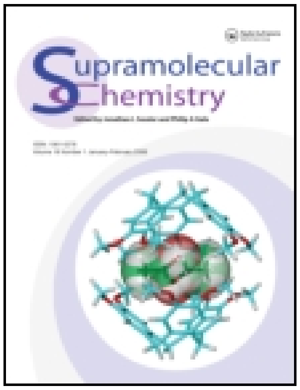

Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
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A mechanical and thermal responsive luminescent liquid crystal forming a colourless film under room light

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To cite this article: Yoshimitsu Sagara & Takashi Kato (2011): A mechanical and thermal responsive luminescent liquid crystal forming a colourless film under room light, Supramolecular Chemistry, 23:03-04, 310-314

To link to this article: http://dx.doi.org/10.1080/10610278.2010.527980

Supramolecular Chemistry
Vol. 23, Nos. 3–4, March–April 2011, 310–314

A mechanical and thermal responsive luminescent liquid crystal forming a colourless film under room light

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(*Received 3 August 2010; final version received 27 September 2010*)

We report here a luminescent liquid crystal that changes the luminescent colour by mechanical and thermal stimuli. The liquid crystal is a 1,5-naphtharene derivative having dendritic moieties and amide groups. This material is colourless due to little absorption in the visible region. The mechanical and thermal stimuli induce a phase transition of this material from the cubic phase to the columnar phase. This exhibits luminescent colour change from light blue to blue.

Keywords: liquid crystals; stimuli-responsive materials; photoluminescence; naphthalene

Introduction

Liquid crystal, which combines order and mobile states, is one of the soft materials (*1*). Incorporation of functional groups into liquid-crystalline (LC) compound is one of the versatile approaches to develop functional soft materials (*2*). For example, photo-functional liquid crystals have attracted much attention because of their variety of applications such as electroluminescent devices (*3*), laser devices (*4*), mechanical devices (*5*), holographic memories (*6*) and stimuli-responsive photoluminescent materials (*2d*, *7*).

We have recently developed several mechanical and/or thermal stimuli-responsive luminescent liquid crystals that switch the luminescent colours on their LC–LC phase transitions (*2d*, *7a–c*). These luminescent liquid crystals have pyrene or anthracene groups that absorb visible light. As a consequence, substrates coated with such liquid crystals are coloured. For some specific applications such as security, introduction of colourless properties to the stimuli-responsive luminescent materials is an important approach. Herein, we report on a colourless stimuli-responsive luminescent naphthalene-based liquid crystal that changes the luminescent colour by mechanical and thermal stimuli.

Results and discussion

We have designed and synthesised 1,5-diethynylnaphthalene (*8*) derivative **1** (Figure 1). Compound **1** is expected to show a stimuli-induced cubic-columnar phase transition with luminescent colour change. We previously used the same dendritic group with **1** to prepare stimuli-responsive anthracene-based liquid crystal **2**, which shows the same phase transition behaviour (*7b*). This dendritic group was reported to exhibit LC behaviour (*9a*). Compound **1** was synthesised by a Sonogashira coupling reaction from 1,5-diethynylnaphthalene (*8*) and the fan-shaped dendron (*7a, b*, *9*).

Compound **1** shows a rectangular columnar phase on slow cooling from the isotropic phase (Figure 2, right). A sandy texture is observed for **1** in the rectangular columnar phase on polarising optical microscopic observation (Figure 3(a)). The X-ray diffraction pattern of **1** at 160°C (Figure 4(a)) shows diffractions at 55.9, 36.5 and 27.4 Å. The diffractions can be ascribed to the (11), (02) and (31) reflections of a *P*2/*a* rectangular columnar phase ($a = 86.9$ and $b = 73.0$ Å). Compound **1** in the columnar phase exhibits blue photoluminescence under UV irradiation (365 nm). We have observed that compound **1** exhibits a cubic phase by rapid cooling procedure from the isotopic phase (Figure 2, left). Light-blue emission is observed for the cubic phase (Figure 5(a), left). No birefringence is observed for the sample at 100°C in the cubic phase (Figure 3(b)). Therefore, under room light, compound **1** in the cubic and columnar phases is colourless in the thin film states (Figure 5(a)), while anthracene-based compound **2** placed between quartz substrates appears yellow (Figure 5(b)). The absorption spectra of **1** in the cubic and columnar phases are shown in the next section. The X-ray diffraction peaks corresponding to (200), (210), (211) and (310) reflections of a *Pm*3*n* cubic phase ($a = 90.7$ Å) are observed in the small-angle region (Figure 4(b)). For the sample of **1** rapidly cooled preserves the cubic structure. On heating the sample, the exothermic peak corresponding to the transition from metastable cubic to stable columnar

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ISSN 1061-0278 print/ISSN 1029-0478 online

DOI: 10.1080/10610278.2010.527980
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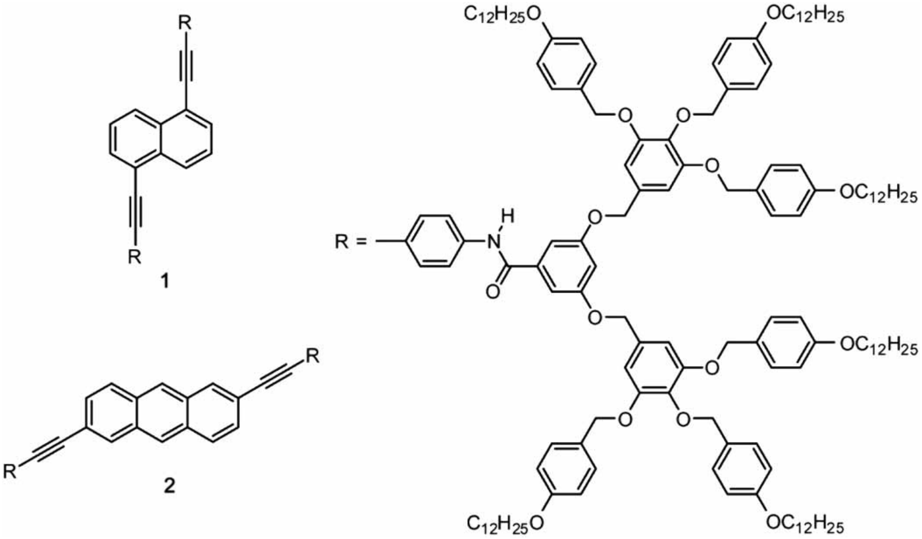

Figure 1. Molecular structures of naphthalene derivative **1** and anthracene derivative **2**.

phases at 128°C is observed (Figure 6(b)). Concurrently, the luminescent colour changes from light blue to blue. At temperatures lower than 128°C, we have found that compound **1** exhibits a shear-induced cubic-columnar phase transition and the same luminescent colour change as that observed on heating the compound in the cubic phase. Only a limited number of organic or organometallic compounds have been reported to exhibit such piezochromic luminescence (*2d*, *7a, b, d*, *10*).

On the basis of the results obtained for the infrared measurements of **1**, its H-bonded self-assembled structures change at molecular level on the cubic-columnar phase transition. The IR spectral features for **1** both in the columnar and cubic phases show that the amide groups are involved in the formation of hydrogen bonding and no free amide C═O and N—H group exists (Figure 7). The C═O stretching band is observed at 1644 cm^{-1} for **1** in the columnar phase, whereas the peak due to C═O stretching appears at 1651 cm^{-1} in the cubic phase. This observation shows that the H-bonded interaction in the cubic phase is weaker than that in the columnar phase. In addition, the peaks corresponding to the C═O and N—H stretching observed in the columnar phase (Figure 7(b)) become narrower than those observed in the cubic phase (Figure 7(c)). These results suggest that more linear H-bonded states form in the columnar phase than those in the cubic phase.

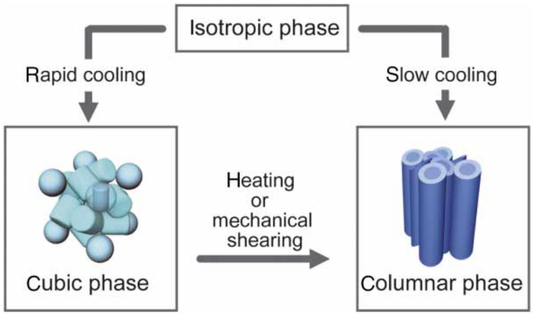

Figure 2. Schematic illustration of the LC phase transition behaviour of **1**.

The absorption spectra of **1** in the columnar and cubic LC phases display absorption bands between 320 and 400 nm as shown in Figure 8(a). Moreover, no apparent absorption in the visible region is observed for **1**. Under UV irradiation, the heated and/or rubbed areas are detected by the change in the photoluminescent colour. These external stimuli-responsive luminescent properties enable compound **1** to be a good candidate for specific sensing materials for security measures. The emission spectrum of **1** in the cubic phase is broadened and red-shifted compared with that of **1** in the columnar phase as shown in Figure 8(b). The emission spectral feature of **1** in the cubic phase is attributed to excimer formation (*11*) of the naphthalene moieties. The emission lifetime of **1** in the cubic phase ($\tau = 3.9$, 15 ns) is longer than those of **1** in the columnar phase ($\tau = 0.1$, 0.8 ns) and chloroform solution ($\tau = 0.2$ ns). This suggests that the emission species in the cubic phase are different from those in the columnar phase, supporting the excimer formation of the naphthalene groups. The excimer formation of compound **1** is also supported by the results of previous studies on excimer emission of various naphthalene derivatives (*12*).

The self-assembled structures of **1** in the columnar and cubic phases are considered to be similar to those of the pyrene derivative in our previous study (*7a*). In the columnar phase, the linear H-bonded formation forms through the amide groups of **1** and naphthalene moieties are fixed in the arrangement in which no naphthalene groups form excimer formation (Figure 9(a)). In the cubic

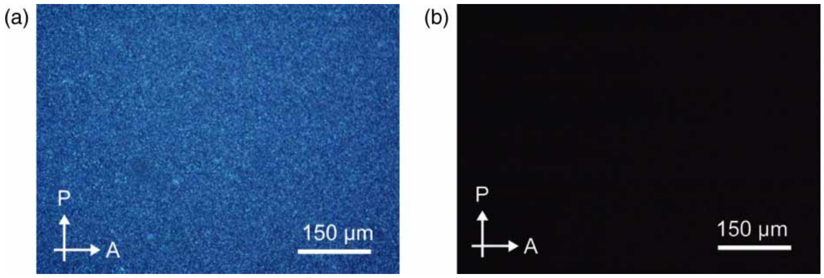

Figure 3. Polarising optical microscopic images of compound **1**: (a) in the columnar phase (140°C) and (b) in the cubic phase (100°C). Directions of A, analyser and P, polariser.

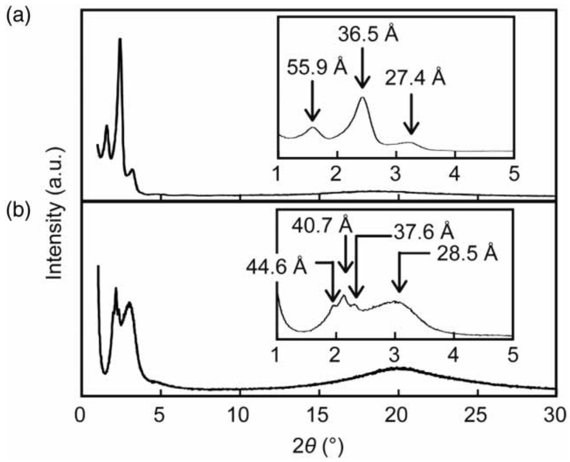

Figure 4. X-ray diffraction patterns of **1**: (a) in the columnar phase at 160°C and (b) in the cubic phase at room temperature.

phase, the luminescent π-conjugated group of compound **1** should be arranged in the disordered stacking (*13*) in the segmented columns, leading to the excimer emission (Figure 9(b)). The segmented columnar structures are surrounded by dendritic moieties with long and flexible alkyl chains.

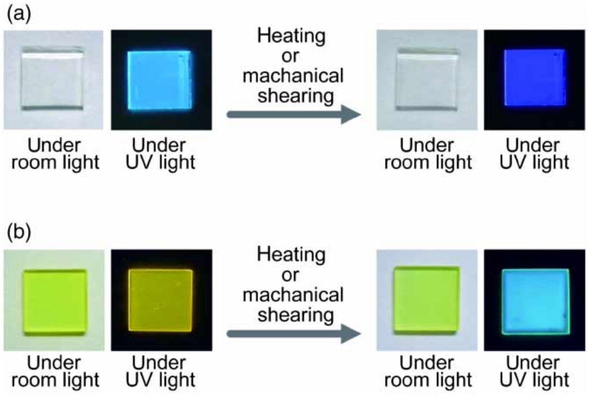

Figure 5. (a) Photographs of **1** placed between quartz substrates under room light and UV irradiation (365 nm) in the cubic phase at 100°C (left) and in the columnar phase at 140°C (right). (b) Photographs of **2** placed between quartz substrates under room light and UV irradiation (365 nm) in the cubic phase at 120°C (left) and in the columnar phase at 170°C (right). The samples for photos under room light were fixed on a white paper.

Conclusion

We have prepared a new stimuli-responsive liquid crystal containing a naphthalene group as a luminescent core. Although this compound is colourless under room light, mechanical–structural change can be detected by luminescent colour change under UV irradiation. This behaviour might broaden the applicability of these stimuli-responsive materials.

Experimental

General methods and materials

All reagents and solvents were purchased from Aldrich (Tokyo, Japan), Tokyo Kasei (Tokyo, Japan), and Wako (Osaka, Japan). They were appropriately purified, if necessary. The reaction was carried out under argon atmosphere in freshly distilled solvents. Silica gel column chromatography was carried out with silica gel 60 from Kanto Chemicals (Tokyo, Japan) (silica gel 60, spherical, 40–50 μm). Recycling preparative GPC was carried out with a Japan Analytical Industry LC-908 chromatograph. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer in $CDCl_3$ solutions (400 and 100 MHz for ^{1}H NMR and ^{13}C NMR, respectively). Chemical shifts of ^{1}H and ^{13}C NMR signals were quoted to internal standard Me_4Si ($\delta = 0.00$) and $CDCl_3$ ($\delta = 77.00$), respectively, and expressed by chemical shifts in ppm (δ), multiplicity, coupling constant (Hz) and relative intensity. Mass spectra were recorded on a PerSeptive Biosystems Voyager-DE STR spectrometer. Elemental analyses were carried out with a Yanaco MT-6 CHN autocorder.

Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH DSC204 Phoenix calorimeter at a scanning rate of 10°C min^{-1}. X-ray diffraction measurements were carried out on a Rigaku

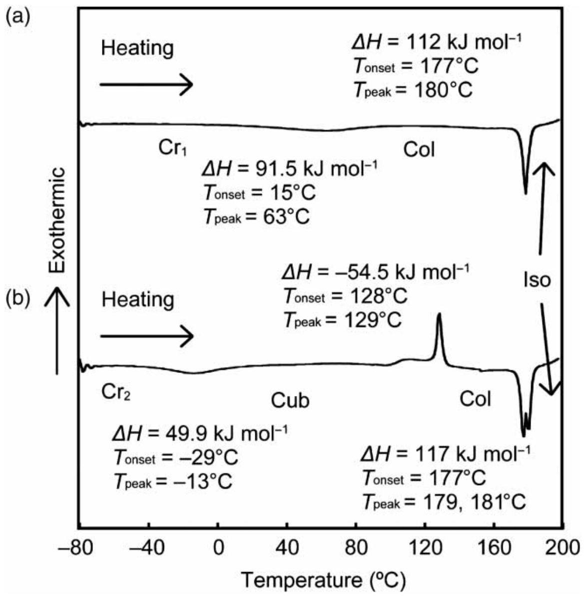

Figure 6. DSC traces of **1**: (a) in the columnar phase on heating at the rate of 10°C min^{-1} and (b) in the cubic phase on heating at the rate of 10°C min^{-1}.

RINT 2500 diffractometer with a heating stage using Ni-filtered Cu Kα radiation. IR measurements were conducted on a Jasco FT/IR-660 Plus using CaF_2 plates equipped with a Mettler FP82HT hot stage. UV–vis absorption spectra were obtained with a Jasco V-670 equipped with a Mettler FP82HT hot stage. Steady-state fluorescence spectra were recorded on a Jasco FP-6300 spectrofluorometer equipped with a hot stage. Time-resolved fluorescence measurements were carried out by exciting samples with a nitrogen laser pulse (337 nm), and the emission was dispersed with a Hamamatsu Photonics C-2830 disperser and monitored on a Hamamatsu Photonics M-2548 streak camera.

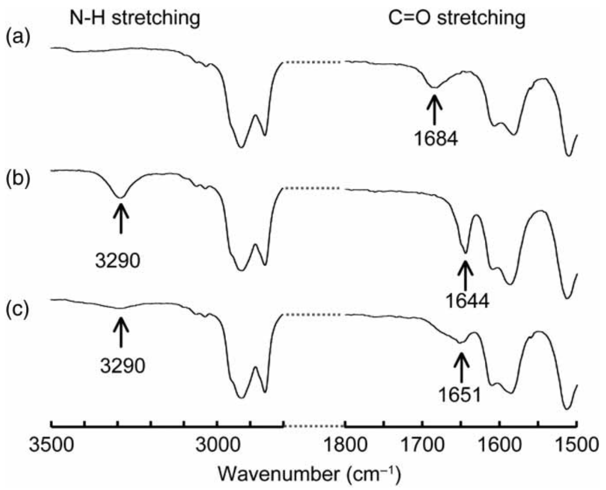

Figure 7. IR spectra of **1**: (a) in the isotropic phase (190°C); (b) in the columnar phase (140°C) and (c) in the cubic phase (100°C).

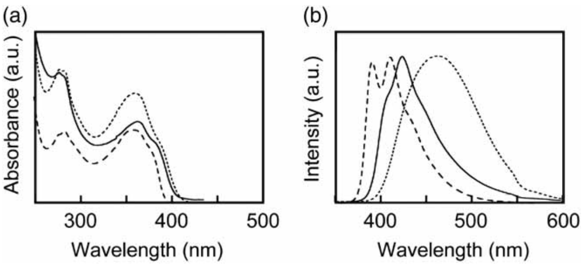

Figure 8. (a) Absorption and (b) emission spectra of **1** in the columnar phase at 160°C (solid line), in the cubic phase at 100°C (dotted line) and in the chloroform solution (1.0×10^{-5} M, dashed line).

Synthesis

The synthetic route used to obtain compound **1** is shown below. *N*-4-Iodophenyl 3,5-bis{3′,4′,5′-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzamide and 1,5-diethynylnaphthalene were obtained according to the reported procedures (*7a*, *8*).

1,5-Bis[p-(3,5-bis{3,4,5-tris[p-(dodecan-1-yloxy)benzyloxy]benzyloxy}benzamido)phenylethynyl] naphthalene (1)

To a suspension of *N*-4-iodophenyl 3,5-bis{3′,4′,5′-tris[*p*-(dodecan-1-yloxy)benzyloxy]benzyloxy} benzamide (600 mg, 0.264 mmol), 1,5-diethynylnaphthalene (21.1 mg, 0.120 mmol), dry toluene (30 ml) and freshly distilled Et_2NH (5 ml) were added CuI (2.28 mg, 1.20×10^{-2} mmol) and $PdCl_2$ $(PPh_3)_2$ (8.40 mg, 1.20×10^{-2} mmol). After stirring for 10 h at 50°C, toluene and Et_2NH were removed with a rotary evaporator. The residue was dissolved in chloroform and this organic phase was washed with 5% hydrochloric acid followed by sat. NH_4Cl aq and sat. NaCl aq, dried over $MgSO_4$, filtered and evaporated. The residue was purified by column chromatography on a silica gel (eluent:chloroform) and GPC (eluent:chloroform) to afford **1** (140 mg, 3.13×10^{-2} mmol) as a transparent colourless solid in 26% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.85$–0.89 (m, 36H), 1.25–1.55 (m, 216H), 1.73–1.79 (m, 24H), 3.90–3.96 (m, 24H), 4.95 (s, 8H), 4.99 (s, 8H), 5.03 (s, 16H), 6.72 (s, 8H), 6.75–6.78 (m, 10H), 6.87 (d, $J = 8.8$ Hz, 16H), 7.04 (d, $J = 2.0$ Hz, 4H), 7.26–7.31 (m, 24H), 7.58 (t, $J = 7.6$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 4H), 7.71 (d, $J = 8.8$ Hz, 4H), 7.81 (d, $J = 6.4$ Hz, 2H), 7.86 (s, 2H), 8.46 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 14.14$, 22.70, 26.10, 29.33, 29.37, 29.47, 29.65, 29.70, 31.93, 68.00, 68.09, 70.54, 71.19, 74.85, 87.25, 94.47, 105.42, 106.23, 107.37, 114.11, 114.43, 119.18, 119.70, 121.46, 126.17, 126.98, 128.87, 129.15, 129.84, 130.25, 130.87, 131.59, 132.60, 133.12, 137.02, 138.15, 138.45, 153.19, 158.94, 160.07, 165.36. MS

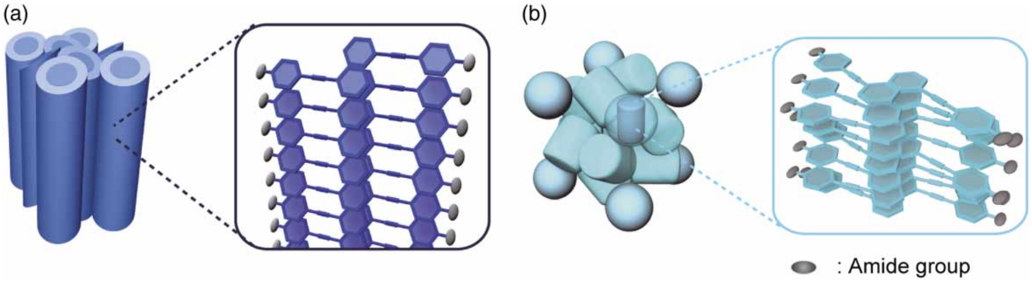

Figure 9. Schematic images of the self-assembled structures of **1**: (a) in the columnar phase and (b) in the cubic phase. The dendritic side chains are omitted in the schematic illustration.

(MALDI): *m/z*: 4498.92 (calcd $[M + Na]^+ = 4496.06$). Elemental analysis: calcd (%) for $C_{296}H_{410}N_2O_{30}$: C, 79.42; H, 9.23; N, 0.63. Found: C, 79.32; H, 9.08; N, 0.65.

Acknowledgements

We thank Prof. K. Araki and Dr T. Mutai for the measurement of emission lifetime. This work was partially supported by Grant-in-Aid for Challenging Exploratory Research (No. 22655061) (T.K.) from the Japan Society for the Promotion of Science (JSPS). Y.S. is thankful for financial support from JSPS Research Fellowships for Young Scientists.

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