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Enhancement of the cholesteric induction power by macrocyclization in liquid crystal dimers with a chiral spacer†

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A liquid crystal dimer with a chiral spacer increases the helical twisting power in a nematic liquid crystal solvent by a factor of four because the two tails are connected. In the macrocyclized dimer, the two mesogens are fixed in a skewed overlapping alignment with the handedness determined by the spacer's chirality.

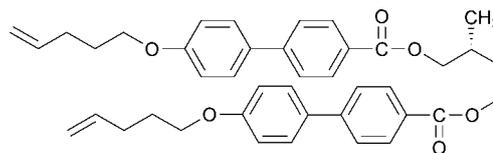
A proven method of obtaining a chiral nematic liquid crystal (LC) is the addition of a chiral dopant to a nematic LC.^{1,2} The chiral nematic (or cholesteric) phase is formed in such a way that the molecular chirality of the dopant is transferred to the nematic phase organization, and the phase formation causes the nematic director to rotate perpendicular to an axis in a helical manner with pitch P inversely proportional to the concentration (molar fraction) of chiral dopant c . The handedness of the helix and the magnitude of P are intrinsic to every chiral compound and are different for every host-guest combination.¹

The efficiency of the dopant in inducing helical organization is expressed by the parameter *helical twisting power* (HTP), defined as $\beta = (Pc)^{-1}$, where r is the enantiometric excess of the dopant. The sign of β is considered positive if the induced cholesteric helix is right-handed. This parameter reflects the amount of dopant needed to reach a cholesteric phase with a certain pitch.

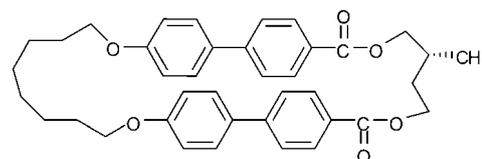
Two approaches have been used to prepare high-HTP chiral dopants. The first approach is mesogenic functionalization of the chiral dopant, where a chiral molecule is functionalized with a mesogenic group resembling the host nematic LC to enhance the solubility and interactions with the LC host.³⁻⁶ For (R)-octane-2-ol, β is $0.8 \mu\text{m}^{-1}$ in an LC host of MBBA (p-methoxybenzylidene-p-butylaniline), but increases to $19.4 \mu\text{m}^{-1}$ by functionalization with a resembling MBBA mesogen.³ The second approach is reduction in the conformation flexibility by the formation of a chiral coordination complex or use of a reasonably rigid backbone.⁷⁻¹⁰ For the tris (pyridyl)amine-based ligand, β is negligibly small, but complexation with Cu(I) or Cu(II) greatly increases it up to $98 \mu\text{m}^{-1}$.⁷ Inherently

chiral molecules, such as binaphthyls,^{11,12} biphenyls¹³ and helicenes,¹⁴ are widely applied as chiral dopants.

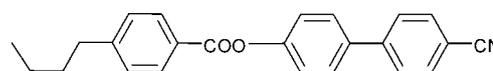
In this paper, we demonstrate that the β value of chiral LC dimers can be enhanced by macrocyclization. The chiral dimer has two mesogenic units connected by an alkyl spacer with a chiral carbon:



This linear (L)-dimer(R) with allyl tails is macrocyclized by ring-closing metathesis under high dilution in the presence of the first Grubbs catalyst to yield the cyclic (C)-dimer(R):¹⁵



Two of these molecules with biphenyl moieties form enantiotropic smectic A LCs, which can be easily dissolved in nematic dopants. We measured the values of β by doping these dimers into a nematic LC of 4'-cyanobiphenyl-4-yl 4-butylbenzoate (CBPBB):¹⁶



For the (C)-dimer(R), β is $-38.4 \mu\text{m}^{-1}$, the absolute value of which is more than four times that of the (L)-dimer(R) ($-9.2 \mu\text{m}^{-1}$). The mechanism of HTP enhancement by macrocyclization is discussed below.

Fig. 1 shows the phase diagrams of the binary mixtures of (C)-dimer(R)/CBPBB and (L)-dimer(R)/CBPBB. As the temperature decreases, CBPBB forms the following phases in the order listed: isotropic liquid (Iso), nematic (N), smectic A (SmA) and finally, crystal. The N phase is formed in a wide temperature range 74–247 °C, which decreases with the addition of the chiral dimer. However, this wide temperature range does not impede the measurement of β , because chiral nematic phases with helical pitches, measured by circular dichroism (CD) spectroscopy, are formed over a sufficiently

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† Electronic Supplementary Information (ESI) available: Synthesis procedure for the dimers, optical micrograph of the BP phase, CD spectra of the mixtures and ¹H-NMR spectra of dimers in chloroform. See DOI: 10.1039/c0jm03161e/

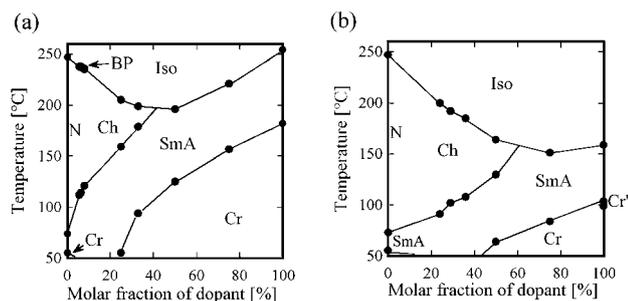


Fig. 1 The phase transition temperatures of (a) (C)-dimer(R)/CBPBB and (b) (L)-dimer(R)/CBPBB mixtures determined by optical microscopy during cooling of the isotropic liquid at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

wide temperature range for (C)-dimer(R)/CBPBB and (L)-dimer(R)/CBPBB mixtures at dimer molar fractions of <10 and <50 mol%, respectively. The (C)-dimer(R)/CBPBB mixture, which is cooled from the Iso phase and observed by polarized optical microscopy, forms a mosaic texture, characteristic of a blue phase over a narrow temperature range ($\sim 1\text{ }^{\circ}\text{C}$, for example, $235\text{--}236\text{ }^{\circ}\text{C}$ at a dimer molar fraction of 8.1%), and then forms the chiral N phase (ESI, Fig. S2[†]).

The value of HTP for (C)-dimer(R) is more than four times larger than that for the (L)-dimer(R). Accordingly, blue-coloured cholesteric LC film can be prepared by doping a dimer in CBPBB. The required doping concentration of the (C)-dimer(R) is just 8 mol%, whereas for the (L)-dimer(R), it is 35 mol%. We doped samples of CBPBB with various molar fractions of (C)- and (L)-dimers and determined the cholesteric pitch using CD spectroscopy of the planar aligned film samples (thickness *ca.* $10\text{ }\mu\text{m}$). All the spectra exhibit a positive peak due to the selective light reflection characteristic of chiral nematic LCs (Fig. 2a), indicating that the induced helical structure is left-handed. The maximum wavelength λ_m of the reflection band is related to the optical pitch nP by $\lambda_m = nP$, where the refractive index n is assumed to be a common value of 1.5. The pitches are weakly dependent on temperature ($-dP/dT < 1.7\text{ nm }^{\circ}\text{C}^{-1}$ in the temperature range $30\text{--}5\text{ }^{\circ}\text{C}$ below the isotropization temperature T_i (ESI, Fig. S3[†]); hence, P measured at $T = T_i - 10$ is regarded as the standard pitch. Fig. 2b shows the plot of reciprocal pitch P^{-1} against the molar fraction of the chiral dimer. The data fall on a straight line in both mixture systems. From the slope of the line and the handedness of the induced helix, we estimate β of the (C)-dimer(R) as $-38.4\text{ }\mu\text{m}^{-1}$, the absolute value of which is more than four times that of the (L)-dimer(R) ($-9.2\text{ }\mu\text{m}^{-1}$).

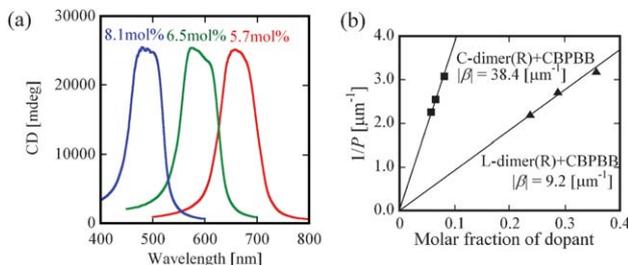


Fig. 2 (a) Typical reflection CD spectra observed at $T = T_i - 10$ in a (C)-dimer(R)/CBPBB mixture system; (b) reciprocal pitch P^{-1} of a cholesteric helix in the chiral nematic LC of (C)-dimer(R)/CBPBB (square) and (L)-dimer(R)/CBPBB (triangle) mixtures as a function of the molar content of the chiral dimer.

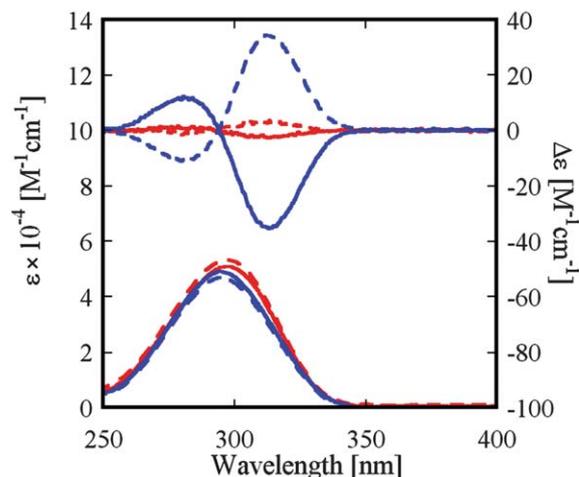


Fig. 3 CD (top) and UV (bottom) spectra of (C)-dimer(R) (blue line) and (L)-dimer(R) (red line) at concentrations of $2 \times 10^{-5}\text{ M}^{-1}$ in chloroform. Dashed lines show the spectra of the enantiomers.

Thus, macrocyclization increases the absolute value of β of the chiral dimer. A possible reason is the skewed arrangement of the two mesogens that face each other in the (C)-dimer. Fig. 3 shows CD and UV spectra of the chiral dimers in chloroform measured at $25\text{ }^{\circ}\text{C}$. In the UV spectra, the (L)- and (C)-dimers(R) are absorbed with similar values of ϵ at a peak wavelength of 295 nm due to $\pi\text{--}\pi^*$ electronic transitions in the biphenyl moiety. In the CD spectra, peaks of the first positive and second negative Cotton effects are evident in the region $250\text{--}350\text{ nm}$, which indicates that the two mesogenic moieties of the (L)- and (C)-dimers(R) overlap counter-clockwise. This is illustrated in Fig. 4.¹⁷ Mirror-image CD spectra are observed for the enantiomers, *i.e.* the (L)- and (C)-dimers(S), indicated that the handedness of such skewed overlapping of the mesogens is determined by the handedness of the chiral spacer.

Interestingly, the CD peaks are much larger for the (C)-dimers than for the (L)-dimers. This phenomenon can be simply explained as

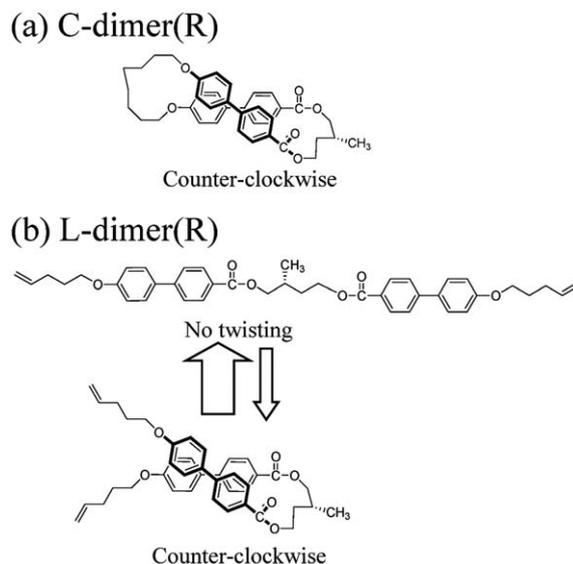


Fig. 4 The proposed configurations of (a) (C)-dimer(R) and (b) (L)-dimer(R) in a nematic solvent.

a direct effect of macrocyclization that causes the two biphenyl moieties to overlap with each other. In fact, a closed side-by-side arrangement of the two mesogenic units has been suggested based on the finding that the aromatic protons shift upfield by 0.1–0.2 ppm from those of the (L)-dimers in the solution $^1\text{H-NMR}$ spectra (ESI, Fig. S5†).^{18,19} Thus, we conclude that for the (C)-dimer, the large absolute value of β is attributed to conformational freezing into a skewed overlap of the two mesogens; for the (L)-dimer, the two mesogenic units can overlap only when the spacer is folded. However, such a configuration is unlikely for a molecule in the nematic LC field (Fig. 4b).

In summary, the HTP of an LC dimer having a chiral spacer is efficiently enhanced by macrocyclization. In the macrocyclized dimer, the two mesogens facing each other are fixed in a skewed arrangement and the handedness is determined by the handedness of the spacer. Such an intermolecular skewed configuration is effective in enhancing the HTP. Macrocyclization of chiral LC dimers can thus be utilized as a new strategy for obtaining high-HTP chiral dopants.

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