of the cooling process shows one exothermic peak. Polarized optical microscopy (POM) of this sample in the temperature range around these peaks revealed that the endothermic peak during the heating process was ascribed to the phase transition from the crystalline (C) phase to the isotropic liquid (ISO) phase, and the exothermic peak during the cooling process was ascribed to the phase transition from the ISO
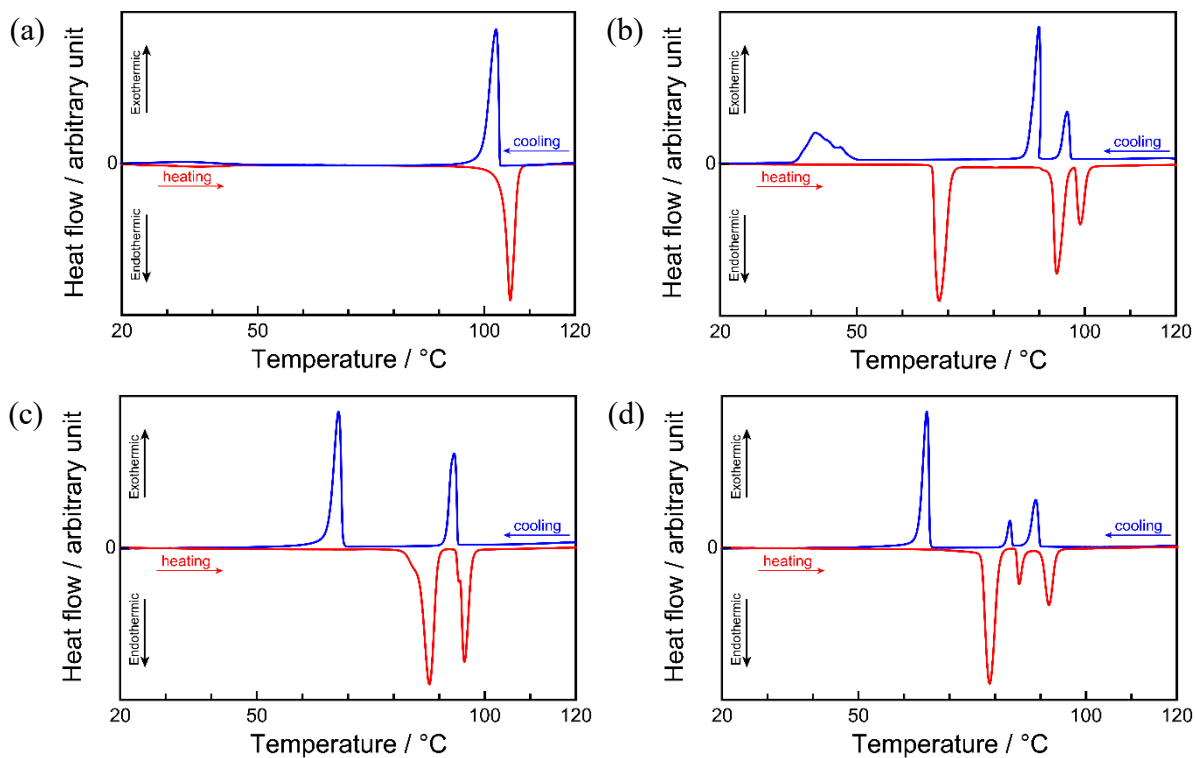
phase to the C phase. This suggests that **SH-4BP5,** with short alkyl spacers (4 + 5 = 9 carbon chains in total), does not exhibit liquid crystallinity. Therefore, we synthesized three compounds with more carbon chains than **SH-4BP5**: **SH-5BP5**, **SH-3BP11,** and **SH-5BP11** with 10, 14, and 16 carbon chains, respectively. DSC measurements of these three compounds showed that all had multiple endothermic peaks during the heating process and exothermic peaks during the cooling process, suggesting the presence of mesophases between the C and ISO phases. For **SH-3BP11**, there were two endothermic peaks upon heating and two exothermic peaks upon cooling, whereas, for **SH-5BP5** and **SH-5BP11**, there were three endothermic peaks upon heating and three exothermic peaks upon cooling. It appears that if the lengths of the two alkyl spacers introduced into the compound differ significantly, the orientation direction of the molecules in the mesophase is not sufficiently maintained; therefore, they may transition to an isotropic liquid without the appearance of a second mesophase. The clearing temperatures from the crystal or mesophase to the isotropic liquid decreased with an increase in the total number of methylene units introduced into the two alkyl spacers. The phase transition temperatures from the crystal to the mesophase and vice versa for **SH-3BP11** were higher than those for **SH-5BP5** and **SH-5BP11**.

Table 1. Summary of phase transition temperatures of **SH-*m*BP*n***.

	heating process[a]			cooling process[a]		
	C → LC1	LC1 → LC2	LC2 → ISO	C ← LC1	LC1 ← LC2	LC2 ← ISO
SH-4BP5	-	-	106[b]	-	-	101[c]
SH-5BP5	66	92	97	43	91	97
SH-3BP11	87[d]	-	95	67[d]	-	92
SH-5BP11	79	85	92	65	83	89

a) 5 degree/min, b) transition temperature from C to ISO, and c) transition temperature from ISO to C.

d) For convenience, a liquid crystalline phase in **SH-3BP11** is referred to as LC1.

Figure 2. DSC curves of (a) **SH-4BP5**, (b) **SH-5BP5**, (c) **SH-3BP11**, and (d) **SH-5BP11**.

In **SH-5BP5**, the POM image (Figure 3 (a)) of the intermediate phase LC1 shows a banded focal conic structure, while that of the intermediate phase LC2 shows a fan-shaped focal conic structure. Variable-temperature powder X-ray diffraction (VT-XRD) measurements were performed to identify the intermediate layers (Figure 3 (b)). The XRD pattern at 30 °C (C phase) shows several sharp diffraction peaks characteristic of the crystalline layer. On the other hand, in the XRD pattern at 80 °C (LC1 phase), a characteristic diffraction peak at $2\theta = 4.22°$ was observed. This 2θ value indicates that there is a d-spacing of 20.8859 Å in LC1. Since this distance is shorter than the molecular length of **SH-5BP5** (about 25 Å) in the long-axis direction, the LC1 phase can be identified as a smectic C (SmC) phase with molecules aligned at about 30° inclination in the long-axis direction. However, as no clear diffraction peaks were observed in the XRD pattern of the LC2 phase, it was most likely a nematic (N) phase. However, because the focal conic structure characteristic of the smectic phase was observed in the POM image, the LC2 phase was characterized as the smectic A (SmA) phase. The reason why clear diffraction patterns characterized by the SmA phase was not observed is unclear and will be investigated later.
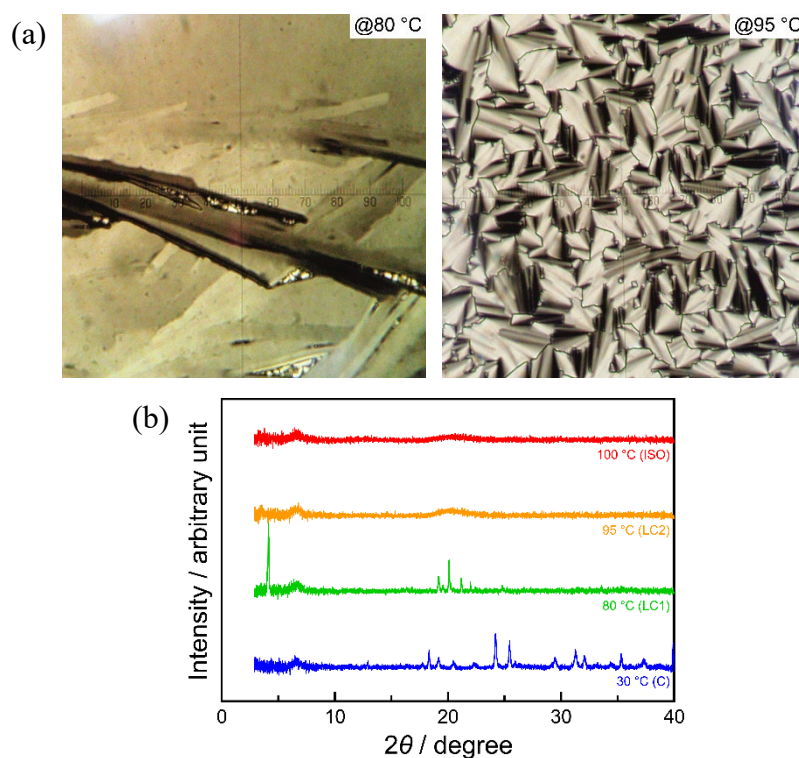
Figure 3. (a) POM images and (b) XRD patterns of **SH-5BP5** measured at various

temperatures.

To orient the LC molecule **SH-*m*BP*n*** in one direction, we first optimized the conditions

for rubbing the LC alignment film. The number of rubbing treatments with the rubbing cloth

was varied from 1 to 15, and the orientation of the LC molecules was investigated by observing

the intensities of the POM light transmitted through the LC compounds using a photodiode

(Figure 4). When the sample was rotated by 45°, the intensities of the polarized light transmitted

through the LC molecules changed, resulting in the brightness and darkness shown in the figure,

confirming that the LC molecules were oriented in the direction of the rubbing of the alignment

film. In the LC molecules formed on the alignment film rubbed thrice, the changes in the

intensities of the transmitted light were somewhat inhomogeneous. In contrast, for the LC

molecules fabricated on the alignment film that was rubbed 15 times, the changes in the

transmitted light intensities were uniform, confirming that the LC molecules were completely
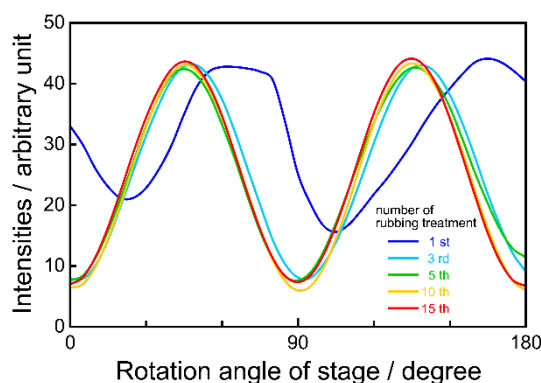
oriented in one direction.

Figure 4. Changes in intensities of transmitted POM light through liquid crystalline

compounds on rubbed films.

Next, we investigated the conditions for the preparation of the SAM films of the LC

compound **SH-*m*BP*n***. The concentration of the LC compounds in dichloromethane was

adjusted to 50 mg/mL. This solution was dropped onto the LC alignment film and heated to

100 °C on a hot plate to evaporate the solvent. At this temperature, all **SH-*m*BP*n*** were in the

ISO phase. After confirming that the solvent was removed and the sample melted, the hot plate

was cooled to the temperature range where **SH-*m*BP*n*** exhibited the LC1 phase. In order to

investigate the influence of cooling rate on the alignment of LC molecules, two samples were

prepared: (1) the first sample was prepared by rapid cooling, and (2) the second sample was

prepared by slow cooling at 0.1 °C/min. The degree of alignment of these samples was also

investigated by monitoring the intensity change of the POM light transmitted through the LC

molecules. The change in the POM light intensity was more obvious when the sample was

cooled slowly (Figure 5), suggesting that the LC compounds obtained by slow cooling showed
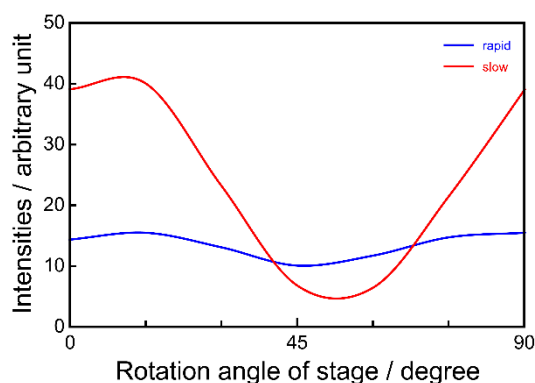
a more homogeneous alignment of molecules.

Figure 5. Changes in intensities of transmitted POM light through liquid crystalline

compounds with different cooling conditions.

Finally, the ability of the LC compounds, as developed in this study, to immobilize on gold

substrates was investigated. A dichloromethane solution of the compound was dropped onto the

LC alignment film that had undergone rubbing treatment 15 times, heated to evaporate the

solvent, melted, and cooled to maintain the LC1 phase. The LC compound was then transferred

to a gold substrate by placing it on the sample in the LC phase. The resulting gold substrate was

washed with dichloromethane and dried. To confirm whether the LC compound was immobilized on the gold substrate surface, cyclic voltammetry (CV) of the potassium ferricyanide solution was performed using the gold substrate as the working electrode with transfer times of 0, 6, 12, and 24 h (Figure 6). A pair of reversible redox waves typical of potassium ferricyanide were observed when a bare gold electrode, to which no liquid crystalline compound was transferred, was used. As the transfer time increased, the redox waves broadened. When an electrode with a transfer time of 24 h is used, the redox waves disappear completely. This can be explained by the fact that as the transfer time was extended, the LC molecules were gradually immobilized on the surface of the gold electrode, and the LC-SAM layer modified on the gold electrode disturbed the electron transfer between the gold electrode and potassium ferricyanide because of the high resistivity of the LC-SAM layer, resulting in a broadening of the peak width.
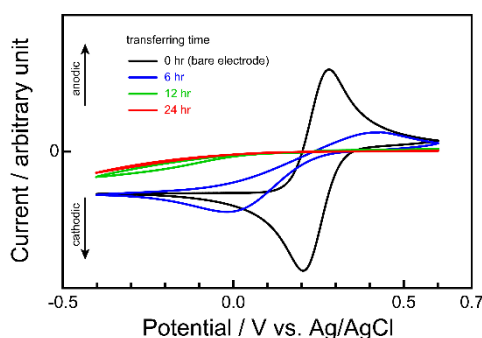

Figure 6. Cyclic voltammograms of $K_3Fe(CN)_6$ using gold electrodes with LC-SAM layers treated with different transferring times as working electrodes.

The LC compounds with thiol groups developed in this study were aligned in one direction on the rubbed alignment film and could be transferred to the gold substrate. The orientation state of the LC-SAM layer, morphology of the organic photo- and electroactive thin films fabricated on top of the LC-SAM layer, and functionality of the photo- and electroactive films originating from orientation control are currently under investigation.

Conclusion

Four compounds with two alkoxy chains and two thiol groups at the alkyl termini were synthesized. The liquid crystallinities of the compounds varied depending on the number of methylene groups in the alkyl chains. Using a liquid crystal alignment film with rubbing treatment, liquid crystalline compounds with thiol groups were aligned in one direction. The degree of alignment ordering can be controlled by cooling the isotropic liquid. When the liquid crystalline compounds aligned in one direction on the liquid crystal alignment film were transferred to a gold substrate, a liquid crystalline monolayer was successfully formed, which was sufficient to cover the gold substrate surface over a transfer time of more than 24 h.

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