Blue Luminescent Naphthalene-based Liquid Crystals

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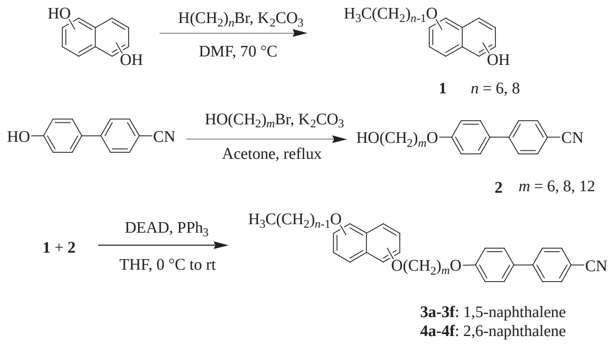
Novel luminescent liquid crystals were synthesized by introducing a mesogenic cyanobiphenylyl side chain to a luminescent naphthalene core. The 1,5-naphthalene derivatives were thermotropic liquid crystals showing monotropic phase transition, while 2,6-naphthalene derivatives showed an enantiotropic behavior. All compounds had an intense bluish emission in the solid, liquid crystal, and isotropic liquid states, which was investigated by UV–vis and PL spectroscopies.

Liquid crystals have a specific property of self-organization in microdomains, which can lead to macroscopic orientation of molecules. Luminescent molecules having liquid crystalline property will be applicable to multifunctional materials for new optical and organic semiconductor devices such as polarized emission, organic lasers, sensors, and so on.[1] Up to the present, a variety of luminescent liquid crystals has been reported, and some of them were applied to organic light-emitting diode (OLED).[2–14] However, they showed only weak electroluminescences under high operation voltages, which was due to poor luminescence, carrier injection, and carrier transport properties of the material in the aggregate state. On the contrary, conjugated polymers such as polyfluorenes and poly(*p*-phenylenevinylene)s that fluoresced efficient in the solid state succeeded to develop polarized OLEDs by the chain alignment.[15–17] However, reorientation of the emitting material by an external force was not possible because of their specific rigid polymer chain.

Since our objective is developing a novel emitting device whose emitting property can be controlled by an external force such as temperature, light, electric field, and magnetic field, we attempt to synthesize novel and intense luminescent liquid-crystalline molecules. From that standpoint, we focused on naphthalene that showed an intense bluish purple luminescence in the crystal state. However in our preliminary investigations, naphthalene itself and some 1,5- and 2,6-dialkoxynaphthalenes did not show any liquid-crystalline behavior. Thus in this paper, we present an approach for synthesis of novel luminescent naphthalene-based liquid crystals by introducing a conventional mesogenic core, cyanobiphenyl, into dialkoxynaphthalene. The linkage used in the synthesis is limited to ether, because the others such as ester having carbonyl group will be unstable during operation of devices such as OLED. In addition, the introduction of such polar mesogenic moiety will have a significance to assist carrier injection.

The synthetic route of 1,5-dialkoxynaphthalene derivatives having cyanobiphenyl **3** and **4** are shown in Scheme 1. Monoalkoxy naphthols **1** were prepared by the reaction of dihydroxynaphthalenes with 1-bromoalkane (1.0 equiv.) in the presence of K_2CO_3 (0.5 equiv.) in DMF at 70 °C overnight. Compounds **2**, 4-cyano-(4′-hydroxyalkoxy)biphenyls, were similarly prepared in good yield by the reaction of 4-cyano-4′-hydroxybiphenyl with *ω*-bromoalcohol (1.5 equiv.) in the presence of K_2CO_3 (1.2 equiv.) in acetone under reflux overnight. Combination of **1** and **2** (1.5 equiv.) by the Mitsunobu reaction in the presence of PPh_3, (1.5 equiv.) and diethyl azodicarboxylate (DEAD) (1.5 equiv.) gave **3a**–**3f** and **4a**–**4f** in 28–86% yields.[18]



Scheme 1. Synthetic route of compounds **3** and **4**.

The phase-transition behavior of **3** and **4** investigated by the thermo-controlled polarized optical microscopy (POM) is summarized in Table 1. The series of 1,5-naphthalene derivatives **3** had a nematic phase that showed monotropic transition, while the series **4** had a nematic phase showing enantiotropic transition besides other unstable mesophases. The appearance of the unstable mesophases was due to disturbance of a molecular interaction between the rod-shape molecules by the presence of the planar naphthalene moiety that had a strong *π*-electronic interaction between the moieties. Introducing the cyanobiphenylyl mesogenic core to one side of the dialkoxynaphthalene was effective to bring about the liquid crystallinity. As a result, the 2,6-naphthalene derivatives **4** that had a more rod-like shape than the 1,5-derivatives **3** showed the distinct phase transitions. A typical Schlieren texture was observed by POM in their nematic phases (Figure 1). In most of the compounds, the larger the numbers of methylene spacer they had, the lower melting point they had.

We chose **4d** to investigate the optical properties, because

Table 1. The phase-transition behavior of **3** and **4**

			T/°C[a]	
	n	*m*	**3**	**4**
a	6	6	C (90 N 100) 140 I	C 133 N 146 I
b	6	8	C (80 N 85) 118 I	C (79 S 80) 135 N 145 I
c	6	12	C (58 N 70) 85 I	C (80 S 107) 134 N 135 I
d	8	6	C (91 N 93) 130 I	C 132 N 135 I
e	8	8	C (70 N 77) 120 I	C 133 N 140 I
f	8	12	C (64 N 78) 97 I	C (115 N 117) 135 I

[a]Abbreviations: C = crystal, N = nematic, S = smectic, and I = isotropic liquid phases. The mesophases and temperatures in parenthesis were observed in the case on rapid cooling.

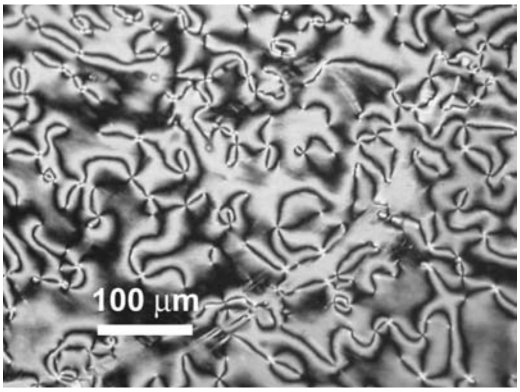


Figure 1. POM texture of **4d** at 100 °C on the cooling process.

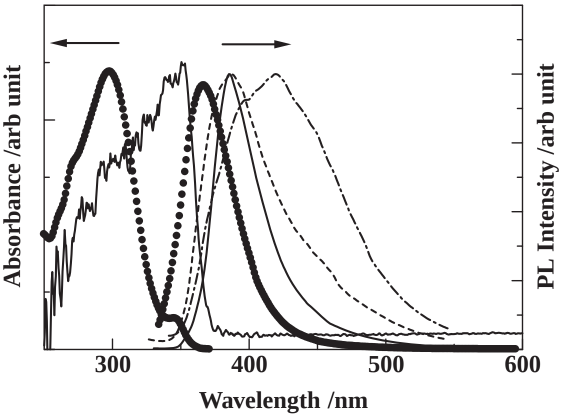


Figure 2. The UV–vis and PL spectra of **4d** on the quartz glass plate in the crystal state at r.t. (solid line), in the nematic state at 100 ± 5 °C (dot-dashed line), in the isotropic liquid state at 150 ± 5 °C (broken line), and in $CHCl_3$ solution (solid circle).

the mesophase appeared in the wider temperature range on the cooling process than the others. The UV–vis and photoluminescence (PL) spectra at each phase are shown in Figure 2. When the UV–vis reflection spectrum for **4d** in the crystal state is compared to the absorption one in $CHCl_3$, a considerable red-shift is observed, which suggests aggregation of molecules caused by intermolecular π-interaction. Additionally, similar molecular interactions are expected to exist in the other phases, since the absorption edges (376 nm) in the nematic and isotropic liquid phases were almost same to that in the crystal phase.

Although **4d** emitted intense blue fluorescence in all phases, some features depending on each phase were found in the PL spectra excited at 298 nm shown in Figure 2. The PL spectrum of isolating **4d** in $CHCl_3$ solution was sharp, and the emission peak maximum (emλ_{max}) was observed shortest in wavelength at 367 nm compared to those in the other states. On the other hand, the emλ_{max} values of aggregating **4d** in the crystal and isotropic liquid phases were almost same, and were observed at 385 and 387 nm, respectively. This result suggests that the luminescent core of **4d** in both phases is affected by a similar intermolecular interaction. On the contrary, the emλ_{max} value in the nematic state was 419 nm, which was considerably longer in wavelength than the others. In order to understand the effect of π-electronic interaction between the naphthalene or cyanobiphenyl moieties in the excited state, we preliminarily investigated the PL spectra of dialkoxynaphthalenes and 4-alkoxy-4′-cyanobiphenyl, respectively. A sharp spectrum with emλ_{max} at 380 nm was observed for 2,6-dihexyloxynaphthalene in the solid and liquid states, as well as 4-hexyloxy-4′-cyanobiphenyl with emλ_{max} at 380 nm in all phases. This result indicates that a specific interaction was generated in the nematic state of **4d**. This specific luminescent behavior in the nematic state was also confirmed in other compounds of this series such as **4a** and **3f**. Consequently, it was considered that a like J-aggregation[19] may arise from a naphthalene–cyanobiphenyl head-to-tail interaction in the nematic phase.

In conclusion, we succeeded to synthesize the novel liquid crystals emitting blue by combining the planar naphthalene and polarizable cyanobiphenyl moieties. Furthermore, it can be shown that the luminescent color can be controlled to some extent by selective formation of the luminescent excitons through phase transition of the molecule.

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18 General procedure for preparation of **3a**–**3f** and **4a**–**4f**: To a solution of monoalkoxynaphthol (2.6 mmol), 4-cyano-4′-(hydroxyalkoxy)biphenyl (3.1 mmol), PPh_3 (3.1 mmol) in THF (10 mL) was added dropwise DEAD (40% in toluene, 3.1 mmol) in THF (5 mL) at 0 °C and stirred at room temperature overnight. After removal of the solvent, the residue was purified by silica-gel column chromatography using EtOAc–hexane (1:2) as an eluent and recrystallization to afford the product.
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