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Helicity control in chiral gelation of achiral coumarin derivatives

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Achiral coumarin derivatives spontaneously undergo chiral gelation to give twisted ribbon-like gels in cyclohexane. This kind of chiral gelation of achiral molecules necessarily forms right- and left-handed helical gels. We successfully controlled the helicity in the presence of small amounts of enantiomerically pure coumarins in the solutions of achiral coumarin derivatives.

Keywords: helicity control; chiral gelation; helical gel; achiral coumarin derivative; chiral dopant

Introduction

In recent years, organogels derived from low-molecular-weight compounds have attracted increased interest (*1*, *2*). Chiral gels can be formed even with achiral molecules, and several examples are known (*3–5*), including our finding of helical gels from achiral coumarin compounds (*6*). This kind of chiral gelation necessarily forms both right- and left-handed helices. The spontaneous formation of both the enantiomorphic structures from achiral molecules is common in various types of chiral supramolecular assemblies, such as crystals (*7*), liquid crystals (*8*, *9*) and surfaces (*10*). Thus, controlling the absolute handedness is important in chemical, biochemical and physical systems, and has many applications.

Seeding has been used to prepare crystals with the same handedness as the seed, and pseudo-seeding is also available, based on the use of enantiomorphous crystals having similar crystal structures (*11*). Doping of chiral compounds, however, is the most direct method for inducing helicity in liquid crystal systems from achiral molecules (*12*). Transfer and amplification of chirality, based on chiral dopants, have been achieved in self-assembled polymers (*13–15*) and gels (*16*). Recently, a review of the amplification of chirality in dynamic supramolecular aggregates was also published (*17*). Here, we report the enantio-control of helical gels of an achiral coumarin compound by doping.

Results and discussion

The achiral coumarin derivative **1** was functionalised with a long alkylamide group (Figure 1a). The compound gelled in non-polar and highly polar solvents (*6*). Particularly, in cyclohexane, scanning electron micrographs revealed that twisted ribbon-like gels were formed, and that right-handed (P) and left-handed (M) helices coexisted randomly (Figure 2a). For example, the spontaneous gelation of **1** in cyclohexane (2.0×10^{-2} M) gave 59 and 56 pieces of P and M helical fibres, respectively, in the different micrographs. The incomplete equivalent ratio (2.8% ee) is likely due to counting insufficient numbers and should not be taken to mean that the statistical probability for the formation of P and M helices is not inherently equivalent (0% ee).

The enantiomerically pure coumarin derivative **2R** (Figure 1b), with an (*R*)-1-phenylethylamide group, partially gelled in cyclohexane (4.3×10^{-3} M) to give cotton-like gels in the upper layer and precipitation at the bottom. The helical morphology of the gels was similar to that of **1**, but the twisted direction was only left-handed (M; Figure 2b). In contrast, P helical fibres alone were observed in the gels of **2S**. The homochiral coumarin derivative **3R** (Figure 1b), with an (*R*)-1-(2-naphthyl)ethylamide group, in cyclohexane (3.7×10^{-3} M) did not form helical gels, but gave a very fine fibre network (Figure 2c), as seen in **3S**.

We first examined the efficiency of **2R** and **2S** as dopants for helicity control. The solution of **1** in cyclohexane (2.0×10^{-2} M) containing different percentages of **2R** (0.01–1.4%) to **1** were allowed to stand at room temperature to afford the gels. The numbers of P and M helical fibres were separately counted one by one in the different scanning electron microscope (SEM) images of the dried gels (a total of about 100), and the values of the enantiomeric excess were calculated (Figure 3a). In the presence of **2R**, M helical fibres formed in excess, the direction of which was coincident with M of **2R** helical fibres. Conversely,

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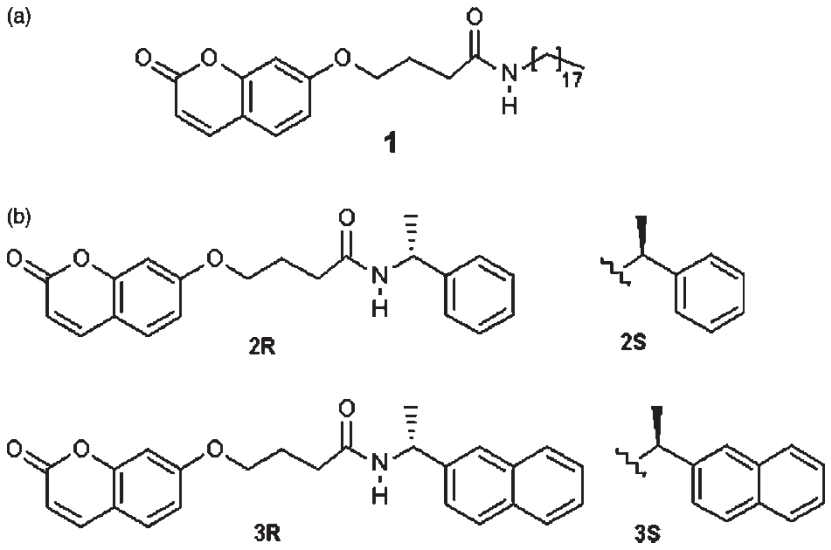

Figure 1. Coumarin gelators. (a) Achiral derivative and (b) chiral derivatives.

the gels doped with **2S** gave P helical fibres in excess, which was in the same direction as that of the **2S** gels. The enantiomeric excess of M helical fibres increased non-linearly with an increase in **2R**; a maximum value of 75% ee was achieved by doping with 1.0% **2R**. Conversely, the presence of 1.0% **2S** afforded 83% ee P helical fibres, indicating a success in controlling the helicity of gels of **1**. However, the presence of more than 1.4% **2R** or **2S** led to a partial combination of neighbouring helical fibres, which made counting the numbers of M and P helical fibres in the SEM images difficult; however, 100% ee, single helicity, was not observed.

Chiral **3R** and **3S** revealed higher efficiencies than **2R** and **2S**. The presence of only 0.13% **3R** or **3S** gave M or P helical fibres in 74 or 68% ee, respectively (Figure 3b). These results confirm that the direction of the helices of achiral gels **1** was controlled by the chirality of the **3R** and **3S** molecules because the gels formed fine fibre networks, and not helical gels (Figure 1c). However, the presence of 0.19% **3R** or **3S** changed the helical fibre morphology slightly to a larger width and helical pitch, to give a lower enantiomeric excess of 56 or 60% ee, respectively. Furthermore, the presence of 0.25% **3R** or **3S** did not result in the formation of helical fibres, but straight ones.

We tried to measure the circular dichroism (CD) spectra of the gels in cyclohexane. However, it was difficult to obtain clear CD spectra even with a 1 mm

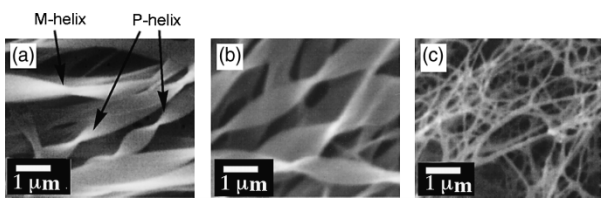

Figure 2. SEM images of dried gels. (a) Coexistence of M and P helices of gels **1**, (b) M helix of gels **2R** and (c) fine fibre network of gels **3R**.

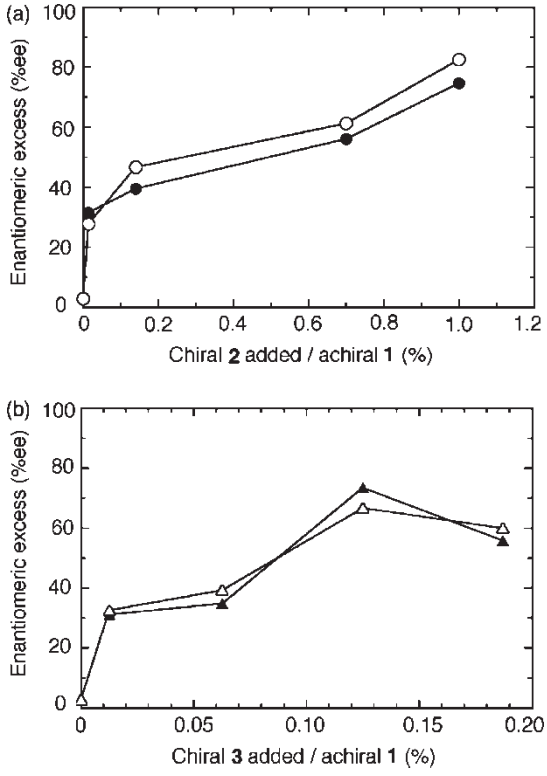

Figure 3. Results of helicity control of the gels of **1** as a function of chiral coumarins in cyclohexane: (a) **2R**, filled circle and **2S**, white circle; (b) **3R**, filled triangle and **3S**, white triangle.

cuvette. Because the helical fibres were relatively large, with widths ranging 1–2 μm, thicknesses ranging 0.1–0.2 μm and helical pitches ranging 1–4 μm, the gels were opaque and not transparent. The CD spectra of the gels were successfully measured by placing the gels in cyclohexane between two quartz plates. Figure 4 shows the CD spectra; the ordinate represents arbitrary units because the thickness of the thin gel layers was not determined. The CD curves (a) and (b) of **2R** and **2S** gels in cyclohexane (4.3×10^{-3} M) revealed good mirror images of each other. Despite the gel morphologies of **3R** and **3S** in cyclohexane (3.7×10^{-3} M) not being helical, but fine fibres, symmetrical CD spectra ((c) and (d)) were observed (Figure 4B), reflecting the molecular chirality of **3R** and **3S**.

Gels of **1** (2.0×10^{-2} M), enantio-controlled (75% ee) by doping with 1.0% **2R** and **2S**, gave CD spectrum (e) and (f) in Figure 4C, respectively. Some resemblance of the curves (a) and (b) with (e) and (f), respectively, suggests that the chirality of **2R** and **2S** molecules was transferred and amplified in the helical gels of achiral **1**. However, with the gels of **1**, doping with **2R** and **2S** in the range 0.7–1.4% gave CD curves almost similar to (e) and (f), resulting in a non-proportional response of the CD effect. As a result, determining the degree of helicity control from the CD spectra quantitatively was difficult. A similar situation was observed for gels of **1** enantio-controlled (around 70% ee) in the presence of 0.13% **3R** or **3S** (Figure 4D).

Infrared spectroscopy of the gels of **1** on a KBr plate showed —CH_2— stretching vibrations at 2920 cm^{-1} (ν_{anti}) and 2850 cm^{-1} (ν_{sym}), indicating that the alkyl chains were closely packed, forming a crystalline domain. Furthermore, the X-ray powder diffraction profile of the dried gels in the absence of dopants revealed that the fibres had a lamellar structure, with a spacing of 2.94 nm (Figure 5a); the 1/2 and 1/4 reflection peaks also appeared. The value of the long period was smaller than the molecular length of **1**, which was 3.64 nm. The coumarin molecules were most probably closely packed, with the long molecular axis parallel to each other through hydrogen bonding among the amide groups to make the lamella structure tilted at 36.1°. The presence of 1.0% **2R** did not change the aggregation mode of the gels of **1**, but the spacing of the lamella slightly increased to 3.00 nm, perhaps due to the decrease in the tilted angle to 35.0° (Figure 5b). The gels of **1** in the presence of 0.13% **3R** also showed a similar lamellar structure (Figure 5c), and a comparable situation was observed in gels doped with the opposite-handed **2S** and **3S**.

Dried gels of chiral **2R** showed similar lamellar structures, with a spacing of 1.69 nm; the 1/2 reflection peak also appeared (Figure 5d). The molecular length was 1.86 nm, and the tilted angle was estimated to be

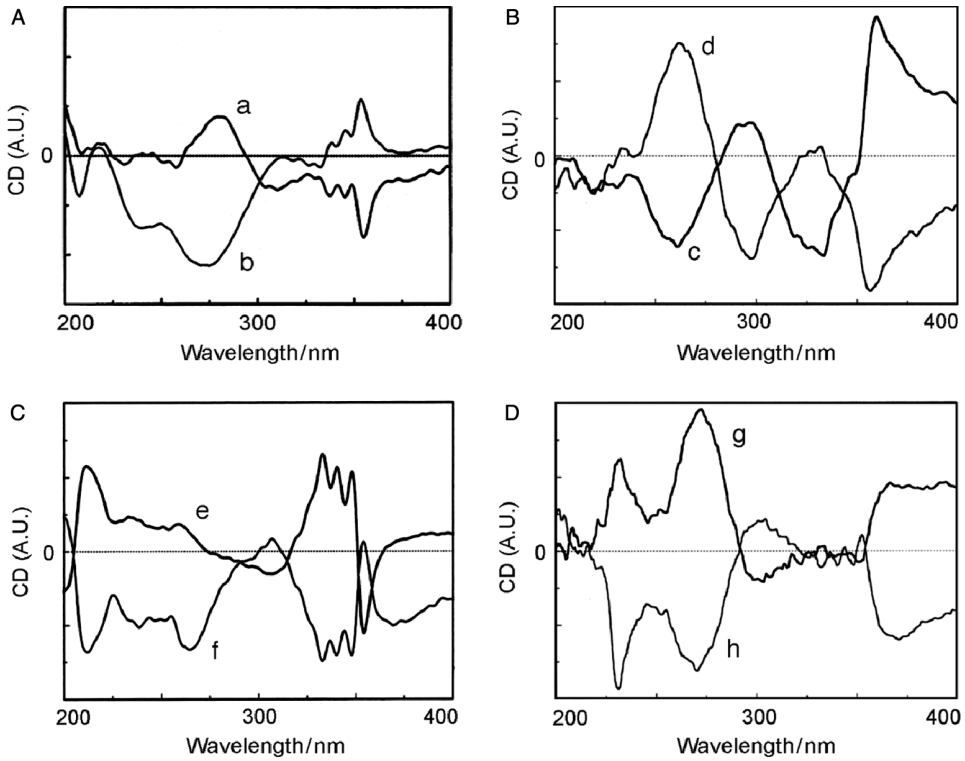

Figure 4. CD spectra of gels in cyclohexane: (A) (a) **2R** and (b) **2S**; (B) (c) **3R** and (d) **3S**; (C) **1** doping with (e) **2R** and (f) **2D**; (D) **1** doping with (g) **3R** and (f) **3S**.

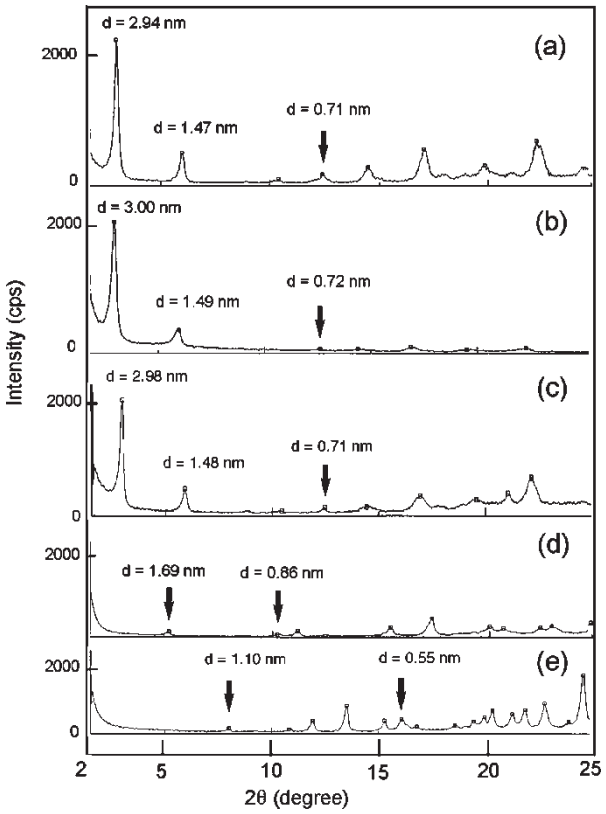

Figure 5. Powder X-ray diffraction profiles of dried gels of (a) **1**, (b) **1** doping with **2R**, (c) **1** doping with **3R**, (d) **2R** and (e) **3R**.

24.7°. The gels of **3R** also had a lamellar structure. Although the molecular distance of **3R** is 1.96 nm, the layer distance was only 1.10 nm, much shorter than that of **2R**; the tilted angle was calculated to be 55.7°. The formation of similar lamellar structures between achiral gels **1** and chiral gels **2R** and **3R** may be the reason that **2R** and **3R** can efficiently act as dopants.

The enantiomeric torsional conformation around the (*R*)-phenylethylamide group in the **2R** molecule arranged the achiral **1** molecules in the same enantiomeric conformation as that of **2R** in the lamellar aggregates. The presence of 1.0% **2R** in gels **1**, which resulted in the M helical fibres in about 80% ee, suggests that one chiral **2R** molecule controlled 90 out of 100 achiral molecules of **1** into the M helical form; one chiral **2S** did the same for the P helical form. Similarly, the result that the presence of 0.13% **3R** in the gels of **1** gave the M helical fibres in about 70% ee suggests that one chiral **3R** molecule could control 680 out of 800 achiral molecules of **1** into the M helical form. Thus, the chiral **2R** and **2S** and **3R** and **3S** molecules apparently control the achiral molecules of **1** (*18*). A subsequent self-organisation of the enantiomeric lamellar aggregates in two and three dimensions forms the M and P helical ribbon-like gels. Thus, the molecular chirality of the chiral dopants was apparently transferred and amplified to the helical fibre gels of achiral **1**.

In conclusion, enantio-control of the helical gels formed from achiral coumarin compounds was achieved by doping with chiral coumarins.

Experimental section

Synthesis of chiral coumarin dopants

Compounds **2R**, **2S**, **3R** and **3S** were synthesised by the procedure described in Ref. 6.

*Compound **2R***. White powder (49% yield), mp 129.6–130.2°C, IR (KBr) 3295, 1737, 1634, 1612 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, $J = 9.3$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 6.80 (d, $J = 2.7$ Hz, 1H), 6.77 (s, 1H), 6.26 (d, $J = 9.6$ Hz, 1H), 5.73 (s, 1H), 5.14 (quint, $J = 6.9$ Hz, 1H), 4.05 (t, $J = 5.9$ Hz, 2H), 2.41 (t, $J = 7.1$ Hz, 2H), 2.21–2.13 (m, 2H) 1.48 (d, $J = 6.9$ Hz, 3H); HR-MS calculated for $C_{21}H_{21}NO_4$ $(M)^+$351.1471, found 351.1469.

*Compound **2S***. White powder (70% yield), mp 119.8–122.6°C, IR (KBr) 3295, 1737, 1634, 1612 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, $J = 9.3$ Hz, 1H), 7.35 (d, $J = 8.1$ Hz, 1H), 6.80 (d, $J = 2.7$ Hz, 1H), 6.77 (s, 1H), 6.26 (d, $J = 9.6$ Hz, 1H), 5.76 (s, 1H), 5.14 (quint, $J = 6.9$ Hz, 1H), 4.05 (t, $J = 5.9$ Hz, 2H), 2.41 (t, $J = 7.1$ Hz, 2H), 2.21–2.13 (m, 2H) 1.48 (d, $J = 6.9$ Hz, 3H); HR-MS calculated for $C_{21}H_{21}NO_4$ $(M)^+$351.1471, found 351.1472.

*Compound **3R***. White powder (90% yield), mp 132.6–133.5°C, IR (KBr) 3296, 1739, 1634, 1613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.84 (dd, $J = 8.1$, 2.0 Hz, 1H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 9.2$ Hz, 1H), 7.52 (td, $J = 6.8$, 2.0 Hz, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 6.70 (dd, $J = 8.2$, 2.8 Hz, 1H), 6.67 (d, $J = 2.4$ Hz, 1H), 6.25 (d, $J = 9.6$ Hz, 1H), 5.95 (quint, $J = 7.1$ Hz, 1H), 5.72 (d, $J = 8.0$ Hz, 1H), 4.00 (m, 2H), 2.37 (m, 2H), 2.16 (quint, $J = 6.5$ Hz, 2H), 1.66 (d, $J = 6.8$ Hz, 3H); HR-MS calculated for $C_{25}H_{23}NO_4$ $(M)^+$401.1627, found 401.1625.

*Compound **3S***. White powder (85% yield), mp 132.3–134.7°C, IR (KBr) 3296, 1738, 1634, 1613 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.85 (dd, $J = 8.1$, 2.0 Hz, 1H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.61 (d, $J = 9.6$ Hz, 1H), 7.52 (td, $J = 6.8$, 2.0 Hz, 1H), 7.49 (d, $J = 7.2$ Hz, 1H), 7.47 (d, $J = 7.6$ Hz, 1H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 8.4$ Hz, 1H), 6.70 (dd, $J = 8.2$, 2.8 Hz, 1H), 6.67 (d, $J = 2.4$ Hz, 1H), 6.25 (d, $J = 9.6$ Hz, 1H), 5.95 (quint, $J = 7.1$ Hz, 1H), 5.72 (d, $J = 8.0$ Hz, 1H), 4.00 (m, 2H), 2.38 (m, 2H), 2.16 (quint, $J = 6.6$ Hz, 2H), 1.66 (d, $J = 6.8$ Hz, 3H); HR-MS calculated for $C_{25}H_{23}NO_4$ $(M)^+$401.1627, found 401.1629.

Helicity control by doping

Typically, to a solution of achiral coumarin **1** (30 mg, 6.0×10^{-5} mol) in cyclohexane (3.0 ml), chiral **2R** (0.002–0.30 mg, 6.0×10^{-9}–8.5×10^{-7} mol) was added and the mixture was dissolved by gentle heating in a covered vessel. The solution was allowed to stand at room temperature to afford gels of **1** (2.0×10^{-2} M) doped with 0.01–1.4% **2R** (2.0×10^{-6}–2.8×10^{-4} M). SEM images of the dried gels were taken and the numbers of P and M twisted ribbon-like fibres were counted one by one, for a total of about 100 in the different SEM images, and the enantiomeric excesses were determined.

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References

(1) van Esch, J.H.; Feringa, B.L. *Angew. Chem. Int. Ed.* **2000**, *39*, 2263.
(2) van Bommel, K.J.C.; Friggeri, A.; Shinkai, S. *Angew. Chem. Int. Ed.* **2003**, *42*, 980.
(3) van Esch, J.H.; De Feyter, S.; Kellogg, R.M.; De Schryver, F.; Feringa, B.L. *Chem. Eur. J.* **1997**, *3*, 1238.
(4) Shimizu, T.; Iwaura, R.; Masuda, M.; Hanada, T.; Yase, K. *J. Am. Chem. Soc.* **2001**, *123*, 5947.
(5) Hill, J.P.; Jin, W.; Kosaka, A.; Fukushima, T.; Ichihara, H.; Shimomura, T.; Ito, K.; Hashizume, T.; Ishii, N.; Aida, T. *Science* **2004**, *304*, 1481.
(6) Yu, H.; Mizufune, H.; Uenaka, K.; Moritoki, T.; Koshima, H. *Tetrahedron* **2005**, *61*, 8932.
(7) Matsuura, T.; Koshima, H. *J. Photochem. Photobiol. C: Photochem. Rev.* **2005**, *6*, 7.
(8) Link, D.R.; Natale, G.; Shao, R.; Maclennan, J.E.; Clark, N.A.; Korblova, E.; Walba, D.M. *Science* **1997**, *278*, 1924.
(9) Sekine, T.; Niori, T.; Sone, M.; Watanabe, J.; Choi, S.-W.; Takanichi, Y.; Takezoe, H. *Jpn J. Appl. Phys.* **1997**, *36*, 6455.
(10) Berg, A.M.; Patrick, D.L. *Angew. Chem. Int. Ed.* **2005**, *44*, 1821.
(11) (a) Koshima, H.; Honke, S.; Miyauchi, M. *Enantiomer* **2000**, *5*, 125, (b) Koshima, H., Miyauchi, M., Shiro, M. *Supramol. Chem.* **2001**, *13*, 137.
(12) Chandrasekhar, S. *Liquid Crystals*; Cambridge University Press: Cambridge, UK, 1992.
(13) Hirschberg, J.H.K.K.; Brunsveld, L.; Ramzi, A.; Vekemans, J.A.J.M.; Sijbesma, R.P.; Meijer, E.W. *Nature* **2000**, *407*, 167.
(14) Brunsveld, L.; Schenning, A.P.H.J.; Broeren, M.A.C.; Janssen, H.M.; Vekemans, J.A. J.M.; Meijer, E.W. *Chem. Lett.* **2000**, 292.
(15) Ajayaghosh, A.; Varghese, R.; George, S.J.; Vijayakumar, C. *Angew. Chem. Int. Ed.* **2006**, *45*, 1141.
(16) de Jong, J.J.; Theodora, D.; Tiemersma-Wegman, T.D.; van Esch, J.H.; Feringa, B.L. *J. Am. Chem. Soc.* **2004**, *127*, 13804.
(17) Palmans, A.R.A.; Meijer, E.W. *Angew. Chem. Int. Ed.* **2007**, *46*, 8948.
(18) Prince, R.B.; Moore, J.S.; Brunsveld, L.; Meijer, E.W. *Chem. Eur. J.* **2001**, *7*, 4150.