A Light-emitting Liquid Crystal Containing *p*-Terphenyl and an Alkylsilyl Group

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A light-emitting liquid crystal containing *p*-terphenyl and a pentylsilyl group was synthesized, and its thermodynamic and photochemical properties were studied. The pentylsilyl group was found to work as a flexible side chain of a thermotropic liquid crystal. This compound shows intense blue fluorescence in hexane and in the liquid crystal state.

Liquid crystal molecules consist of rigid central cores and flexible side chains.[1] As rigid central cores, aromatic rings have usually been used, and as flexible side chains, alkoxy, acyloxy, carboalkoxy, alkylthio, and alkyl groups have been used. Recently, organosilicon liquid crystals have been reported, including oligosilanes,[2] polysilanes,[3] and bicyclo[2.2.2]octasilane derivatives.[4] Also, lyotropic liquid crystalline polymers containing trimethylsilyl and long alkyldimethylsilyl groups have recently been reported.[5]

In the course of our studies on silyl-substituted aromatic compounds, we found that silyl groups increase extinction coefficients of UV absorption bands and fluorescence or phosphorescence quantum yields of aromatic compounds.[6] We also reported that silyl groups improve photochemical properties of porphyrin dyes for photodynamic therapy[7] and dye-sensitized solar cells.[8] We report herein the first example that an alkylsilyl group can be used as a flexible side chain of a thermotropic liquid crystal containing *p*-terphenyl.[9] As silyl groups improve fluorescence quantum yields of aromatic compounds, pentylsilyl-substituted *p*-terphenyl can be used as a highly effective light-emitting liquid crystal.

The synthetic route is described in Scheme 1. The Suzuki–Miyaura coupling of 4-bromo-4′-hexyloxybiphenyl and 4-(trimethylsilyl)phenylboronic acid gave 4-hexyloxy-4″-trimethylsilyl-*p*-terphenyl (**1**). Compound **1** was iodinated with iodine monochloride to give 4-hexyloxy-4″-iodo-*p*-terphenyl (**2**). The reaction of **2** and dichloropentylsilane in the presence of magnesium followed by reduction with lithium aluminum hydride gave 4-hexyloxy-4″-pentylsilyl-*p*-terphenyl (**3**).[10] For comparison, 4-hexyloxy-*p*-terphenyl (**4**) was synthesized by lithiation of **2** with butyllithium and hydrolysis with methanol. Also, 4-hexyloxy-4″-pentyloxy-*p*-terphenyl (**5**) was synthesized by the Suzuki–Miyaura coupling of 4-bromo-4′-hexyloxybiphenyl and 4-pentyloxyphenylboronic acid.

The phase transition temperatures and the enthalpy changes (ΔH) of **3**–**5** were measured by differential scanning calorimetry (DSC). In the heating process, compound **3** shows crystal phases below 190.4 °C, a mesophase between 190.4 and 206.1 °C, and an isotropic liquid phase above 206.1 °C (Figure 1).[11] In the cooling process, reverse phase transitions were observed. In Figure 2, the texture of the mesophase observed with a polarizing microscope is shown. Fan-shaped texture which is characteristic of the smectic phase was observed. The smectic
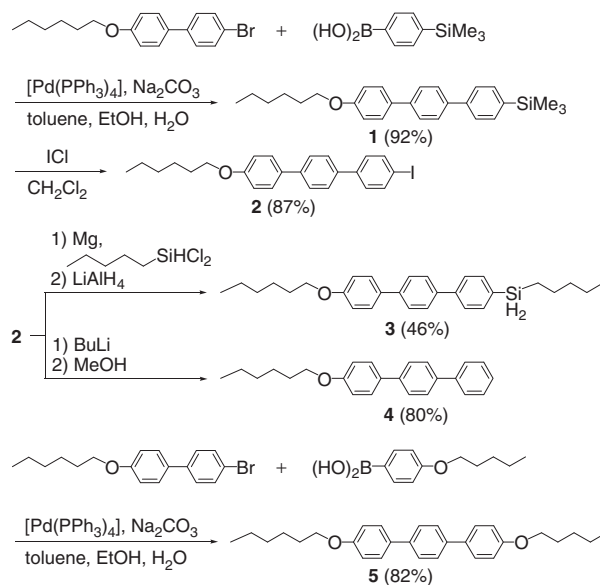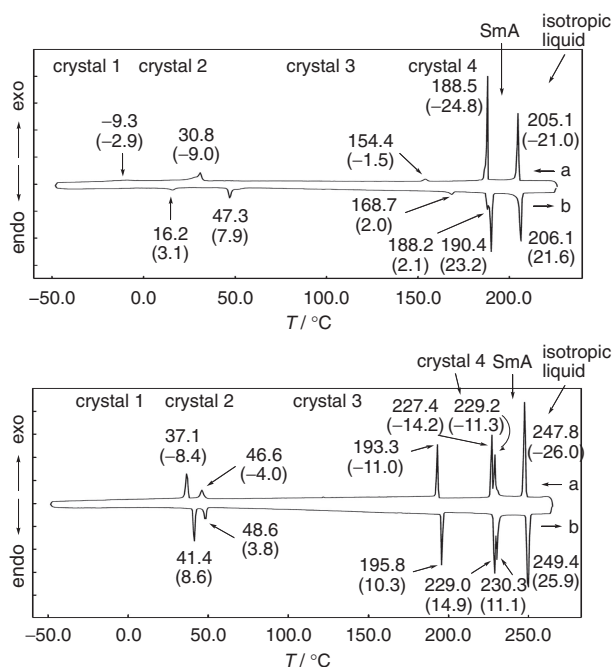
Scheme 1.

Figure 1. DSC thermograms of **3** (top) and **5** (bottom). (a) Cooling curve, (b) second heating curve. Phase transition temperatures (°C) and enthalpy changes (J g⁻¹, in parentheses) are designated beside peaks.

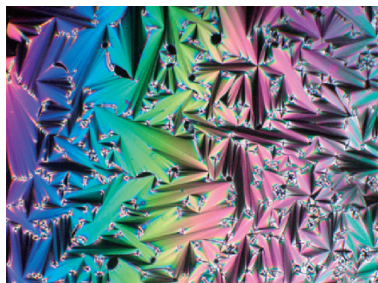**Figure 2.** Fan-shaped texture of **3** observed with a polarizing microscope at 195.0 °C in the cooling process.
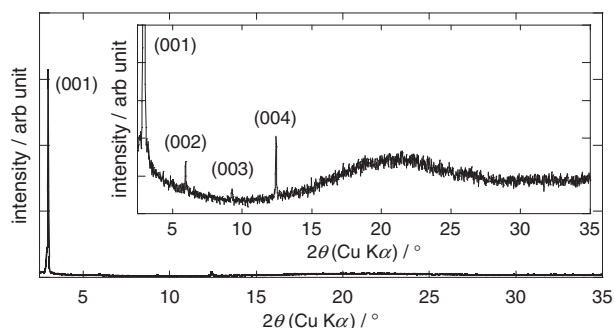

Figure 3. X-ray diffraction pattern of **3** at 190 °C.

phase is reasonable because the enthalpy changes in the phase transitions from the crystal phase to the mesophase (23.2 J g^{-1}) and from the mesophase to the isotropic liquid phase (21.6 J g^{-1}) are comparable. This means that in the mesophase, the crystal structure is considerably disrupted, but the ordered structure still remains.

In order to determine the type of the smectic phase, we measured X-ray diffraction of **3** at 190 °C (Figure 3). The liquid crystal phase exhibits sharp reflections at 2.98, 5.96, 9.28, and 12.44°. These reflections are due to the (001), (002), (003), and (004) reflections of the smectic structure, respectively. From these angles, the layer spacing was calculated to be 29.1 Å, which corresponds to the length of the molecular long axis. Other reflections were not observed except for a broad halo at ca. 10–30°. This means that the ordered structure is not present inside each layer. Furthermore, the broken structure, which is typical of the SmC phase,[1c] was not observed in the fan-shaped texture in Figure 2. From these results, the smectic phase of **3** is assigned to a SmA phase.

Compound **4** does not show a mesophase between the crystal phase and the isotropic liquid phase.[12] Compound **5** shows a mesophase between 230.3 and 249.4 °C in the heating process, and reverse phase transitions were observed in the cooling process (Figure 1). Observation of fan-shaped texture with a polarizing microscope and X-ray diffraction showed that the mesophase is a SmA phase.[12] As the temperature range of this SmA phase is by ca. 40 °C higher than that of **3**, this SmA phase fumes and becomes pale brown in a few minutes, while the SmA phase of **3** remains unchanged. This is an advantage of the pentylsilyl group as a flexible side chain. The relatively low temperature range of the SmA phase of **3** may be ascribed to the long silicon–hydrogen bond: two hydrogen atoms on the silicon
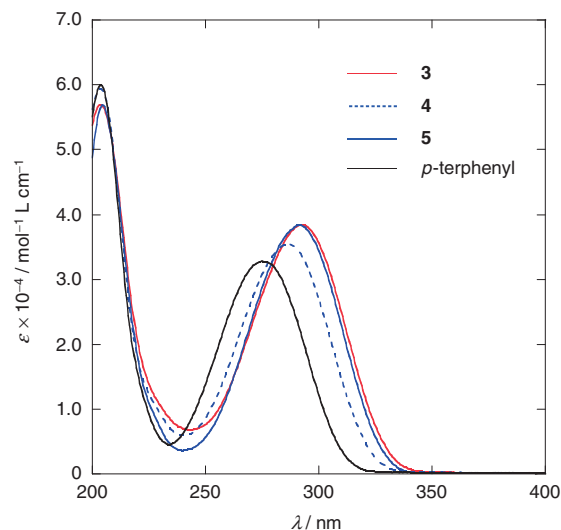

Figure 4. UV spectra of **3**–**5** and *p*-terphenyl in hexane at room temperature.

Table 1. Photophysical parameters of **3**–**5** and *p*-terphenyl in hexane at room temperature

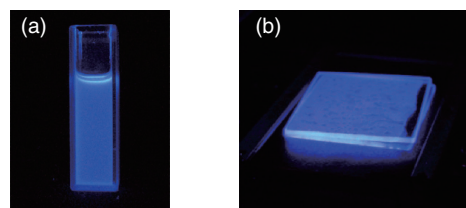| Compound	UV absorption		Fluorescence	
	λ_{max}/nm	ε	λ_{max}/nm	Φ_f
3	293	38000	344, 360	0.83
4	287	35000	337, 351	0.72
5	292	38000	341, 358	0.69
p-terphenyl	275	33000	325, 339	0.77

Figure 5. The light emission of **3** in hexane at room temperature (a) and in a liquid crystal state at 195 °C (b). Excitation was carried out with a low-pressure mercury lamp.

atom behave like "lateral substituents" and destabilize the SmA phase.

The UV spectra of **3**–**5** are shown in Figure 4. In Table 1, the wavelengths of the lowest energy absorption maxima and the extinction coefficients are summarized. The lowest energy absorption band of **3** shows a slight bathochromic shift compared with that of **4** and has a little larger extinction coefficient than that of **4**. These changes are explained by the cooperative effect of the σ–π conjugation in the HOMO and the σ*–π* conjugation in the LUMO as reported in other silyl-substituted aromatic compounds.[6e] Compound **5** shows the wavelength and the extinction coefficient similar to those of **3**.

Compound **3** shows intense blue fluorescence as shown in Figure 5. Fluorescence spectra of **3**–**5** and their parameters are shown in Figure 6 and Table 1. The fluorescence bands shift
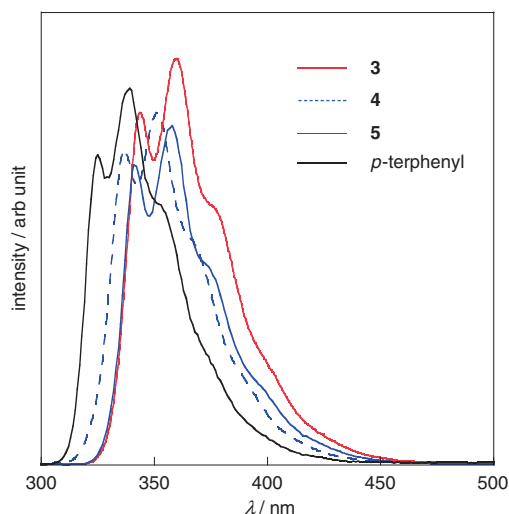
Figure 6. Fluorescence spectra of **3**–**5** and *p*-terphenyl in hexane at room temperature. The excitation wavelength is 281 nm.

bathochromically in the order of *p*-terphenyl, **4**, and **3**. The wavelengths of the fluorescence maxima of **5** are almost the same as those of **3**. These results correspond to the absorption bands of the UV spectra. When *p*-terphenyl is substituted by alkoxy groups, the fluorescence quantum yield decreases in the order of *p*-terphenyl (0.77), **4** (0.72), and **5** (0.69). On the other hand, the fluorescence quantum yield of **3** (0.83) is higher than that of *p*-terphenyl, **4**, and **5**. Therefore, the alkylsilyl group improves the fluorescence quantum yield of *p*-terphenyl as reported in other silyl-substituted aromatic compounds.[6a,6d] From these results, the alkylsilyl group seems to be a favorable flexible side chain for light-emitting liquid crystals. Unfortunately, the fluorescence spectrum of **3** in a liquid crystal state could not be observed because temperature should be kept at ca. 200 °C during measurement.

In summary, we synthesized a light-emitting organosilicon liquid crystal **3**. The pentylsilyl group was found to be able to be used as a flexible side chain of a liquid crystal. Compound **3** shows intense blue fluorescence in hexane and in the liquid crystal state. Further studies on the application of this light-emitting liquid crystal are now in progress.

References and Notes

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9 We attempted to use alkyldimethylsilyl groups as flexible side chains, but they did not induce common liquid crystal phases. Details of this result will be reported elsewhere.

10 **3**. Mp: 186–189 °C. ^{1}H NMR (CDCl$_3$): δ 0.89 (t, 3H, J = 7.0 Hz), 0.92 (t, 3H, J = 7.3 Hz), 0.95–1.00 (m, 2H), 1.30–1.40 (m, 8H), 1.46–1.53 (m, 4H), 1.82 (qui, 2H, J = 6.9 Hz), 4.01 (t, 2H, J = 6.9 Hz), 4.33 (t, 2H, J = 4.0 Hz), 6.99 (d, 2H, J = 8.8 Hz), 7.57 (d, 2H, J = 8.8 Hz), 7.63–7.67 (m, 8H). ^{13}C NMR (CDCl$_3$): δ 10.0, 14.0, 14.1, 22.3, 22.6, 24.8, 25.7, 29.2, 31.6, 35.0, 68.1, 114.8, 126.5, 127.0, 127.4, 128.0, 131.4, 132.8, 135.7, 139.0, 140.0, 141.8, 158.8. ^{29}Si NMR (C$_6$D$_6$): δ −31.1. IR (KBr): 3030, 2960, 2920, 2860, 2120, 1600, 1510, 1490, 1470, 1390, 1290, 1250, 1180, 1120, 940, 860, 810 cm^{-1}. MS (EI, 70 eV): m/z 430 (M$^+$, 100), 275 (11), 246 (28). Anal. Calcd for C$_{29}$H$_{38}$OSi: C, 80.87; H, 8.89%. Found: C, 80.82; H, 8.66%.

11 The phase of **3** observed between 188.2 and 190.4 °C and the phase of **5** observed between 229.0 and 230.3 °C in the heating processes were not fully characterized because of the very narrow temperature ranges of 1–2 °C.

12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.