Journal of
Materials Chemistry C

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *J. Mater. Chem. C*, 2014, **2**, 6467

Received 20th May 2014
Accepted 18th June 2014

DOI: 10.1039/c4tc01049c

www.rsc.org/MaterialsC

A fluorinated binaphthyl chiral dopant for fluorinated liquid crystal blue phases†

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A 6,6′-fluorinated binaphthyl enantiomer, (*R*)-**1**, was applied as a chiral dopant to produce cholesteric blue phases (BPs). A fluorinated nematic liquid crystal doped with (*R*)-**1** showed lower critical chirality to induce a BP and a larger temperature range of BPs than that doped with a conventional chiral dopant.

Blue phases (BPs),[1–12,14–18,20,21] one of the chiral liquid crystal (LC) phases, appear usually in a small temperature range between chiral nematic (N*) and isotropic (Iso) phases, when the N* phase has a relatively short helical pitch. There are three different types of BPs: BP I, BP II, and BP III, in the order of increasing temperature. The temperature range of a BP has been reported to be enlarged remarkably in the polymer-stabilized blue phase (PSBP),[2] by which the BP state is retained at a low temperature where the N* phase should inherently be the stable phase in the absence of polymer-stabilization. The PSBP is a promising candidate as a next-generation LC display (LCD) material because it exhibits a fast electro-optic effect represented by an optical switching between isotropic and anisotropic states, without surface alignment treatment. The PSBP can be prepared by *in situ* photo-polymerization of an appropriate amount of monomers in a BP state. In the photo-polymerization process, a precursor solution basically consisting of a host LC, chiral dopant, monomer, and photoinitiator is irradiated with UV light. The temperature of the precursor must be adjusted very precisely to hold the BP state during the photo-polymerization process. From the viewpoint of a "process window" in the manufacturing of BP-LCDs, the temperature range of the BP before photo-polymerization should be as large as possible, even if the enlarging range is only 1 °C. Several attempts to enlarge the temperature range of BPs have been made, for example, dimeric LC molecules,[3] hydrogen-bonded self-assembled LC complexes,[4] a binaphthyl type LC molecule,[5] gold nanorod dispersed BPs,[6] an additive bend-core molecule,[7] dendron-stabilized BPs,[8] and so on.[9–12] However, an additional dopant other than the basic components of the precursor or a large change in chemical structure of the components often depresses the display performance. It is required to combine a large temperature range of BPs before polymer-stabilization with high electro-optical performances of BPs. In this study, we focus our attention on a chiral dopant, which is a key material, because large chirality and short helical pitch are needed to induce the BP. If a chiral dopant is able to enlarge the temperature range of BPs, both requirements of the BP temperature range and electro-optic performance could be satisfied simultaneously, without depressing the display performance. Furthermore, a practical chiral dopant should be compatible with fluorinated host LCs because fluorinated LCs are indispensable for thin film transistor (TFT) driving to retain the high voltage holding ratio in display devices.

In our previous study, we synthesized a novel fluorinated chiral dopant, 6,6′-fluorinated binaphthyl, denoted as (*R*)-**1** (Fig. 1), and found that it demonstrated a high helical twisting power (HTP) and high miscibility with a fluorinated nematic LC.[13] Here, we present the phase behavior and electro-optic properties of the fluorinated BPs induced by the chiral dopant (*R*)-**1**, and compare them with BPs induced by a conventional chiral dopant.

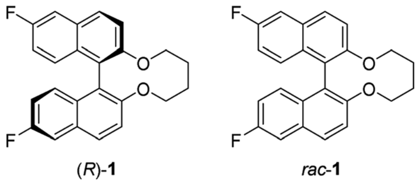

Fig. 1 Chemical structures of 6,6′-difluorinated binaphthyl derivatives.

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† Electronic supplementary information (ESI) available: The syntheses, measurements, polarizing optical microscopy images, elastic constants data, and electro optical properties. See DOI: 10.1039/c4tc01049c

A chiral dopant, 2,5-bis[4′-(hexyloxy)-phenyl-4-carbonyl]-1,4;3,6-dianhydride-D-sorbitol (ISO-$(6OBA)_2$, the chemical structure of which is shown in Fig. S1 in the ESI†), was used as a conventional dopant for comparison with (*R*)-**1**. A nematic mixture of fluorinated biphenyl cyclohexyl systems, JC-1041XX (Fig. S1 in ESI†), was used as the host fluorinated LC. The temperature range of BPs depends on the chirality, *i.e.*, the reciprocal of the helical pitch of the chiral LC phase.[14–18] The helical pitches for each sample were evaluated based on HTP, which was measured by the Grandjean-Cano wedge cell method in the N* phase at 5 °C below the clearing point, *i.e.* the LC phase-isotropic liquid transition temperature T_c. The phase transition behavior of BP samples was observed by polarizing optical microscopy (POM) and UV-Vis micro-spectrophotometry. The melting points of chiral dopants were measured by differential scanning calorimetry. The physical properties of (*R*)-**1** and ISO-$(6OBA)_2$ are as follows: the HTPs (in the N* phase at $T_c - 5$ °C) are −51.5 and 58.4 μm^{-1}, the melting points are 185.1 and 88.3 °C, respectively.

Fig. 2 shows the phase diagrams and the reduced phase transition temperatures as functions of the reciprocal of the helical pitch in the N* phase of (a) JC-1041XX/ISO-$(6OBA)_2$ and (b) JC-1041XX/(*R*)-**1** mixtures. The reduced temperature $T - T_c$ represents the temperature difference from the clearing point. The transition temperatures were measured during the heating process to exclude the effect of supercooling, which is often observed for a phase transition from a BP to the N* phase. The reciprocal of the helical pitch is indicative of the strength of chirality. In general, BPs appear between N* and isotropic liquids when the chirality is higher than a critical point. The critical reciprocals of the helical pitch for JC-1041XX/ISO-$(6OBA)_2$ and JC-1041XX/(*R*)-**1** mixtures were 2.33 and 2.03 μm^{-1}, respectively, and the corresponding critical pitches were 428 and 491 nm, respectively. The critical chirality of BPs is governed by a thermodynamic energy balance between the N* phase and a BP. Low critical chirality corresponds to a readily obtained BP. Furthermore, the temperature range of BPs in the JC-1041XX/(*R*)-**1** mixture was larger than that in the JC-1041XX/ISO-$(6OBA)_2$ mixture.

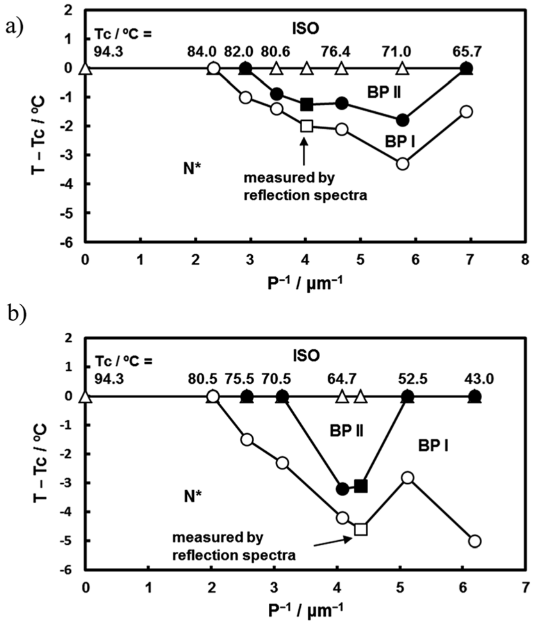

Fig. 2 Phase diagrams and the reduced phase transition temperatures as a function of the reciprocal of the helical pitch in the N* phase of (a) JC-1041XX/ISO-$(6OBA)_2$ and (b) JC-1041XX/(*R*)-**1** mixtures.

Due to Bragg diffraction from the cubic lattice, BPs exhibit characteristic selective light reflections in the visible wavelength range. The temperature dependences of the Bragg wavelengths for the mixtures of (a) JC-1041XX/ISO-$(6OBA)_2$ = 93.1/6.9 wt% (sample 1) and (b) JC-1041XX/(*R*)-**1** = 91.5/8.5 wt% (sample 2) were measured with a UV-Vis micro-spectrophotometer. The temperature range of BPs is known to depend on the chirality, the helical pitch, and/or the lattice constant of the BP. To eliminate the effect owing to the differences in chirality, the helical pitches of the two BPs induced by (*R*)-**1** and ISO-$(6OBA)_2$ were adjusted to be approximately identical by controlling the doping amounts of the chiral dopants in JC-1041XX. The temperature dependences of the Bragg wavelengths for BP I (110) and for BP II (100) are shown in Fig. 3 for the JC-1041XX/ISO-$(6OBA)_2$ and JC-1041XX/(*R*)-**1** mixtures. For the two samples shown in Fig. 3, the Bragg wavelengths are close to each other, *i.e.* the lattice constants of both BPs are comparable. Nevertheless, the temperature ranges of the BPs of JC-1041XX/(*R*)-**1** are larger than those of JC-1041XX/ISO-$(6OBA)_2$. The results shown in Fig. 2 and 3 clearly indicate that the chiral dopant (*R*)-**1** stabilizes a BP more effectively than ISO-$(6OBA)_2$.

Fig. 4 shows the relationships between the concentration of the chiral dopant and the reciprocal of the Bragg wavelength in BP I for the JC-1041XX/ISO-$(6OBA)_2$ and JC-1041XX/(*R*)-**1** mixtures. A linear relation should be satisfied when a chiral dopant is dissolved completely on a molecular level in a host nematic LC. Although the JC-1041XX/ISO-$(6OBA)_2$ mixture showed good linearity over a ISO-$(6OBA)_2$ concentration range of 5 to 10 wt%, a slight downward deviation was observed at 12 wt%, as shown in plot 1 of Fig. 4. On the other hand, the JC-1041XX/(*R*)-**1** mixture obtained good linearity over the entire concentration range of 5 to 12 wt%, as shown in plot 2 of Fig. 4. These results indicate that the miscibility of (*R*)-**1** is higher than

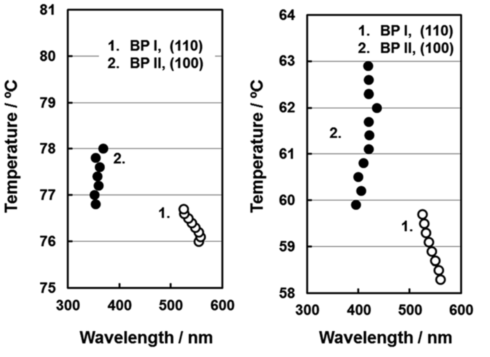

Fig. 3 Temperature dependences of the Bragg wavelengths for (a) JC-1041XX/ISO-$(6OBA)_2$ = 93.1/6.9 wt% (sample 1) and (b) JC-1041XX/(*R*)-**1** = 91.5/8.5 wt% (sample 2) mixtures.

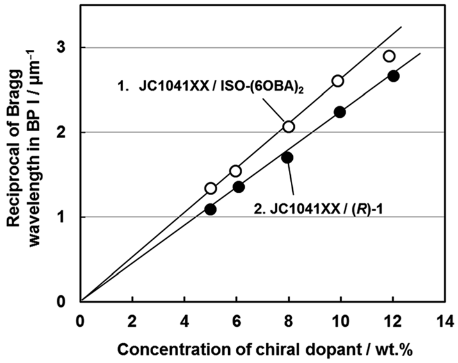

Fig. 4 Relationships between the concentration of the chiral dopant and the reciprocal of the Bragg wavelength of BP I for JC-1041XX/ISO-$(6OBA)_2$ and JC-1041XX/(*R*)-**1** mixtures.

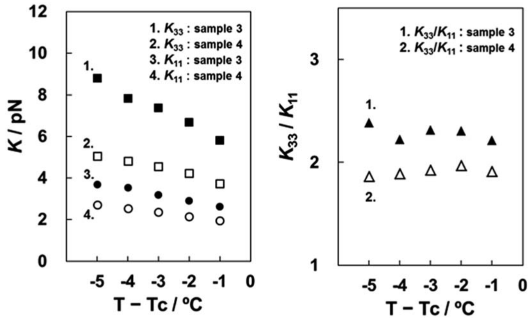

Fig. 5 Temperature dependences of K_{11} and K_{33} as well as the ratio K_{33}/K_{11} for samples 3 and 4. The temperature T_c indicates the clearing point of sample 3 or the nematic-coexisting phase transition temperature of sample 4.

that of ISO-$(6OBA)_2$ in BP I. The temperature range of the BPs of JC-1041XX/ISO-$(6OBA)_2$ is reduced in the high chiral region, as shown in Fig. 2a. Generally, the temperature range of BPs increases with increasing chirality. The low miscibility of ISO-$(6OBA)_2$ to JC-1041XX could be responsible for this unusual reduction of the BP temperature range at high chirality. On the other hand, such a phenomenon was not observed for the JC-1041XX/(*R*)-**1** mixture because of the sufficiently high miscibility of (*R*)-**1** to JC-1041XX.

The thermodynamic stability of BPs is theoretically shown to depend significantly on the value of the Frank elastic constants, splay (K_{11}), twist (K_{22}), and bend (K_{33}), of the host LC materials. Therefore, evaluating the influence of doping with (*R*)-**1** on the value of the Frank elastic constants of the host LC is meaningful. However, the elastic constants are typically measured with uniformly aligned LCs, and therefore these constants can be difficult to determine for a highly twisted LC. To overcome this difficulty, we synthesized the racemic binaphthyl compound, *rac*-**1** (for details, see ESI†), that has an identical chemical structure to (*R*)-**1** (Fig. 1), but which does not induce twist alignment in the LC. We measured the elastic constants, K_{11} and K_{33}, of the pure JC-1041XX without dopant (sample 3, $T_{NI} = 94.3$ °C) and the JC-1041XX/*rac*-**1** = 91.5/8.5 wt% mixture (sample 4) by means of the capacitance method.[19] The phase transition temperatures of sample 3 were 59.7 °C (N to N + Iso.) and 65.5 °C (N + Iso. to Iso), which were observed by POM as discussed later. Fig. 5 shows the temperature dependences of K_{11} and K_{33} as well as their ratio K_{33}/K_{11} for samples 3 and 4. The differences in the values of K_{11} between samples 3 and 4 were relatively small. In contrast, the respective values of K_{33} were very different, wherein the K_{33} values of sample 4 were lower than those of sample 3. The ratio K_{33}/K_{11} of sample 4 was also smaller than that of sample 3 over the entire measuring temperature range. Thus, the chiral dopant (*R*)-**1** is demonstrated to more readily cause bend deformation of LC directors. Assuming that a similar situation could occur for local directors in the BPs of JC-1041XX/(*R*)-**1** is reasonable. The thermodynamic stability of BPs has been shown to theoretically and experimentally be greatly enhanced when K_{33} is smaller.[7,8,20,21] This tendency is in agreement with our experimental results. Therefore, considering that the temperature range of BPs in JC-1041XX/(*R*)-**1** was enlarged by a decrease of K_{33} by doping with (*R*)-**1** is reasonable.

Sample 4 showed a relatively large temperature range, over which the nematic and isotropic phases coexisted as a result of the addition of *rac*-**1** (Fig. S5 in ESI†). The coexisting phase ranged over a span of 5.8 °C, which is much wider in comparison with the host LC (sample 3). Producing a disclination line requires excess thermal energy below the clearing point because the orientational order within the disclination cores is low like an isotropic phase.[18,20] It has been reported that the orientational order in a LC is associated with the ratio of the length *L* to the width *D* (*L*/*D*) of the constituent molecules, and the orientational order decreases as the *L*/*D* of a LC molecule decreases.[22] The *L*/*D* of the compound *rac*-**1**, owing to its wide shaped binaphthyl skeleton, is smaller than both that of the host LC molecule and ISO-$(6OBA)_2$. Hence, the addition of the chiral dopant (*R*)-**1** having a small *L*/*D* might be able to facilitate the formation of disclination lines below the clearing point and to lower the free energy of the BPs. This could be a possible mechanism of the stabilization effect by addition of (*R*)-**1**. When a dendron molecule with a small *L*/*D* is added to a BP sample, the temperature ranges of the BPs and nematic-isotropic coexisting phases is enlarged with an increasing amount of the added dendron molecule.[8]

As shown in Fig. 2, the clearing point T_c of JC-1041XX/(*R*)-**1** is lower than that of JC-1041XX/ISO-$(6OBA)_2$, suggesting that (*R*)-**1** has the larger effect of lowering the order parameter of the host LC than ISO-$(6OBA)_2$. The blue phase must coexist with disclinations to form the double twist alignment. The order parameter in the core of disclination should be lowered as mentioned above. Therefore, the effect of lowering the order parameter by (*R*)-**1** might be also responsible for the observed larger temperature range of blue phases.

The electro-optical properties of the BPs of samples 1 and 2 were investigated. The transmittances of the BPs were measured upon an applied electric field driven by a 1 kHz square wave with comb type electrodes under crossed Nicols. Response times at the voltage at which the BP I exhibited maximum

Table 1 Electro-optical properties of samples 1 and 2

	Kerr coefficient/10^{-11} m V^{-2}	τ_{rise}/μs	τ_{decay}/μs
Sample 1	9.5	966	455
Sample 2	10.5	442	406

transmittance (V_{max}) and Kerr coefficients were measured at the intermediate temperature between $T_{\text{N*–BP I}}$ and $T_{\text{BP I–BP II}}$ for samples 1 and 2. The results are summarized in Table 1. The Kerr coefficients and the response times depend strongly on the helical pitch of BPs. Therefore, by controlling the doping concentration, the helical pitches of samples 1 and 2 were adjusted to be nearly identical. The maximum transmittance, Kerr constants, and response time for the voltage-off state (τ_{decay}) were comparable between the two samples, whereas the response time of the voltage on state (τ_{rise}) of the BP I of sample 2 was less than half that of sample 1, as shown in Table 1. Thus, the electro-optical performance of JC-1041XX/(*R*)-**1** is concluded to be equal to or greater than that of the conventional system, JC-1041XX/ISO-(6OBA)$_2$.

Conclusions

A novel chiral fluorinated binaphthyl derivative, (*R*)-**1**, which was previously synthesized by us, was applied as a chiral dopant to produce fluorinated cholesteric blue phases. A lower critical chirality to induce a blue phase and a larger temperature range of blue phases were produced in a chiral fluorinated nematic liquid crystal doped with (*R*)-**1**. Compared with a conventional sorbitol type chiral dopant, (*R*)-**1** showed a high ability to stabilize blue phases. To understand the stabilizing effect of (*R*)-**1**, Frank elastic constants were measured with a mixture of the fluorinated nematic liquid crystal and *rac*-**1**. The racemic binaphthyl compound *rac*-**1** induced a low elastic constant of bend deformation and an extended temperature range over which the nematic phase coexisted with the isotropic phase, and these could be possible mechanisms of the high stabilizing effect of (*R*)-**1** on blue phases. Most electro-optical properties of JC-1041XX/(*R*)-**1** were comparable with those of the conventional materials, but the rise response was faster.

Acknowledgements

This work was partially supported by JSPS KAKENHI Grant Numbers 21245037, 25248021, and 24750130, Grant-in-Aid for Scientific Research (no. 22107008) on the Innovative Areas: "Fusion Materials" (Area no. 2206) and The Global COE program, Novel Carbon Resource Sciences, Kyushu University.

Notes and references

1 P. P. Crooker, in *Chirality in Liquid Crystals*, ed. H.-S. Kitzerow and C. Bahr, Springer, New York, 2001, ch. 7, pp. 186–222.

2 H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang and T. Kajiyama, *Nat. Mater.*, 2002, **1**, 64–68.

3 H. J. Coles and M. N. Pivnenko, *Nature*, 2005, **436**, 997–1000.

4 W. He, G. Pan, Z. Yang, D. Zhao, G. Niu, W. Huang, X. Yuan, J. Guo, H. Cao and H. Yang, *Adv. Mater.*, 2009, **21**, 2050–2053.

5 A. Yoshizawa, Y. Kogawa, K. Kobayashi, Y. Takanishi and J. Yamamoto, *J. Mater. Chem.*, 2009, **19**, 5759–5764.

6 J.-M. Wong, J.-Y. Hwanga and L.-C. Chien, *Soft Matter*, 2011, **7**, 7956–7959.

7 S.-T. Hur, M.-J. Gim, H.-J. Yoo, S.-W. Choi and H. Takezoe, *Soft Matter*, 2011, **7**, 8800–8803.

8 S. Shibayama, H. Higuchi, Y. Okumura and H. Kikuchi, *Adv. Funct. Mater.*, 2013, **23**, 2387–2396.

9 L. Wang, W. He, X. Xiao, Q. Yang, B. Li, P. Yang and H. Yang, *J. Mater. Chem.*, 2012, **22**, 2383–2386.

10 L. Wang, L. Yu, X. Xiao, Z. Wang, P. Yang, W. He and H. Yang, *Liq. Cryst.*, 2012, **39**, 629–638.

11 L. Wang, W. He, X. Xiao, F. Meng, Y. Zhang, P. Yang, L. Wang, J. Xiao, H. Yang and Y. Lu, *Small*, 2012, **8**, 2189–2193.

12 L. Wang, W. He, X. Xiao, M. Wang, M. Wang, P. Yang, Z. Zhou, H. Yang, H. Yu and Y. Lu, *J. Mater. Chem.*, 2012, **22**, 19629–19633.

13 K. Kakisaka, H. Higuchi, Y. Okumura and H. Kikuchi, *Chem. Lett.*, 2014, **43**, 624–625.

14 M. A. Marcus and J. W. Goodby, *Mol. Cryst. Liq. Cryst.*, 1982, **72**, 297–305.

15 K. Tanimoto, P. P. Crooker and G. C. Koch, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1985, **32**, 1893–1895.

16 D. K. Yang and P. P. Crooker, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1987, **35**, 4419–4423.

17 M. B. Bowling, P. J. Collings, C. J. Booth and J. W. Goodby, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 1993, **48**, 4113–4115.

18 P. de Gennes and J. Prost, in *The Physics of Liquid Crystals*, Oxford University Press, Oxford, 2nd edn, 1993, ch. 6, pp. 263–336.

19 G. Czechowski and J. Jadâyn, *Acta Phys. Pol., A*, 2001, **99**, 579–591.

20 S. Meiboom, J. P. Sethna, P. Anderson and W. Brinkman, *Phys. Rev. Lett.*, 1981, **46**, 1216–1219.

21 J. Fukuda, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2012, **85**, 020701.

22 H. Kimura, *J. Phys. Soc. Jpn.*, 1974, **36**, 1280–1287.