A thermoresponsive photoluminescent smectic liquid crystal: change of photoluminescent color on the smectic–smectic phase transition†

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An anthracene derivative having forklike side chains shows a change of photoluminescent color from green to light blue at the smectic–smectic phase transition.

Soft materials have attracted much attention because of their dynamic properties.[1] Liquid crystals are among soft materials combining fluidity and ordered structures.[2] Based on such unique properties of liquid crystals, a number of liquid-crystalline (LC) photoluminescent materials have been developed for various applications such as organic light emitting diodes,[3] laser devices,[4] and sensing devices.[5] Our intention here is the development of a new type of photo-functional smectic liquid crystals exhibiting change of the photoluminescent color by external stimuli. In general, photoluminescent properties observed for molecular materials depend on their assembled structures.[5–7] Therefore, liquid crystals can be good candidates for stimuli-responsive photoluminescent materials because LC–LC phase transitions are often accompanied by a dynamic change of the assembled structures.

Herein we report on a change of photoluminescent color of anthracene derivative **1** (Fig. 1) from green to light blue upon smectic–smectic phase transition. In our previous studies,[5a,b] pyrene and anthracene derivatives having dendritic side chains showed changes of photoluminescent color on the cubic–columnar phase transitions induced by mechanical shearing and heating. However, until now, only limited numbers of LC materials are known to change their photoluminescent colors on LC–LC phase transitions with dynamic change of the assembled structures.[5a–c] Moreover, to the best of our knowledge, no photo-functional liquid crystals that show smectic–smectic phase transitions associated with change of the photoluminescent colors have been prepared.

Our molecular design is shown in Fig. 1. Compound **1** has a 2,6-diethynylanthracene[8] group as a photoluminescent core. Up to now anthracenes have been incorporated into several LC molecules.[9] Compound **1** also has a block structure consisting of six side chains of tetra(ethylene oxide) and *p*-(4-*trans*-pentylcyclohexyl)phenyl moieties. A compound having a block structure composed of the two moieties has been reported to exhibit the smectic A phase originating from the nanosegregation between the two different moieties.[10] In addition, similar forklike side chains consisting of rodlike mesogens induced smectic phases for complex molecular moieties such as interlocked catenane and rotaxane structures.[11] Therefore, compound **1** is expected to show smectic A phases. Compound **2** was also designed to examine the effects of side chains on the LC behavior.

The LC properties of compounds **1** and **2** are summarized in Table 1. Compound **1** exhibits a smectic A (SmA) phase and three unidentified smectic (Sm1, Sm2 and Sm3) phases. On heating, this compound shows a highly viscous smectic (Sm1) phase from −14 to 83 °C. Two subsequent unidentified smectic (Sm2 and Sm3) phases with low viscosity are observed from 83 to 104 °C. The Sm2–Sm3 phase transition is observed at 94 °C. On further heating, compound **1** shows an SmA phase from 104 to 132 °C. Focal conic textures characteristic of SmA phases are observed on cooling from the isotropic phase (see ESI†). The focal conic textures change slightly on the SmA–Sm3 and Sm3–Sm2 phase transitions on cooling (see ESI†).

Under UV irradiation (365 nm), compound **1** shows green photoluminescence in both the Sm3 (Fig. 2, left) and Sm2 phases. In contrast, light-blue photoluminescence is shown in the SmA phase (Fig. 2, right). This phenomenon is an example of thermochromic luminescence in ordered structures.[5b–d,7c,d] The absorption and emission spectra (Fig. 3) have been obtained to examine the origin of the color change. As shown in Fig. 3(a), the absorption bands of **1** in the Sm2 and Sm3 phases are almost identical to that of **1** in the SmA phase. These absorption spectra, having well-resolved vibronic structures, are similar to that of **1** in chloroform (1.0×10^{-5} M, see ESI†), indicating that no obvious ground-state interactions occur between the luminescent cores of **1** in the Sm2, Sm3 and SmA phases. Compared to the absorption spectral features, the emission spectra for **1** in the Sm2 and Sm3 phases are different from that for **1** in the SmA phase. The broad and structureless emission bands observed for **1** in the Sm2 and Sm3 phases (Fig. 3(b), green dotted and solid lines) are ascribed to excimer formation of the anthracene moieties of **1**. To date, a number of anthracene derivatives have been reported to show excimer emission.[12] As for the SmA phase,

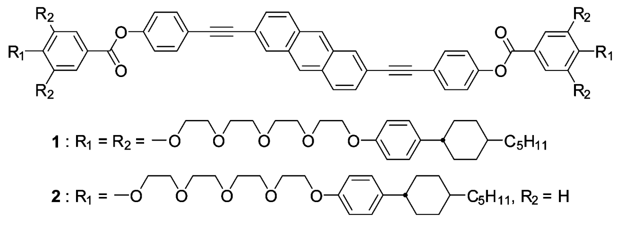

Fig. 1 Molecular structures of anthracene derivatives **1** and **2**.

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Table 1 Liquid-crystalline properties of compounds **1** and **2**

Compound	Phase transition behaviour[a]
1	G•−14•Sm1•83•Sm2•94•Sm3•104•SmA•132•Iso
2	G•−26•Sm4•206•N[b]

[a] Transition temperatures (°C) determined by DSC (second heating; 5 °C $\min^{-1}$), POM observation and X-ray diffraction patterns. G: glass; Sm1, Sm2, Sm3 and Sm4: unidentified smectic; SmA: smectic A; N: nematic; Iso: isotropic. [b] Thermal decomposition occurred above 270 °C before reaching the isotropic state.

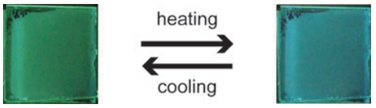

Fig. 2 Photoluminescent images of **1** in the Sm3 phase at 98 °C (left) and in the SmA phase at 120 °C (right) under UV irradiation (365 nm). Compound **1** is sandwiched between quartz substrates.

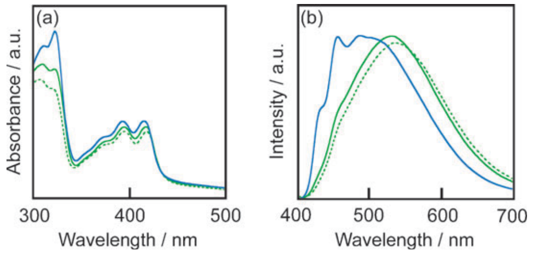

Fig. 3 Absorption spectra (a) and emission spectra (b) of **1** in the Sm2 phase at 88 °C (green dotted line), in the Sm3 phase at 98 °C (green solid line) and in the SmA phase at 120 °C (blue line).

the emission peaks and shoulders appear at 430, 454 and 487 nm besides the excimer emission band (Fig. 3(b), blue line). These peaks are attributed to the monomeric emission of **1**, because the emission spectrum of a chloroform solution of **1** (1.0×10^{-5} M, see ESI†) displays the peaks at the same positions. The decrease of relative ratio of the excimer emission on the Sm3–SmA phase transition results in the change of the photoluminescent color from green to light blue on the phase transition. On the other hand, no obvious change in the relative ratio of the excimer emission occurs on the Sm2–Sm3 phase transition (Fig. 3(b), green dotted and solid lines).

X-Ray diffraction (XRD) measurements have been performed to examine the relationship between the self-assembled structure and the luminescent color. The XRD patterns of **1** in the Sm2 and Sm3 phases show several diffractions in the small angle region (Fig. 4(a) and (b)). In the Sm3 phase at 98 °C, the XRD pattern shows the diffraction peaks at 86.5, 42.6, 27.7, 20.5 and 16.2 Å corresponding to (100), (200), (300), (400) and (500) reflections, respectively (Fig. 4(b)). The layer spacing is 8.5 nm, which almost coincides with the estimated molecular length, 8.2 nm for compound **1** in its extended form (see ESI†). It is assumed that a monolayer self-assembled structure (Fig. 5, left) is formed in the Sm3 phase. As the diffraction peaks for the Sm2 and Sm3 phases are very similar (Fig. 4(a) and (b)), the self-assembled structures of **1** in the Sm2 phase are similar to those of **1** in the Sm3 phase, leading to small ΔH compared to the other phase transitions observed for compound **1**. To fill the gap between the anthracene moieties and fork-like side chains, a part of side chains may be in the layer of anthracene cores by bending of the oxyethylene chain. In the self-assembled structure for the Sm2 and Sm3 phases, the emitting cores are close to each other. Therefore, excited luminescent cores form excimers with adjacent luminescent cores and the energy transfer may occur from most of the excited luminescent cores to the excimer sites.[13] As a consequence, no obvious monomeric emission appears in the emission spectra of **1** in the Sm2 and Sm3 phases (Fig. 3(b), green dotted and solid lines). On the other hand, the XRD pattern in the SmA phase (Fig. 4(c)) reveals that the self-assembled structure of **1** in the SmA phase is different from the monolayer structure observed for **1** in the Sm2 and Sm3 phases. As shown in Fig. 4(c), only one peak appears at 38.2 Å in the diffraction pattern obtained at 120 °C. Because the layer spacing is less than half of the estimated molecular length, compound **1** is considered to form an interdigitated structure in the SmA phase (Fig. 5, right). In this self-assembled structure, luminescent groups are surrounded by the side chains, leading to separation of the luminescent cores from each other (Fig. 5, right). In this case, the deactivation of excited states with monomeric emission

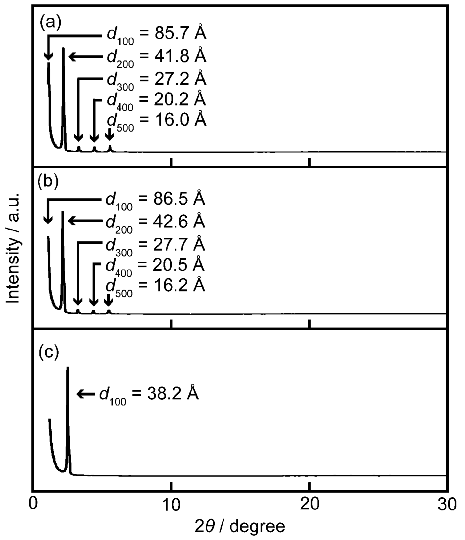

Fig. 4 X-Ray diffraction patterns of **1** in the Sm2 phase at 88 °C (a), in the Sm3 phase at 98 °C (b) and in the smectic A phase at 120 °C (c).

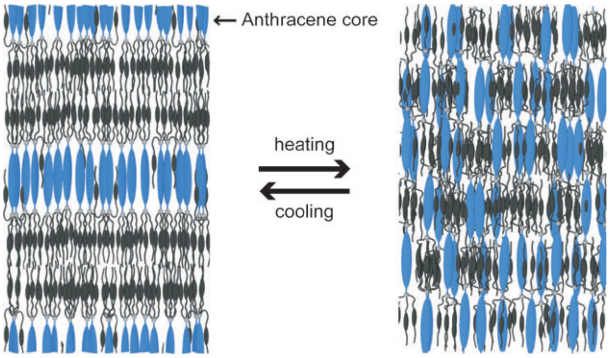

Fig. 5 Schematic illustrations of the self-assembled structures of **1** in the Sm3 (left) and SmA (right) phases.

(around 454 nm) occurs for some of the excited luminescent cores, before they form excimers or the energy transfer occurs. As a consequence, both monomeric and excimer emissions are observed in the emission spectrum of **1** in the SmA phase (Fig. 3(b), blue line).

Based on the XRD measurements and emission spectra of compound **1** (Fig. 3 and 4), the induction of the Sm3–SmA phase transition can be explained as follows. In the Sm3 phase, nanosegregation between the tetra(ethylene oxide) and *p*-(4-*trans*-pentylcyclohexyl)phenyl moieties of the forklike side chains is the dominant driving force to induce the smectic LC behavior, leading to the formation of a monolayer self-assembled structure (Fig. 5, left). Since the occupied volume of the forklike side chains increases with increase of temperature, an interdigitated structure forms to complement the difference of spatial volume between the forklike side chains and the luminescent cores. Consequently, the Sm3–SmA phase transition occurs (Fig. 5, left → right). A dumbbell-shaped molecule having similar structures to compound **1** was reported to also show Sm–Sm phase transitions.[14] Moreover, the phase transitions are observed for various types of LC compounds.[15] Compared to compound **1**, compound **2** having a linear molecular shape shows no Sm–Sm phase transition (see ESI†).

In summary, we have developed an anthracene-based smectic liquid crystal showing the change of photoluminescent color from green to light blue on the Sm3–SmA phase transition. The luminescent color change is ascribed to the decreasing of the ratio of the excimer emission, which arises from the change of the self-assembled structures on the Sm3–SmA phase transition. This liquid crystal could be used as a stimuli-responsive polarized photoluminescent material if it is uniaxially aligned.

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