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ARTICLE

Simple and highly efficient chiral dopant molecules possessing both rod- and arch-like units

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A simple chiral dopant molecule (*R*)-1 with both rod- and arch-like units was prepared, and extremely large helical twisting powers (HTPs) (+123–228 μm^{-1}) in nematic liquid crystal phases were achieved. We have demonstrated that the introduction of an arch-like unit in addition to rod-like units is highly effective in controlling the helical molecular alignment. As an application of the dopant, induction of blue phases by addition of a small amount of it was indicated.

Introduction

Generation of helical structures is an important topic in chemistry, physics, biology and materials science.¹ To generate helical structures, nematic (*N*) liquid crystals (LCs) which are the sensitive fluid matters with a one-directional order.² By adding a small amount of a chiral compound, an MLC phase becomes a chiral *N* (*N*^{*}) LC phase which has a single helical superstructure, observable as fingerprint textures by polarized-light optical microscopy (POM). The pitch lengths of the helical superstructures are easily measured by the Cano wedge method, and the strengths of the helicities are quantified by their HTPs. ($\text{HTP} = (\partial p^{-1}/\partial x)_{x \rightarrow 0}$ (p : pitch length, x : mole fraction)).³ For decades, many scientists have been faced with the challenge of synthesizing chiral dopants with larger HTPs. However, the HTPs of the majority of the reported dopants are less than 100 μm^{-1} ,⁴ and no methodology to achieve an HTP larger than 200 μm^{-1} has been described.

It was reported that taddols (*trans*-4,5-bis(diarylhydroxymethyl)-1,3-dioxycyclopentane (534 μm^{-1})⁵ and some metal complexes (Ti(IV) (400–740 μm^{-1})⁶ and Ru(III) (176 μm^{-1})⁷) possess large HTPs. It is assumed that the hydrogen bonds or the metal coordination bonds play an important role in these large HTPs. However, the molecular shapes of these compounds are so intricate that it is difficult to determine the origin of their large HTPs.

It was reported that several chiral dopants possessing two rod-like units in a twisted parallel manner showed rather large HTPs without using hydrogen bonding or metal coordination. For example, 2,2'-disubstituted biphenyl derivatives possessing two rod-like units (46 μm^{-1}),⁸ binaphthol derivatives possessing two rod-like units (154 μm^{-1}),⁹ cyclic molecules consisting of two rod-like units linked with spacers (104 μm^{-1})¹⁰ and

isobornide derivatives with two rod-like units (80.2 μm^{-1})¹¹ showed large HTPs. In these dopants, it is advantageous for the helical senses to be easily predicted from the relative spatial arrangement of their two rod-like units. Namely, each of the two rod-like units play a role as a “director control site,” which controls the alignment of the rod-like LC molecules in parallel around it, and the two rod-like units twist in a parallel manner to generate the helical molecular alignment based on the spatial arrangement. However, the HTPs of those two-rod systems are much smaller than those of the above-mentioned taddols or metal complexes. A binaphthol derivative possessing four rod-like units recently reported by Goh, et al. showed a large HTP (757 μm^{-1}).¹² However, the molecules are relatively large, and the molecular structures calculated by a semi-empirical method (AM1) in their report were complicated because of the flexibility in the alkyl spacers and central binaphthyl units. Other chiral dopants, such as dithienylperfluorocyclopentene,¹³ rocked cyclic conformers,¹⁴ oligonaphthalenes,¹⁵ dihydrodibenz[*c,e*]thiepin,¹⁶ spirobi(2H-naphtho[1,2-*b*]pyran)¹⁷ and chelated borane imine complexes¹⁸, are known, but none of these chiral dopants possesses a HTP greater than 100 μm^{-1} . Hence, a simple and effective molecular design strategy for chiral dopants has not yet been established.

In this study, we designed novel chiral dopants based on the following concepts: 1) to generate a strong helicity, an arch-like unit should be used as one of the director control sites in the molecule, 2) the director control sites should be fixed with a rigid skeleton to control the LC director effectively and 3) the molecular shape should be simple so that the helical sense generated can be easily estimated. We designed compounds (*R*)-1, (*R*)-2 and (*R*)-3 (Fig. 1), which possess both rod- and arch-like units, based on the above concepts.

In this series, bicyclo[2.2.2]octane is used as the rigid skeleton, and two rod-like units are introduced at its 7 and 8-positions. These compounds were easily synthesized from commercially available fumaryl chloride in 4–5 steps, and the stereochemistry of the adducts is controlled by the Diels-Alder reaction of a chiral fumarate with dienes, as reported by Hartmann, et al.,¹⁹ and Zacconi, et al.²⁰ In the molecule (*R*)-1, the pair of rod-like units were arranged almost in a line to generate a one-directional molecular alignment in the *N* phases, as shown in Fig. 2(a).

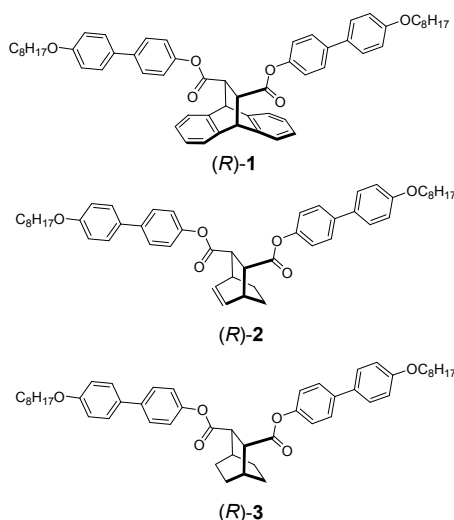


Fig. 1 Molecular structures of (*R*)-1, (*R*)-2 and (*R*)-3

Further, the arch-like unit generates another molecular alignment whose direction is perpendicular to the arch (Fig. 2(b)). Molecule (*R*)-1 contains both rod- and arch-like units in it (Fig. 2(c)). The molecular alignment of triptycene derivatives in an NLC phase caused by the minimization of the free volume in a mixture of the triptycene and the LC molecules reported by Swager et al. is known,²¹ and the triptycene units are aligned strongly in one-direction because of the interaction of the LC molecule and each of the three concave surfaces. From the report, it is suggested that a concave surface can be used as a director control site. In our molecule (*R*)-1, generation of *P*-helicity was predicted, as shown in Fig. 3. The LC molecules around each of the biphenyl moieties are aligned parallel to it, while the LC molecules around the concave surface of the arch are aligned parallel to the perpendicular direction to the bent direction. It is estimated that this twisted molecular alignment of LC molecules around the (*R*)-1 induces a large HTP. The HTPs of (*R*)-2 and (*R*)-3 possessing a small arch unit were compared with those of (*R*)-1.

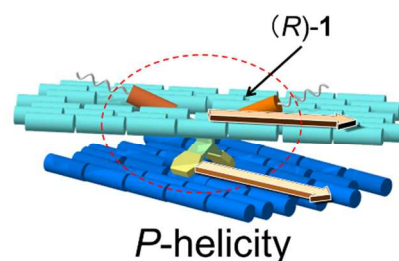


Fig. 3 Schematic representation for controlling the molecular alignments by the two rod-like and one arch-like units of (*R*)-1. Light-blue and blue rods indicate LC molecules.

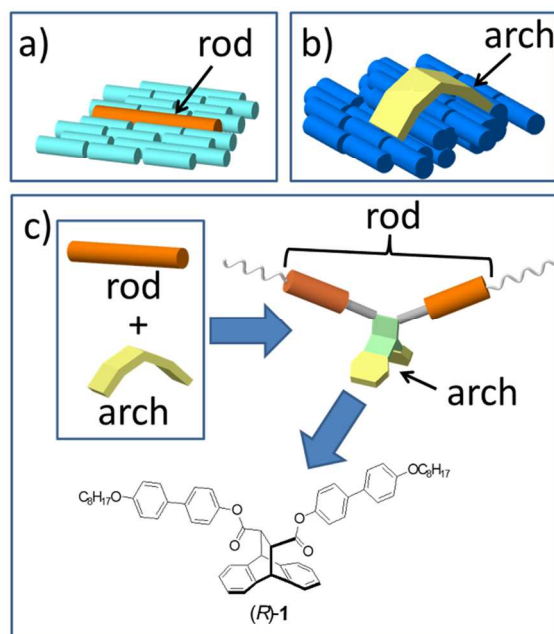


Fig. 2 Molecular design of (*R*)-1: (a) rod-like unit and LC molecules, (b) arch-like unit and LC molecules and (c) molecular design of (*R*)-1 possessing both rod and arch-like units. Light-blue and blue rods in (a) and (b) are LC molecules.

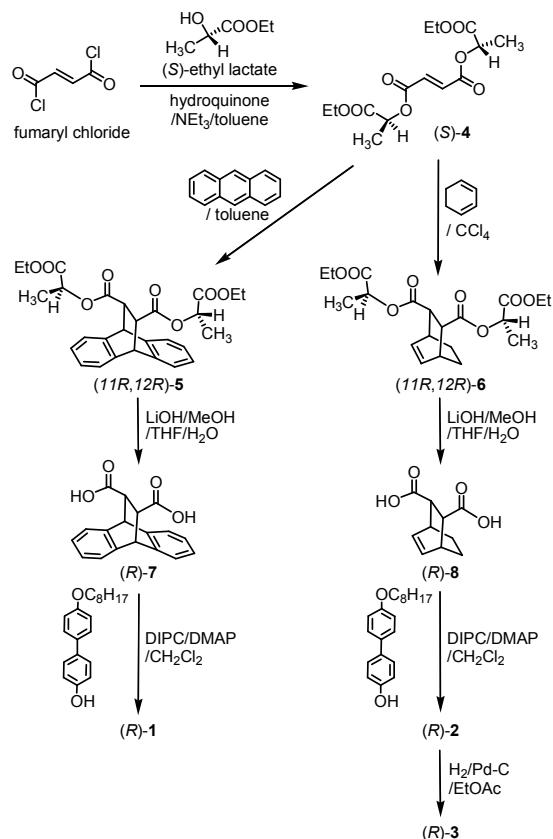


Fig. 4 Synthetic route of (R)-1, (R)-2 and (R)-3.

Results and discussion

Synthesis of dopants and estimation of their conformation.

Compounds (R)-1, (R)-2 and (R)-3 were synthesized as follows (Fig. 4). The condensation of fumaryl chloride and (S)-ethyl lactate gave chiral fumarate (S)-4. The Diels-Alder reaction of (S)-4 with anthracene and 1,3-cyclohexadiene produced **5** and **6** as the major diastereomeric adducts, respectively.^{19,20} The products were purified by silica gel column chromatography or recrystallization to afford **5** and **6** as the pure stereoisomers. Hydrolysis of **5** and **6** afforded (11*R*,12*R*)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid ((*R*)-**7**) and (7*R*,8*R*)-bicyclo[2.2.2]oct-5-ene-7,8-dicarboxylic acid ((*R*)-**8**), respectively. Esterification of (*R*)-**7** and (*R*)-**8** with 4-(4-octyloxyphenyl)phenol yielded (R)-**1** and (R)-**2**, respectively. Compound (R)-**3** was obtained through hydrogenation of (R)-**2**. (S)-**1**, (S)-**2** and (S)-**3** were synthesised in the same synthetic route using ethyl (*R*)-lactate as the chiral starting material.

To confirm that the (*R*)- and (*S*)-isomers of **1**, **2** and **3** obtained by our procedure were a pair of enantiomers, their CD spectra were measured, respectively. There were no difference between the UV spectra of (*R*)- and (*S*)-isomers in each of **1**, **2** and **3**. In Fig. 5(a), the UV spectra of (R)-**1**, (R)-**2** and (R)-**3** in THF are shown and they have a peak at around 270 nm. The CD spectra of the (*R*)- and (*S*)-enantiomers of **1**, **2** and **3** (Fig. 5(b)-(d)) in THF show peaks that have equal magnitudes in

opposite directions, respectively. This confirmed that each pair is a pair of enantiomers. The CD spectrum of each molecule has a large peak at about 280 nm, which originates from the UV absorption of the two -O-CO-C₆H₄-C₆H₄-OC₈H₁₇ moieties at approximately 270nm. The ee of each enantiomer was measured using HPLC on a chiral column, and the purities of (R)-**1**, (S)-**1**, (R)-**2**, (S)-**2**, (R)-**3** and (S)-**3** were 98.6, >99.5, 96.7, 99.4, 98 and >99.5% ee, respectively.

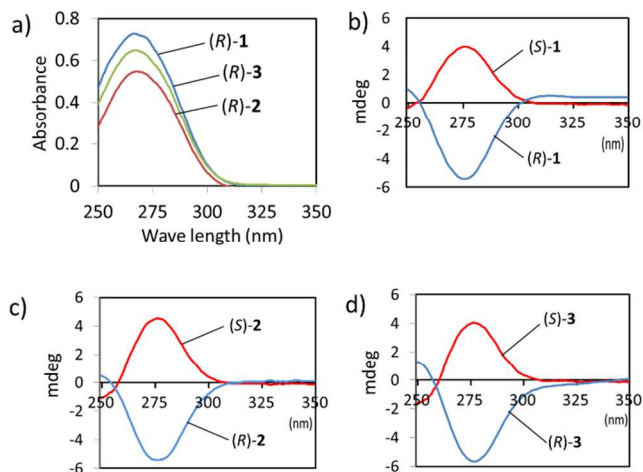


Fig. 5 UV and CD spectra of **1** (1.1×10^{-5} M), **2** (1.0×10^{-5} M) and **3** (1.2×10^{-5} M) in THF; (a) UV spectra of (R)-**1**, (R)-**2** and (R)-**3**, (b) CD spectra of (R)- and (S)-**1**, (c) CD spectra of (R)- and (S)-**2** and (d) CD spectra of (R)- and (S)-**3**. The spectra were measured at room temperature.

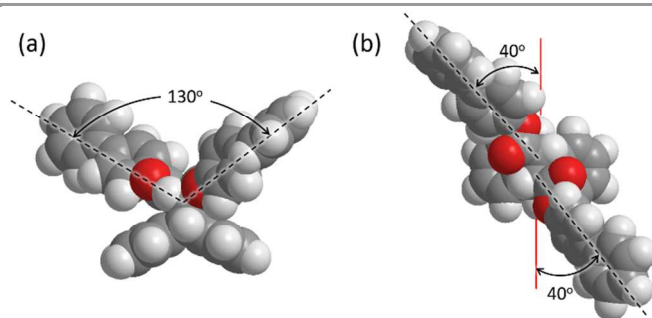


Fig. 6 Most stable conformer of di(4-biphenyl) (11*R*,12*R*)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (R)-**1'** calculated by DFT (B3LYP/6-31G(d)) method: side (a) and top (b) views.²² The axis of each biphenyl group is indicated by a dotted black line. The perpendicular direction to the bent direction of the arch site is indicated a solid red line.

To investigate the most stable conformation of (R)-**1**, the density functional theory (DFT) calculation (B3LYP/6-31G(d))²² of di(4-biphenyl) (11*R*,12*R*)-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate (R)-**1'** was performed. The resulting conformation is shown in Fig. 6. As shown in Fig. 6(a), the angle generated by the two biphenyl-long axes is about 130°. The long axes of the two biphenyl moieties are almost on a plane as shown in Fig. 6(b), and the angle generated by the plane and the perpendicular direction to the bent direction of the arch is approximately 40°. The

conformation obtained by the calculation was similar to the abovementioned model in Fig. 3. Accordingly, it was strongly predicted that *P*-helicity was generated in the doping of (*R*)-1, (*R*)-2 and (*R*)-3 into an achiral *N* LC host.

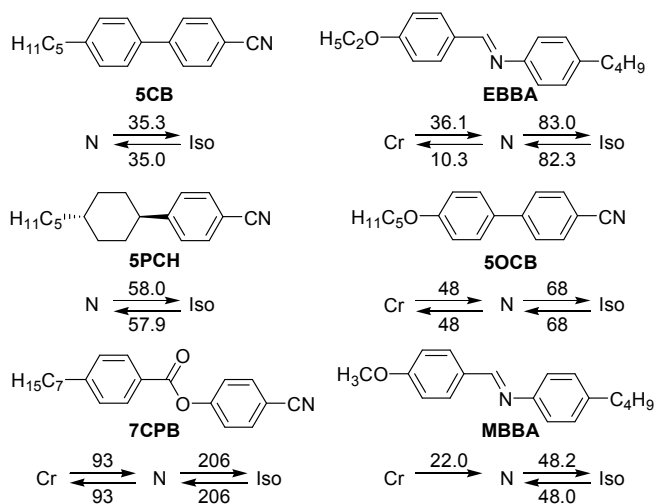


Fig. 7 Molecular structures of the mother LC compounds and their phase transition behaviours

Determination of HTP of the dopant and the helical sense induced by it in the *N** phase.

As the mother LC compounds 5CB, EBBA, 5PCH, 5OCB and 7CPB were used, and their structures and phase behaviours are shown in Fig. 7. LC compounds were doped with 0.5mol% of each of chiral dopants (*R*)-1, (*R*)-2 and (*R*)-3, and their HTPs were measured at $T = T_{IN} - 2$. The results are shown in Table 1. In the case of (*R*)-1, the HTPs in 5CB, 5OCB, 5PCH and 7CPB gave extremely large HTPs around $+200 \mu\text{m}^{-1}$. In the case of 5PCH, the maximum HTP in this study, $+228 \mu\text{m}^{-1}$, was observed. EBBA showed a relatively small HTP ($+123 \mu\text{m}^{-1}$) in these LC compounds.

Table 1 HTPs of (*R*)-1, (*R*)-2 and (*R*)-3 in the LC compounds

Dopant	LC compound	HTP (μm^{-1})
(<i>R</i>)-1	5CB	+213
	EBBA	+123
	5PCH	+228
	5OCB	+211
	7CPB	+192
(<i>R</i>)-2	5CB	+73
	EBBA	+105
	5PCH	+52
	5OCB	+69
	7CPB	+74
(<i>R</i>)-3	5CB	+63
	EBBA	+63
	5PCH	+59
	5OCB	+59
	7CPB	+46

^a The HTPs were measured at $T = T_{IN} - 2$ (K) using a wedge-cell.

Each helical sense of the HTPs were determined in POM by contact experiments with the *N**LC phase of cholesteryl oleyl carbonate which has *M*-helicity.²³ In Fig. 8, the contact experiment of cholesteryl oleyl carbonate and EBBA doped with (*R*)-1 is shown. There is a boundary between the two LC materials. This means that EBBA doped with (*R*)-1 has *P*-helicity which is the opposite helical sense to cholesteryl oleyl carbonate. All *N**LC samples prepared exhibited a discontinuity with that of cholesteryl oleyl carbonate at the boundary. Accordingly, all of the HTPs in Table 1 are written as positive values. Further, *P*-helicity was also suggested by the induced CD spectrum of MBBA⁷ doped with (*R*)-1. As shown in Fig. 9, MBBA doped with (*R*)-1 and (*S*)-1 indicates positive and negative signals, respectively. This also means that dopants (*R*)-1 and (*S*)-1 generate *P*- and *M*-helicity in the *N* phases.

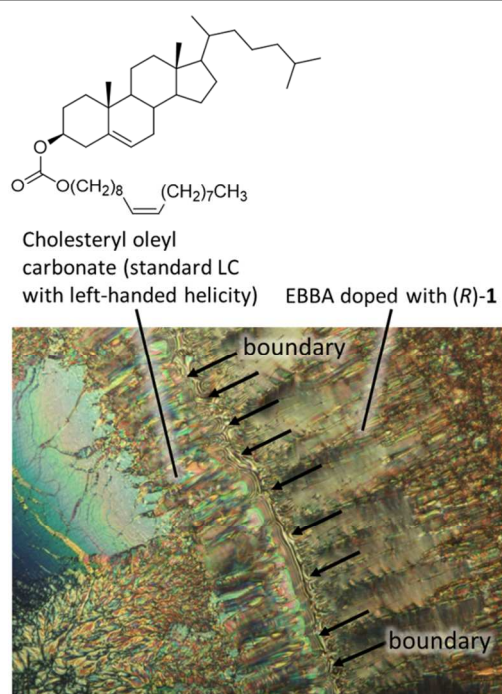


Fig. 8 Microphotograph in the contact experiment of cholesteryl oleyl carbonate (standard LC with *M*-helicity) and EBBA doped with 4wt% of (*R*)-1 (30.9 °C, X200). The boundary of the two LC materials are indicated by black arrows. The existence of the boundary means that the two LC materials have opposite handedness in their helicities.

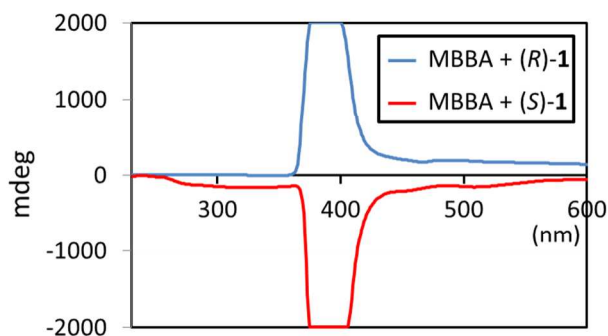


Fig. 9 Induced CD spectra of MBBA doped with 0.4wt% of (*R*)- and (*S*)-1.

It is known that a CN group has a large permanent dipole moment and interacts intermolecularly with other CN groups and benzene rings in LC phases.²⁴ Accordingly, the difference in the HTPs between EBBA and 5CB may originate in the difference in the interaction strengths of $-\text{C}\equiv\text{N}$ and $-\text{C}=\text{N}-$ with the benzene rings at the arch-like unit of (*R*)-1.

In the case of dopant (*R*)-2, which possesses one double bond at its arch-unit, the HTPs in the *N** phases of the cyano-substituted LC compounds (5CB, 5PCH, 5OCB and 7CPB) were +73, +52, +69 and +74 μm^{-1} , respectively. These values are much smaller than those of (*R*)-1. However, the HTP (+105 μm^{-1}) of (*R*)-2 in EBBA is similar to that of (*R*)-1 in EBBA

(+123 μm^{-1}). Dopant (*R*)-3 does not give high HTP values (+46-63 μm^{-1}) in any of the LC compounds.

These results show that the benzene rings at the arch unit of (*R*)-1 play a significant role in aligning the cyano LC molecules. In the case of EBBA, it is assumed that the double bond at the arch of (*R*)-2 has a rather strong interaction with the EBBA molecules, from the comparison of (*R*)-2 and (*R*)-3. The arch of (*R*)-3 has neither a large enough size to control the molecular direction nor a strong interaction with the LC molecules. These results strongly suggest that both the rod- and arch-like units are necessary to generate the strong helicity in the *N**LC phases.

Induction of blue phases by addition of the dopants.

As an application of these dopants, induction of blue phases was attempted. It is known that the phase appears between the isotropic state and the *N** phase with a strong helicity. 5CB doped with only 2 mol% (*R*)-1 exhibited an enantiotropic blue phase at 35.8-36.1 °C as shown in Fig. 10 which indicates platelet textures indicating green selective reflections as their typical textures. It is known that chiral dopants with large HTP can effectively induce blue phases by small amount.²⁵ However, to the best of our knowledge, no example has not been reported on induction of blue phases by addition of a dopant with an extremely large HTP (more than 200 μm^{-1}). EBBA doped with 3 mol% (*R*)-1 also exhibited an enantiotropic blue phase at 75.1-75.7 °C (Fig. 11). In the samples of 5CB doped with (*R*)-2 and (*R*)-3, the enantiotropic blue phases were observed at a dopant concentration of 4 mol%.²⁶ EBBA doped with (*R*)-2 and (*R*)-3 exhibited blue phases at 4 mol% doping.²⁶ Thus, it was found that these dopants effectively induced blue phases. Further, in the case of EBBA doped with 6mol% (*R*)-2, as shown in Fig. 12, both platelet (A and B: blue phase-I and blue phase-II) and fog (C: blue phase-III) textures were observed. It has been reported that a blue phase-III is induced above the temperature range of the *N** phase with strong chirality.²⁷

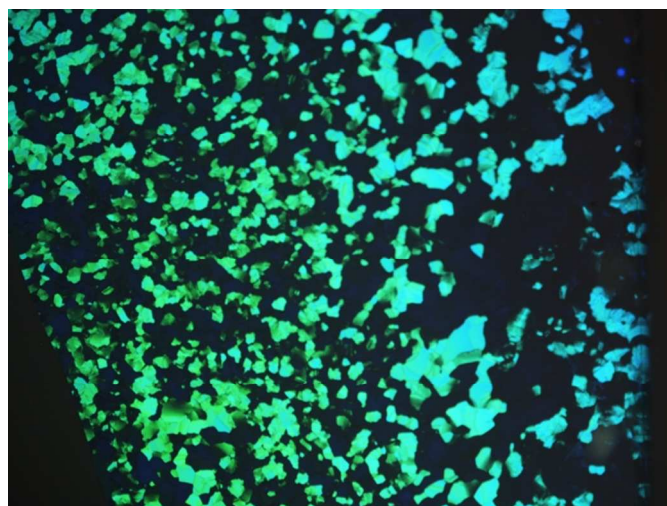


Fig.10 Polarized microphotograph of the blue phase of 5CB doped with 2 mol% (*R*)-1 (36.1 °C on cooling, $\times 100$).

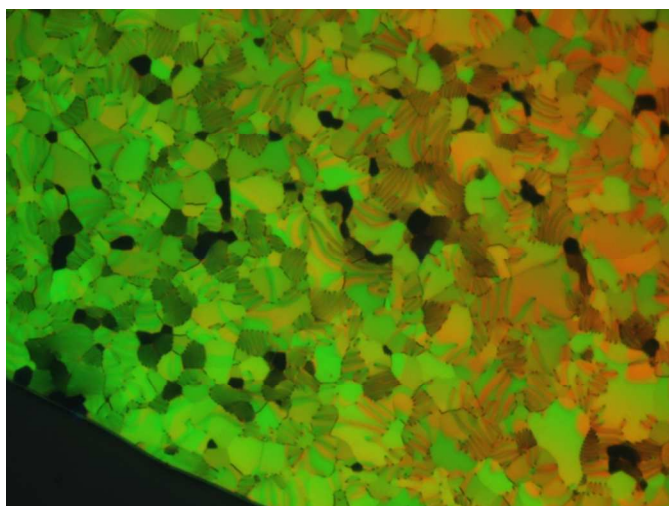


Fig.11 Polarized microphotograph of the blue phase of EBBA doped with 3 mol% (*R*)-1 (75.3°C on heating, $\times 500$).

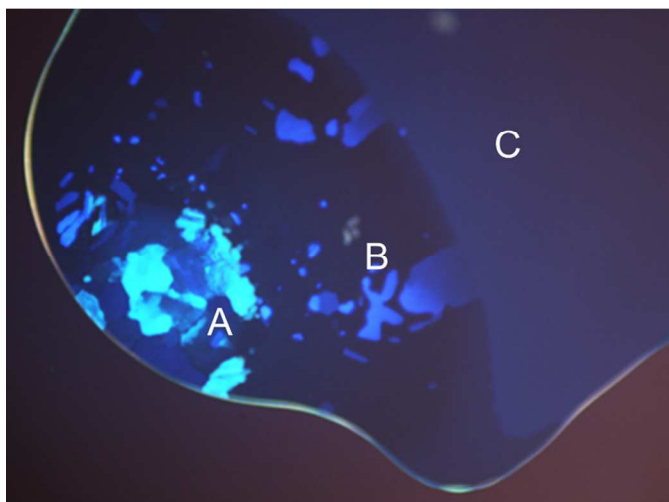


Fig.12 Polarized microphotograph of the blue phase of EBBA doped with 6 mol% (*R*)-2 (72.9°C on cooling, $\times 100$). Platelet (A and B: blue phase-I and blue phase-II) and fog (C: blue phase-III) textures.

Conclusions

We showed that our methodology, the introduction of both arch and rod-sites into a chiral dopant molecule, is highly effective in generating helicity in *N* phases. In this study, as we expected, the *N**LC phases generated by the chiral dopants (*R*)-1, (*R*)-2 and (*R*)-3 had *P*-helical superstructures. Accordingly, the generation of *M*-helical superstructures is also possible by the addition of (*S*)-1, (*S*)-2 and (*S*)-3 which are easily preparable from (*R*)-ethyl lactate using the same synthetic route. We believe that it is highly valuable to prepare both (*R*)- and (*S*)-enantiomers as highly efficient chiral dopants in the field of LC materials chemistry.

Experimental

Synthesis of compound (*R*)-1

Compound (*R*)-7 (0.199 g, 0.676 mmol), 4-(4-octyloxyphenyl)phenol (0.403 g 1.35 mmol), and dry CH_2Cl_2 (25 mL) were placed in a 100mL three-necked round-bottom flask equipped with a CaCl_2 tube. DIPC (0.21 mL, 1.4 mmol) and DMAP (8.2 mg 0.067 mmol) were added and stirred at room temperature for 24 h. The organic phase was washed with water (100 mL) and saturated NaHCO_3 aq (50 mL), and dried over MgSO_4 anhydrous. The solution was filtrated and the solvent was removed by evaporation. The crude product was purified by silica gel column chromatography eluting with *n*-hexane-ethyl acetate to give (*R*)-1 as a white solid (0.440 g, yield 76.9%).

(*R*)-1: mp 112°C (from *n*-hexane-ethyl acetate); $R_f = 0.51$ (hexane : EA = 5 : 1); $\nu_{\text{MAX}}(\text{KBr})/\text{cm}^{-1}$ 3041(C-H), 2927(C-H), 2855(C-H), 1757(C=O); $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.89 (m, 6H, Me), 1.22-1.54 (20H, m, $-\text{CH}_2-$), 1.81 (4H, quint, $J_{1,2} = 6.6 \text{ Hz}, -\text{CH}_2-$), 3.89 (2H, s, CH), 3.99 (4H, t, $J_{1,2} = 6.6 \text{ Hz}, -\text{OCH}_2-$), 5.03 (2H, s, CH), 6.97 (8H, m, aromatic-CH), 7.21 (4H, m, aromatic-CH), 7.48 (12H, m, aromatic-CH); $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.57, 23.11, 26.50, 29.70, 29.81, 32.26, 47.32, 48.35, 68.53, 115.23, 122.05, 124.76, 125.09, 127.06, 127.29, 128.12, 128.51, 133.01, 139.28, 140.66, 142.05, 150.04, 159.23, 171.49; HRMS (ESI) calcd for $\text{C}_{58}\text{H}_{62}\text{O}_6\text{Cl}[(\text{M}+\text{Cl})^+]$ 889.4229, found 889.4276; $[\alpha]_{\text{D}}^{26} -114.36$ (*c* 1.02 in CHCl_3); enantiomeric purity: 98.6 %ee.

(*S*)-1: $[\alpha]_{\text{D}}^{27} +114.35$ (*c* 1.01 in CHCl_3); enantiomeric purity: >99.5 %ee.

Synthesis of compound (*R*)-2

Compound (*R*)-8 (0.130 g, 0.663 mmol), 4-(4-octyloxyphenyl)phenol (0.396 g 1.33 mmol), and dry CH_2Cl_2 (15 mL) were placed in a 200mL three-necked round-bottom flask equipped with a CaCl_2 tube. DIPC (0.21 mL, 1.4 mmol) and DMAP (8.1 mg 0.066 mmol) were added and stirred at room temperature for 24 h. The organic phase was washed with water (100 mL) and saturated NaHCO_3 aq (50 mL), and dried over MgSO_4 anhydrous. The solution was filtrated and the solvent was removed by evaporation. The crude product was purified by silica gel column chromatography eluting with *n*-hexane-chloroform to give (*R*)-2 as a white solid (0.288 g, yield 57.4%).

(*R*)-2: mp 115-118°C (from *n*-hexane-chloroform); $R_f = 0.56$ (hexane : EA = 5 : 1); $\nu_{\text{MAX}}(\text{KBr})/\text{cm}^{-1}$ 3039(C-H), 2928(C-H), 2871(C-H), 2855(C-H), 1752(C=O); $\delta_{\text{H}}(300 \text{ MHz}, \text{CDCl}_3; \text{Me}_4\text{Si})$ 0.89 (6H, m, Me), 1.22-1.53 (22H, m, $-\text{CH}_2-$) 1.80 (6H, m, $-\text{CH}_2-$), 3.31 (3H, m, CH), 3.57 (1H, m, CH), 3.99 (4H, t, $J_{1,2} = 6.6 \text{ Hz}, -\text{OCH}_2-$), 6.45 (2H, m, double bond-CH), 6.96 (4H, m, aromatic-CH), 7.13 (4H, m, aromatic-CH), 7.51 (8H, m, aromatic-CH); $\delta_{\text{C}}(75 \text{ MHz}, \text{CDCl}_3; \text{Me}_4\text{Si})$ 14.51, 21.05, 23.07, 24.59, 26.47, 29.66, 29.69, 29.77, 32.23, 33.05, 33.15, 46.08, 46.40, 68.50, 115.20, 122.03, 122.09, 128.04, 128.11, 128.48, 128.49, 132.78, 133.04, 133.07, 135.34, 139.08, 139.22, 150.14, 150.17, 159.18, 159.21, 173.14; HRMS (ESI) calcd for $\text{C}_{50}\text{H}_{60}\text{O}_6\text{Cl}[(\text{M}+\text{Cl})^+]$ 791.4073, found 791.4088; $[\alpha]_{\text{D}}^{28} -118.30$ (*c* 0.50 in CHCl_3); enantiomeric purity: 96.7 %ee.

(*S*)-**2**: $[\alpha]_D^{28} +126.20$ (*c* 1.00 in CHCl₃) ; enantiomeric purity: 99.4 %ee.

Synthesis of compound (*R*)-**3**

Into a 50 mL round bottom flask were added compound (*R*)-**2** (0.140 g, 0.185 mmol), CHCl₃ (10 mL), and 30% palladium-carbon (0.042 g). The solution was hydrogenated under hydrogen atmosphere with stirring at room temperature. After the reaction, the solution was filtered with celite, and the celite was washed with CHCl₃ (50 mL). The combined CHCl₃ solution was concentrated in vacuo to give (*R*)-**3** (0.127 g) as a crude product. The crude product was purified by silica gel column chromatography eluting with chloroform-hexane to give (*R*)-**3** as a white solid (0.127 g, yield 92.5%).

(*R*)-**3**: mp 120-121°C (from chloroform-*n*-hexane); R_f = 0.77 (chloroform); $\nu_{\text{MAX}}(\text{KBr})/\text{cm}^{-1}$ 3037(C-H), 2930(C-H), 2860(C-H), 1749(C=O); $\delta_{\text{H}}(300 \text{ MHz, CDCl}_3; \text{Me}_4\text{Si})$ 0.89 (6H, m, Me), 1.20-1.89 (32H, m, -CH₂-), 2.38 (2H, s, CH), 3.52 (2H, s, CH), 3.99 (4H, t, $J_{1,2} = 6.6 \text{ Hz, -OCH}_2\text{-}$), 6.96 (4H, m, aromatic-CH), 7.14 (4H, m, aromatic-CH), 7.52 (8H, m, aromatic-CH); $\delta_{\text{C}}(75 \text{ MHz, CDCl}_3; \text{Me}_4\text{Si})$ 14.49, 21.84, 23.06, 25.66, 26.46, 28.07, 29.64, 29.68, 29.76, 32.21, 44.54, 68.51, 115.21, 122.09, 128.08, 128.48, 133.09, 139.11, 150.20, 159.18, 173.97; HRMS (ESI) calcd for C₅₀H₆₂O₆Cl [(M+Cl)⁻] 793.4229, found 793.4246; $[\alpha]_D^{28} -68.46$ (*c* 0.30 in CHCl₃) ; enantiomeric purity: 98.8 %ee.

(*S*)-**3**: $[\alpha]_D^{28} +72.95$ (*c* 0.31 in CHCl₃) ; enantiomeric purity: >99.5 %ee.

An example of measurement of HTPs by the Cano's method
5CB doped with 0.5 mol% of (*R*)-**1** was put in a Cano wedge cell. The pitch length was measured by using a polarized optical microscope. Plots of the inversed pitch length (p^{-1}) against the mole fraction (*x*) of the dopant gave the magnitude of HTP. The sign of β_M was determined by POM observation in the contact experiment with cholesteryl oleyl carbonate.

Observation of induced CD of MBBA doped with (*R*)-**1** and(*S*)-**1**

The induced CD spectra were measured by Hoshino's method.⁷ MBBA doped with 0.4 mol% of **1** was placed between two quartz plates in the N*LC phase. The induced CD was measured by using a CD spectrometer.

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Notes and references

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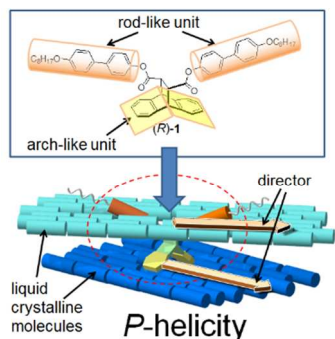
† Electronic Supplementary Information (ESI) available: Phase transition behaviors of 5CB and EBBA doped with (*R*)-**1**, (*R*)-**2** and (*R*)-**3** (Tables 1S, 2S and 3S) and polarized microphotographs of blue phases of

5CB and EBBA doped with (*R*)-**1**, (*R*)-**2** and (*R*)-**3** (Fig. S1–S5). See DOI: 10.1039/b000000x/

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Table of contents entry



Simple chiral dopant molecule (*R*)-1 possessing both rod- and arch-like units was prepared and indicated extremely large HTPs (+123–228 μm^{-1}) with *P*-helicity in nematic liquid crystal phases.