DOI: 10.1002/anie.201100914

Brightly Tricolored Mechanochromic Luminescence from a Single-Luminophore Liquid Crystal: Reversible Writing and Erasing of Images**

*Yoshimitsu Sagara and Takashi Kato**

Luminescent materials that switch their photoluminescent properties in response to various external stimuli have attracted much attention for a decade because of their potential application for memory devices, sensors, security materials, and informational displays.[1–5] To induce change in the luminescent colors of organic and organometallic materials, one could switch the molecularly assembled structures.[4–7] Crystals,[8–24] liquid crystals,[25–28] and polymers[29–32] have been reported to change their luminescent colors by mechanical and thermal stimuli. The observed phenomena are referred to as piezo(mechano)chromic or thermochromic luminescence. Such materials contain just one type of luminophore and they form only two luminescent states. In the condensed states, to date, multiemission colors that are generated from a single luminophore and switch between their colors using external stimuli have not been achieved for organic and organometallic materials; the one exception is a crystalline compound.[16] If such materials are prepared using liquid crystals, it leads to new applications of stimuli-responsive luminescent materials that are flexible, sophisticated, and highly functional.

Liquid crystals are functional soft materials that exhibit mobile and ordered states.[33] Because of their dynamic properties, liquid crystals are good candidates for stimuli-responsive luminescent materials.[25–28] In our previous studies, we have prepared pyrene-, anthracene-, and naphthalene-based liquid crystals that show piezo(mechano)chromic luminescence and thermochromic luminescence in liquid-crystalline (LC) states.[25,26] However, multiluminescent colors have not been achieved for these LC materials.

Herein we report a new type of stimuli-responsive luminescent liquid crystal that exhibits three luminescent colors, which can be switched by mechanical and thermal stimuli (Figure 1). The liquid crystal is composed of equimolar amounts of the dumbbell-shaped compound **1** and compound **2** (Scheme 1). The three luminescent colors observed are reddish-orange, yellow, and green, which are easily distinguished by the naked eye. Moreover, the LC mixture of **1** and **2** contains only one type of luminophore, 9,10-bis(phenylethynyl)anthracene,[34,35] and no additives are required to induce the luminescent color changes. Unlike crystalline materials, the thin-film states are easily prepared (see below). The change in the luminescent colors and the phase-transition behavior of the LC mixture are summarized in Figure 1.

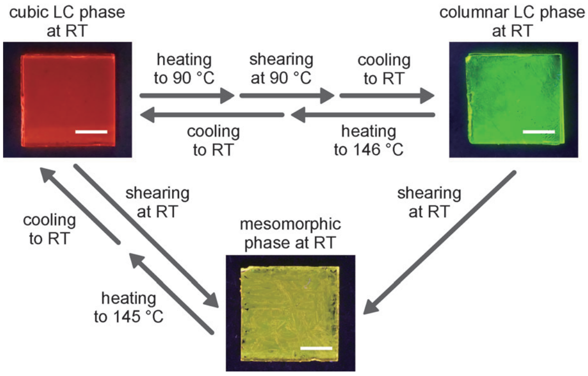


Figure 1. Procedures for obtaining the three different luminescent colors exhibited by a mixture of compounds **1** and **2**. The photoluminescent images were taken for the mixtures between quartz substrates under UV irradiation at 365 nm. Scale bar: 5 mm.

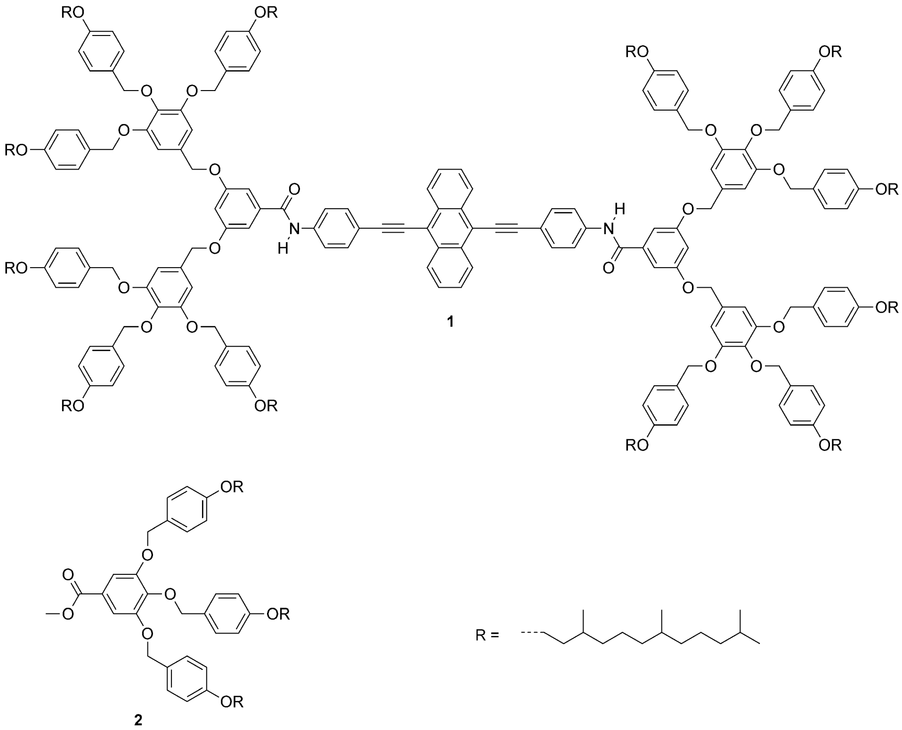
The mixture forms a thermotropic micellar cubic phase upon heating from room temperature to 146 °C. Recently thermotropic cubic phases classified as micellar cubic phases were reported.[25,36] The characterization of the LC phases is discussed in the Supporting Information. Under UV irradiation (365 nm), reddish-orange photoluminescence is observed for the micellar cubic phase (Figure 1, top left). We have found that mechanical shearing to the mixture in the cubic phase at 90 °C triggers a change in the luminescent color from reddish-orange to green (Figure 1, top left→top right). The piezo(mechano)chromic luminescent behavior is accompanied by a shear-induced phase transition from the micellar cubic phase to the columnar phase.[25] The shear-induced columnar phase is stable from room temperature to 146 °C

---

[*] Dr. Y. Sagara, Prof. T. Kato
Department of Chemistry and Biotechnology
School of Engineering, The University of Tokyo
Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
E-mail: kato@chiral.t.u-tokyo.ac.jp
Homepage: http://kato.t.u-tokyo.ac.jp/index-e.html

[**] We thank Prof. K. Araki and Dr. T. Mutai for measurements of emission lifetime and quantum efficiency. This work was partially supported by the Grant-in-Aid for Scientific Research on Innovative Areas of "Fusion Materials: Creative Development of Materials and Exploration of Their Function through Molecular Control" (No. 2206) (T.K.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), and The Global COE Program (Chemistry Innovation through Cooperation of Science and Engineering) (T.K.) from MEXT. Y.S. is grateful for financial support from the Japan Society for the Promotion of Science Research Fellowship for Young Scientists.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201100914.



Scheme 1. Molecular structures of compounds **1** and **2**.

and shows no isothermal transition back to the micellar cubic phase. The increase of the transition enthalpy corresponding to clearing points suggests that the shear-induced columnar phase is more thermodynamically stable than the cubic phase (see the Supporting Information). However, once the mixture of compounds **1** and **2** forms the isotropic phase, the columnar phase does not appear without mechanical shearing. We have also found that the mixture exhibits another change in luminescent color. When the mixtures in the micellar cubic or columnar phases are mechanically sheared at room temperature, the mixtures show an unidentified mesomorphic phase exhibiting yellow emission (Figure 1, bottom). Upon heating the mixture in the mesomorphic phase, the mixture shows a transition to the isotropic phase at 145 °C. On subsequent cooling, reddish-orange emission is observed again from the mixture in the micellar cubic phase. And on heating the mesomorphic phase from −50 °C, a few of exothermic peaks were observed on the differential scanning calorimetry trace (see the Supporting Information). The results imply the mesomorphic phase is a thermodynamically metastable phase.

By following proper procedures (see the Supporting Information), the tricolored luminescent pattern in Figure 2 was obtained at room temperature. The quantum yields of the mixture in the condensed state are lower than that observed for compound **1** in a chloroform solution (Table 1). However, these values are sufficient for various applications such as mechano-sensors, indicators of mechano-history, security papers, optoelectronic devices, and data storage.

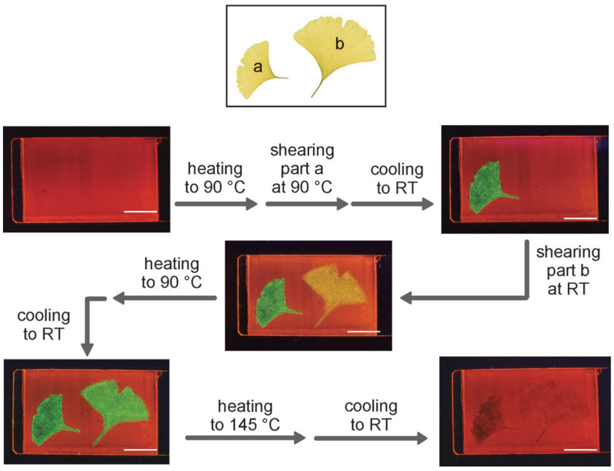


Figure 2. Procedures of writing and erasing tricolored luminescent images. Photoluminescent images were taken for the mixtures on a glass substrate under UV irradiation at 365 nm. Scale bar: 1 cm. Top panel shows two mechanically sheared sections a and b.

Table 1: Emission lifetime and quantum efficiency of the mixture of compounds **1** and **2**.[a]

	Lifetime [ns]	Quantum efficiency
compound **1** in chloroform solution	2.0	0.80
mixture in the cubic phase	1.8, 20	0.05
mixture in the columnar phase	1.6, 4.0	0.13
mixture in the mesomorphic phase	1.4, 9.3	0.15

[a] All measurements were carried out at room temperature. The concentration of compound **1** in chloroform is 1×10^{-6} M.

The spectroscopic measurements of the material were performed to obtain insight into the change in the luminescence of the mixture. The absorption spectrum of **1** in a chloroform solution (1×10^{-5} M; Figure 3 a, gray line) displays an absorption band with vibronic structures between 400 and 500 nm ($S_0\rightarrow S_1$ transition). For the mixture in the assembled states, the absorption bands ascribed to the $S_0\rightarrow S_1$ transition broaden compared to that of **1** in the chloroform solution (Figure 3 a, green, yellow, and red lines), thus indicating that ground-state electronic interactions between luminescent groups occur in the assembled states. In addition, the spectral features for the three assembled states are different from each other. These observations suggest that the arrangements of the luminescent groups of compound **1** change on the shear-induced phase transitions.

The spectral features of the emission in these states are obviously different. In the emission spectrum of **1** in a

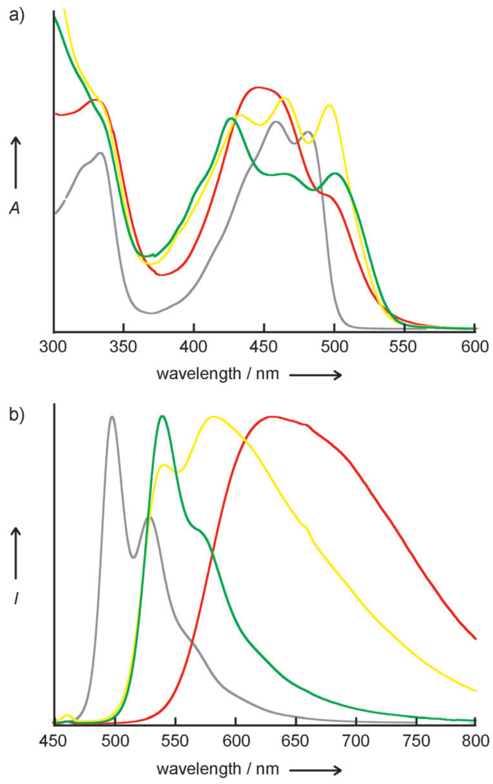


Figure 3. a) Absorption spectra of **1** in chloroform (1×10^{-5} M; gray line), the mixture of compounds **1** and **2** in the cubic (red line), columnar (green line), and mesomorphic (yellow line) phases. b) Normalized emission spectra of **1** in chloroform (1×10^{-5} M; gray line), the mixture in the cubic (red line), columnar (green line), and mesomorphic (yellow line) phases. $\lambda_{ex}=440$ nm. All absorption and emission spectra were obtained at room temperature.

chloroform solution (1×10^{-5} M; Figure 3b, gray line), a well-resolved vibronic structure indicative of the monomeric state of **1** is observed ($\lambda_{max}=497$ nm). As for the cubic phase, the emission band is significantly red-shifted and broadened (Figure 3b, red line) compared to that of **1** in the chloroform solution. The broad and structureless emission band at $\lambda_{max}=630$ nm (red line) is attributed to the excimer formation of the luminescent cores, 9,10-bis(phenylethynyl)anthracene moieties. The emission decay time measurements of the samples (Table 1) support the excimer formation. Compared to the emission lifetime for **1** in chloroform solution (2.0 ns), a longer lifetime component of 20 ns is observed for the mixture in the cubic phase at room temperature. 9,10-Bis(phenylethynyl)anthracene derivatives have been reported to exhibit excimer emission.[35] The emission spectrum of the mixture in the columnar phase (Figure 3b, green line) displays an emission band ($\lambda_{max}=540$ nm) at shorter wavelengths relative to that of the mixture in the cubic phase. The large hypsochromic shift of the emission band on the shear-induced phase transition from the cubic phase to the columnar phase leads to apparent change in luminescent color from reddish-orange to green (Figure 1, top left→top right). For the columnar phase, the longer lifetime component like that observed for the cubic phase cannot be detected (Table 1).

As for the mixture in the mesomorphic phase, two peaks appear in the emission spectrum (Figure 3b, yellow line). The broad peak with $\lambda_{max}=583$ nm can be attributed to partial-overlap excimers of the emission cores. A partial-overlap excimer is an excimer with partial overlap of the aromatic cores.[37] Compared to normal excimers, the partial-overlap excimers exhibit emission bands at shorter wavelengths than those observed for normal excimers. In addition, the emission lifetime of the partial-overlap excimers is often shorter than that of normal excimers. The partial-overlap excimers have been observed in the highly viscous medium such as polymers and Langmuir–Blodgett films.[38] The photophysical properties of the mixture in the mesomorphic phase support the formation of the partial-overlap excimers. From emission lifetime measurements, the mixture contains a lifetime component (9.3 ns) that is shorter than that of the excimer in the cubic phase and longer than that observed for the columnar phase. The position of the other peak with $\lambda_{max}=541$ nm (Figure 3b, yellow line) is identical to that of the peak in the emission spectrum for the mixture in the columnar phase (Figure 3b, green line). In addition, similar lifetime components are detected for the mixture in the columnar and mesomorphic phases (Table 1). Therefore, we concluded that the yellow emission observed for the mesomorphic phase is composed of the emissions from partial-overlap excimers and the same emission spices as in the columnar phase. Notably, possibility that twisting of the chromophores may have a little influence on the change of luminescent colors cannot be ruled out.

The self-assembled structures of compounds **1** and **2** in the LC phases and the mesomorphic phase are proposed in Figure 4. In the cubic phase, compounds **1** and **2** form micellar structures (Figure 4a). Each micelle contains an equal number of compounds **1** and **2**.

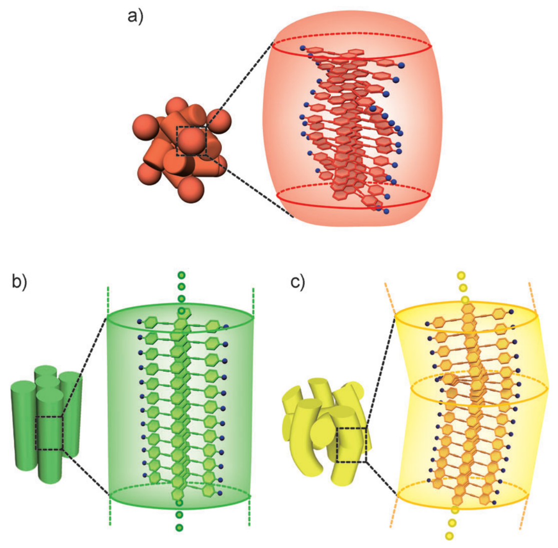


Figure 4. Schematic illustration of the assembled structures of compounds **1** and **2**. a) Cubic phase, b) columnar phase, and c) mesomorphic phase. Amide groups of compound **1**: blue spheres. Compound **2** and dendritic moieties of compound **1** are omitted in the detailed illustration to the right of each structure.

The total number of molecules forming each micelle is approximately 32, which is calculated based on the results of the X-ray measurements (see the Supporting Information). In each micelle approximately 16 molecules of compound **1** form the segmented column. The segmented columnar structure is built through both the formation of π–π stacked structures of the emission cores and the formation of hydrogen bonding between the amide groups of adjacent molecules (see the Supporting Information). The emission cores should be arranged in a disordered stacking arrangement in the segmented columns, because the distance between adjacent arenes forming the π–π stacked structures is generally shorter than the length of H-bonded amide groups.[25] The combination of the dumbbell-shaped compound **1** with compound **2** leads to the formation of stable segmented columnar assembly. As a consequence, reddish-orange excimer emission occurs in the cubic phase (Figure 1, top left). Such assembled structures are supported by our previous results on the assembled structures of pyrene, anthracene, and naphthalene derivatives having similar molecular structures to compound **1**.[25]

The molecularly assembled structures in the columnar phase are depicted in Figure 4b. In each column, compound **1** forms columnar structures through the formation of a linear hydrogen-bonding array that is not observed in the cubic phase. The luminescent cores are spaced by 5 Å (approx.) intervals, thus leading to the interference with the excimer formation of 9,10-bis(phenylethynyl)anthracene moieties. These proposed assembled structures of compound **1** are supported by previous reports on the crystal structures for some arenedicarboxamides.[39] Green photoluminescence of the mixtures in the columnar phase (Figure 1, top right) is attributed to these depicted assembled structures. Upon formation of the shear-induced columnar phase, compound **2** may exist among the hydrogen-bonded columns formed by the dumbbell-shaped compound **1**. The existence of **2** may stabilize the columnar structures consisting of compound **1**. Without compound **2**, compound **1** does not form a columnar phase (see the Supporting Information).

In the mesomorphic phase (Figure 4c), it is assumed that compound **1** forms less-ordered columnar structures, though no clear peaks appear in the X-ray diffraction pattern (see the Supporting Information). This assumption is based on the fact that almost all of the amide groups of compound **1** are involved in the formation of linear hydrogen bonds similar to that in the columnar phase (see the Supporting Information). In addition, a lifetime component similar to that observed in the columnar phase was also detected in the mesomorphic phase (Table 1). These results suggest that the luminescent cores in the mesomorphic phase are partially arranged in a linear arrangement similar to that in the columnar phase. In addition, some of the cores are partially overlapped, thus leading to the partial-overlap excimer emission (Figure 4c). Energy migration and energy transfer may occur from non-overlapped luminescent cores to the partial-overlap excimer sites. Therefore, the mixture exhibits yellow emission in the mesomorphic phase (Figure 1, bottom).

In conclusion, the present results reveal that materials containing only a single luminophore component can switch between three different luminescent colors in the condensed state depending upon the molecularly assembled structures. Moreover, these luminescent images are capable of being written and erased. If a single luminophore component is sufficient to achieve a multiluminescent color device, it can lead to cost reduction in the production of multicolor luminescent displays and sophisticated stimuli-responsive luminescent materials. Our results also imply that the switching of assembled structures of luminescent groups is one of the most promising ways to obtain external-stimuli-responsive luminescent materials, which adds to the conventional approaches of inducing change to the molecular structures itself by light, pH, redox, and mechanical stimuli.

Received: February 5, 2011
Revised: April 16, 2011

Keywords: liquid crystals · luminescence · materials science · phase transitions · supramolecular chemistry

---

[1] C. Weder, C. Sarwa, A. Montali, C. Bastiaansen, P. Smith, *Science* **1998**, *279*, 835 – 837.

[2] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, *Nature* **2002**, *420*, 759 – 760.

[3] X. Zhang, S. Rehm, M. M. Safont-Sempere, F. Würthner, *Nat. Chem.* **2009**, *1*, 623 – 629.

[4] T. Mutai, H. Satou, K. Araki, *Nat. Mater.* **2005**, *4*, 685 – 687.

[5] Y. Sagara, T. Kato, *Nat. Chem.* **2009**, *1*, 605 – 610.

[6] A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, *Chem. Soc. Rev.* **2008**, *37*, 109 – 122.

[7] F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer, A. P. H. J. Schenning, *Chem. Rev.* **2005**, *105*, 1491 – 1546.

[8] A. L. Balch, *Angew. Chem.* **2009**, *121*, 2679 – 2682; *Angew. Chem. Int. Ed.* **2009**, *48*, 2641 – 2644

[9] Y.-A. Lee, R. Eisenberg, *J. Am. Chem. Soc.* **2003**, *125*, 7778 – 7779.

[10] S. Mizukami, H. Houjou, K. Sugaya, E. Koyama, H. Tokuhisa, T. Sasaki, M. Kanesato, *Chem. Mater.* **2005**, *17*, 50 – 56.

[11] Y. Sagara, T. Mutai, I. Yoshikawa, K. Araki, *J. Am. Chem. Soc.* **2007**, *129*, 1520 – 1521.

[12] H. Ito, T. Saito, N. Oshima, N. Kitamura, S. Ishizaka, Y. Hinatsu, M. Wakeshima, M. Kato, K. Tsuge, M. Sawamura, *J. Am. Chem. Soc.* **2008**, *130*, 10044 – 10045.

[13] J. Kunzelman, M. Kinami, B. R. Crenshaw, J. D. Protasiewicz, C. Weder, *Adv. Mater.* **2008**, *20*, 119 – 122.

[14] Y. Ooyama, Y. Kagawa, H. Fukuoka, G. Ito, Y. Harima, *Eur. J. Org. Chem.* **2009**, 5321 – 5326.

[15] T. Abe, T. Itakura, N. Ikeda, K. Shinozaki, *Dalton Trans.* **2009**, 711 – 715.

[16] G. Zhang, J. Lu, M. Sabat, C. L. Fraser, *J. Am. Chem. Soc.* **2010**, *132*, 2160 – 2162.

[17] T. Tsukuda, M. Kawase, A. Dairiki, K. Matsumoto, T. Tsubomura, *Chem. Commun.* **2010**, *46*, 1905 – 1907.

[18] S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin, J.-P. Boilot, *J. Am. Chem. Soc.* **2010**, *132*, 10967 – 10969.

[19] S.-J. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M.-G. Choi, D. Kim, S. Y. Park, *J. Am. Chem. Soc.* **2010**, *132*, 13675 – 13683.

[20] a) R. Davis, N. P. Rath, S. Das, *Chem. Commun.* **2004**, 74 – 75; b) R. Davis, N. S. S. Kumar, S. Abraham, C. H. Suresh, N. P. Rath, N. Tamaoki, S. Das, *J. Phys. Chem. C* **2008**, *112*, 2137 – 2146; c) N. S. S. Kumar, S. Varghese, N. P. Rath, S. Das, *J. Phys. Chem. C* **2008**, *112*, 8429 – 8437.

[21] Y. Dong, J. W. Y. Lam, A. Qin, J. Sun, J. Liu, Z. Li, J. Sun, H. H. Y. Sung, I. D. Williams, H. S. Kwok, B. Z. Tang, *Chem. Commun.* **2007**, 3255–3257.

[22] T. Mutai, H. Tomoda, T. Ohkawa, Y. Yabe, K. Araki, *Angew. Chem.* **2008**, *120*, 9664–9666; *Angew. Chem. Int. Ed.* **2008**, *47*, 9522–9524.

[23] Y. Zhao, H. Gao, Y. Fan, T. Zhou, Z. Su, Y. Liu, Y. Wang, *Adv. Mater.* **2009**, *21*, 3165–3169.

[24] M. Osawa, I. Kawata, S. Igawa, M. Hoshino, T. Fukunaga, D. Hashizume, *Chem. Eur. J.* **2010**, *16*, 12114–12126.

[25] a) Y. Sagara, T. Kato, *Angew. Chem.* **2008**, *120*, 5253–5256; *Angew. Chem. Int. Ed.* **2008**, *47*, 5175–5178; b) Y. Sagara, S. Yamane, T. Mutai, K. Araki, T. Kato, *Adv. Funct. Mater.* **2009**, *19*, 1869–1875; c) Y. Sagara, T. Kato, *Supramol. Chem.* **2011**, *23*, 310–314.

[26] S. Yamane, Y. Sagara, T. Kato, *Chem. Commun.* **2009**, 3597–3599.

[27] V. N. Kozhevnikov, B. Donnio, D. W. Bruce, *Angew. Chem.* **2008**, *120*, 6382–6385; *Angew. Chem. Int. Ed.* **2008**, *47*, 6286–6289.

[28] A. Kishimura, T. Yamashita, K. Yamaguchi, T. Aida, *Nat. Mater.* **2005**, *4*, 546–549.

[29] a) C. Löwe, C. Weder, *Adv. Mater.* **2002**, *14*, 1625–1629; b) B. R. Crenshaw, C. Weder, *Chem. Mater.* **2003**, *15*, 4717–4724.

[30] A. Pucci, F. D. Cuia, F. Signori, G. Ruggeri, *J. Mater. Chem.* **2007**, *17*, 783–790.

[31] S. Srinivasan, P. A. Babu, S. Mahesh, A. Ajayaghosh, *J. Am. Chem. Soc.* **2009**, *131*, 15122–15123.

[32] J. R. Kumpfer, J. Jin, S. J. Rowan, *J. Mater. Chem.* **2010**, *20*, 145–151.

[33] a) *Handbook of Liquid Crystals* (Eds.: D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess V. Vill), Wiley-VCH, Weinheim, **1998**; b) *Thermotropic Liquid Crystals* (Ed.: G. W. Gray), Wiley, Chichester, **1987**; c) T. Kato, N. Mizoshita, K. Kishimoto, *Angew. Chem.* **2006**, *118*, 44–74; *Angew. Chem. Int. Ed.* **2006**, *45*, 38–68; d) T. Kato, *Science* **2002**, *295*, 2414–2418; e) T. Kato, T. Yasuda, Y. Kamikawa, M. Yoshio, *Chem. Commun.* **2009**, 729–739; f) C. Tschierske, *J. Mater. Chem.* **2001**, *11*, 2647–2671.

[34] M. Levitus, M. A. Garcia-Garibay, *J. Phys. Chem. A* **2000**, *104*, 8632–8637.

[35] A. D. Malakhov, M. V. Skorobogatyi, I. A. Prokhorenko, S. V. Gontarev, D. T. Kozhich, D. A. Stetsenko, I. A. Stepanova, Z. O. Shenkarev, Y. A. Berlin, V. A. Korshun, *Eur. J. Org. Chem.* **2004**, 1298–1307.

[36] a) K. Borisch, S. Diele, P. Göring, H. Kresse, C. Tschierske, *Angew. Chem.* **1997**, *109*, 2188–2190; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2087–2089; b) D. Fazio, C. Mongin, B. Donnio, Y. Galerne, D. Guillon, D. W. Bruce, *J. Mater. Chem.* **2001**, *11*, 2852–2863; c) T. Kato, T. Matsuoka, M. Nishii, Y. Kamikawa, K. Kanie, T. Nishimura, E. Yashima, S. Ujiie, *Angew. Chem.* **2004**, *116*, 2003–2006; *Angew. Chem. Int. Ed.* **2004**, *43*, 1969–1972; d) Y. Kamikawa, M. Nishii, T. Kato, *Mol. Cryst. Liq. Cryst.* **2005**, *435*, 755–765.

[37] F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587–614.

[38] a) F. M. Winnik, N. Tamai, J. Yonezawa, Y. Nishimura, I. Yamazaki, *J. Phys. Chem.* **1992**, *96*, 1967–1972; b) Y. Tsujii, T. Itoh, T. Fukuda, T. Miyamoto, S. Ito, M. Yamamoto, *Langmuir* **1992**, *8*, 936–941.

[39] a) F. D. Lewis, J.-S. Yang, C. L. Stern, *J. Am. Chem. Soc.* **1996**, *118*, 2772–2773; b) F. D. Lewis, J.-S. Yang, C. L. Stern, *J. Am. Chem. Soc.* **1996**, *118*, 12029–12037.