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Photoswitching in chiral nematic liquid crystals: interaction-selective helical twist inversion by a single chiral dopant

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Photoisomerization of a chiral azobenzene dopant possessing only one asymmetric carbon, (*R*)-3-(1-methylhexyloxy)-3′-octyloxy-2,2′-dimethylazobenzene, was found to be able to specifically induce a helical twist inversion in liquid crystals having alkenyl terminal substituents, an alkenyl-selective interaction which was not found in conventional *para*-substituted azobenzenes.

Reversible switching of electro-optical properties of liquid crystals (LCs) by photochromic materials has been the subject of a wide range of investigations.[1] Azobenzene is an attractive photochromic material because of its simple photochemistry and ease of chemical modification. Azobenzene dissolved in a chiral nematic (cholesteric) LC provides photocontrollability of the helical pitches as a result of *trans–cis* photoisomerization, as was first demonstrated by Sackmann.[2] On the other hand, a chiral azobenzene derivative dissolved in a nematic LC can act as both a chiral dopant to induce a chiral nematic phase and a phototrigger to control the generated helical pitch. Recently, we have shown that the photoswitching behavior of helical pitches in chiral nematic phases doped with azobenzene derivatives is determined by the interaction between the LC molecules and the conformations of the *trans* and *cis* isomeric configurations of the azobenzenes, coupled with the thermal characteristics of the chiral nematic nature.[3] Other photochromic materials, such as fulgides,[4] diarylethenes,[5] and overcrowded alkenes,[6] have also been reported to modify the helical pitch of chiral nematic LCs. In this paper, we describe a specific interaction-selective helical twist (handedness) inversion of chiral nematic LCs induced by photoisomerization of a simple chiral azobenzene, (*R*)-3-(1-methylhexyloxy)-3′-octyloxy-2,2′-dimethylazobenzene (mMeAz) (Fig. 1).

Temperature-dependent and dopant concentration-dependent helical twist inversion for chirally doped LC systems have been found in chiral nematic and chiral smectic C phases.[7] This intriguing reversal phenomenon occurs mostly to chiral dopants having various chiral centers in one molecule. Although some 2,2′-dialkylazobenzenes having two chiral centers doped into nematic LCs have also been reported to show helical twist inversion upon *trans–cis* photoisomerization,[8] the role of host–guest interactions in the inversion phenomenon was unclear. We believe that this is the first example of a single pure chiral dopant with only one chiral center that can exhibit clear LC host-dependent, more precisely, functional group-dependent, helical twist inversion by photoisomerization. The structures of the nematic LC hosts (purchased either from RODIC or Merck) are also shown in Fig. 1.

The chiral azobenzene dopant is prepared *via* reaction of 3,3′-dihydroxy-2,2′-dimethylazobenzene with the corresponding alcohols.[9] The *trans* and *cis* isomers were isolated by liquid chromatography and their UV-vis spectra are shown in Fig. 2. Photoisomerization in a nematic LC (DON-103) toward the photostationary states of UV (365 nm) and visible (436 nm) light produced *ca.* 83 and 0.5% *cis* isomer, respectively. The helical twisting power, $\beta = 1/pc$, is measured using wedge cells (p/μm^{-1} and c/mol% are the pitch and concentration of dopant, respectively). The helical twist sense is determined by observing the extinction zone shift upon rotating the analyzer, or by the contact method.[10,11]

At the lower limit of dopant concentration, a strongly linear correlation relation between c and $1/p$ was found (Fig. 3). Our previous effort involved nematic hosts having alkyl, alkoxy, or

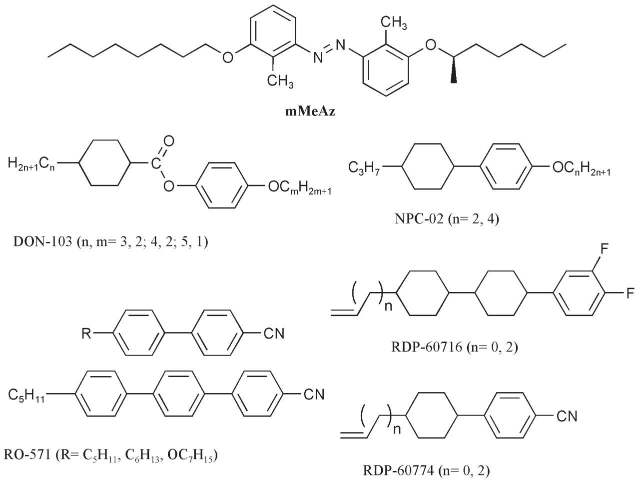

Fig. 1 Chemical structures of the chiral dopant mMeAz and the nematic host mixtures.

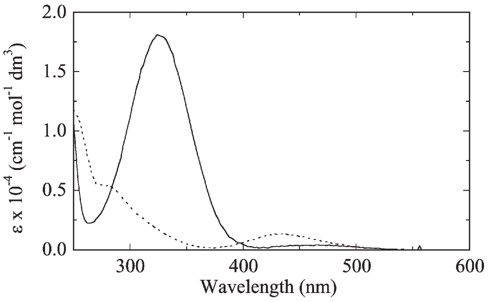

Fig. 2 UV-vis spectra of the isolated *trans*- (solid line) and *cis*-isomers (dotted line) of mMeAz in ethylacetate–hexane (1 : 9) solution.

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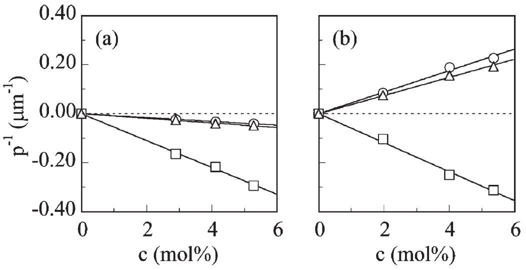

Fig. 3 Reciprocal helical pitch as a function of concentration of mMeAz dopant in nematic (a) RO-571 and (b) RDP-60774 at the initial state (○), and the photostationary states of visible (△) and UV light (□). Positive and negative p^{-1} values represent right- and left-handed helical twists, respectively. The horizontal dotted lines indicate the infinite helical pitch.

Table 1 The helical twisting powers (β/μm^{-1}) of mMeAz at the initial state (β_{trans}), and the photostationary states of visible (β_{vis}) and UV light (β_{UV}) in different nematic LC hosts. Positive and negative values represent right- and left-handed helical twists, respectively

Nematic LC	β_{trans}	β_{vis}	β_{UV}
RO-571	−0.77	−0.93	−5.4
DON-103	−2.6	−3.1	−8.9
NPC-02	−1.2	−1.9	−7.8
RDP-60716	+4.4	+3.7	−5.9
RDP-60774	+1.6	+0.77	−8.0
MLC-2039[a]	+0.81[b]	+0.47[b]	−4.3[b]

[a] MLC-2039 ($\Delta\varepsilon = -4.1$) is a nematic mixture having fluoro and alkenyl groups at the terminal substitutions. [b] Value from the dopant concentration in wt%, due to unknown composition of components in the LC mixture.

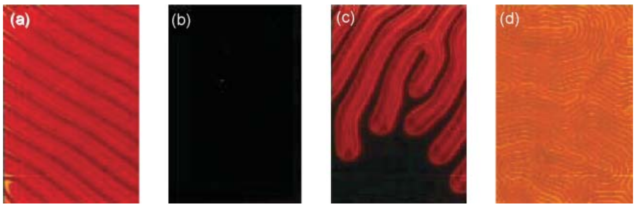

Fig. 4 Polarized microphotographs (size: 380 × 550 μm^2) showing the switching behavior of the chiral nematic phase induced by dissolving 6 wt% of mMeAz in nematic MLC-2039 upon irradiation with UV light for (a) 0 (b) 4, and (c) 5 min, and (d) toward the photostationary state.

polar groups connected to the mesogenic cores.[12] Considering the *cis* content at the UV photostationary state (*ca.* 83%) in these LCs, both the *trans* and *cis* isomers of mMeAz have the same helical twist sense, *i.e.* left-handed [see, for example, Fig. 3(a)]. However, to our surprise, when mMeAz interacts with LC hosts having alkenyl substituents, such as RDP-60774 [Fig. 3(b)], inversion of the helical sense from right-handed to left-handed is observed upon *trans*-to-*cis* photoisomerization with UV light. The authenticity of this phenomenon was also examined with other nematic LCs. Table 1 summarizes the observed β at the initial state (β_{trans}), and the photostationary states of visible (β_{vis}) and UV light (β_{UV}) in different nematic hosts.

Interestingly, we observed the opposite twist sense (right-handed) of β_{trans}, with respect those of other nematic LCs, only in nematic LCs having alkenyl groups (RDP-60716, RDP-60774, MLC-2039). Note also that the *trans*-mMeAz in these alkenyl nematic LCs does not follow the rule of Gray and McDonnell (SED, ROD, SOL, REL)[11] which describes the relation between the absolute configuration (*S* or *R*), the parity of asymmetric carbon from the core [O (odd) or E (even)], and the twist sense [D (*dextro* = right-handed) or L (*laevo* = left-handed)]. On the other hand, chiral 4,4′- or 2,2′-substituted azobenzenes do adopt the rule.[8,12,13] From the β_{UV} values in Table 1, it is concluded that pure *cis*-mMeAz has a left-handed sense, independent of the nematic host.

In a similar fashion to the temperature-dependent inversion phenomenon,[7] the reversal helical twist in our case is most likely to be the consequence of the competition between different interconvertable rotational species of the chiral alkyl chain relative to the core. Molecular orbital calculations predict that rotation around the O–C1 bond will be greatly hindered due to the presence of the methyl group attached to the *ortho* position of the azo core.[14] Thus, the rotation mainly about C1–C2 bond of the chiral terminal chain may produce species with different β and some may be stabilized upon specific interaction with the host molecules. For the same azobenzene without methyl groups in the *ortho* positions, the energy barrier for the rotation around the O–C1 bond should be lowered. In this case, no inversion phenomenon was observed. The methyl groups at the *ortho* positions providing steric hindrance which amplifies the β of *cis*-mMeAz and its analogs with respect to their *trans* isomers ($\beta_{cis} > \beta_{trans}$) has been described to be a specific conformational effect, not found in other type of chiral azobenzenes.[12]

By utilizing this interaction-selective effect, we can switch not only the helical pitch, but also the twist sense of the chiral nematic phase. Consequently, reversible photoswitching among three different optical LC phases is readily performed *via* light irradiation. Fig. 4 shows the changes in the optical phases formed by dissolving mMeAz in MLC-2039 in an LC cell[15] upon continuous irradiation with UV light. The right-handed sense of the fingerprint textures (a) diminished and the dark image (b), which corresponds to the compensated nematic phase with homeotropic alignment appeared, followed afterward by the growth of new left-handed fingerprint textures (c), whose pitch length shrank at the photostationary state (d). It should also be emphasized that, in contrast to other conventional azobenzenes, *cis*-mMeAz and its analogs do not destabilize the mesophases at all.

In conclusion, an interaction-selective helical twist inversion of chiral nematic LCs by photoisomerization of a single chiral azobenzene which functions as both chiral and photosensitive dopants has been described. The clear interaction-selective effect here should provide a new concept for the molecular design of photoswitchable LC systems. Although the inversion of chirality-dependent LC properties is a complicated phenomenon and merits further investigation, it is undoubtedly a unique and promising methodology for practical use in optical switching.

Notes and references

1 For leading reviews, see: (*a*) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (*b*) Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1717; (*c*) B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.*, 2000, **100**, 1789; (*d*) K. Ichimura, *Chem. Rev.*, 2000, **100**, 1847.
2 E. Sackmann, *J. Am. Chem. Soc.*, 1971, **93**, 7088.
3 C. Ruslim and K. Ichimura, *J. Phys. Chem. B*, 2000, **104**, 6529.
4 (*a*) S. Janicki and G. B. Schuster, *J. Am. Chem. Soc.*, 1995, **117**, 8524; (*b*) Y. Yokoyama and T. Sagisaka, *Chem. Lett.*, 1997, 687.
5 (*a*) C. Denekamp and B. L. Feringa, *Adv. Mater.*, 1998, **10**, 1080; (*b*) K. Uchida, Y. Kawai, Y. Shimizu, V. Vill and M. Irie, *Chem. Lett.*, 2000, 654; (*c*) T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie and M. Irie, *Chem. Mater.*, 2000, **12**, 869.
6 (*a*) B. L. Feringa, N. P. N. Huck and H. A. van Doren, *J. Am. Chem. Soc.*, 1995, **117**, 9929; (*b*) N. P. M. Huck, W. F. Janger, B. de Lange and B. L. Feringa, *Science*, 1996, **273**, 1686.
7 (*a*) P. Styring, J. D. Vuijk, I. Nishiyama, A. J. Slaney and J. W. Goodby, *J. Mater. Chem.*, 1993, **3**, 399; (*b*) H. Stegemeyer, A. Sprick, M. A. Osipov, V. Vill and H.-W. Tunger, *Phys. Rev. E*, 1995, **51**, 5721; (*c*) V. Vill, H. M. von Minden and D. W. Bruce, *J. Mater. Chem.*, 1997, **7**, 893.

8 G. Heppke, H. Marschall, P. Nürnberg, F. Oestreicher and G. Scherowsky, *Chem. Ber.*, 1981, **114**, 2501.

9 The azobenzene mMeAz was prepared from 2,2′-dimethyl-3-hydroxy-3′-octyloxyazobenzene (0.30 g; 0.85 mmol), potassium carbonate (0.35 g; 2.60 mmol), and (*S*)-1-methylhexyl-*p*-toluenesulfonate (0.30 g; 1.11 mmol) in DMF at 80 °C, to give an orange product in a 66% yield. ^{1}H-NMR (CDCl) δ (ppm): 0.90 (t, J = 6.46, 3H), 1.32–1.92 (m, 23H), 2.60 (ds, 6H), 4.02 (t, J = 6.35 Hz, 2H), 4.33–4.45 (m, 1H), 6.88–7.28 (m, 6H). Found: C, 76.86; H, 9.83; N, 6.03; calc. for $C_{29}H_{44}N_2O_2$: C, 76.93; H, 9.82; N, 6.19%.

10 N. Isaert, B. Soulestin and J. Malthete, *Mol. Cryst. Liq. Cryst.*, 1976, **37**, 321.

11 G. W. Gray and D. G. McDonald, *Mol. Cryst. Liq. Cryst. Lett.*, 1977, **34**, 211.

12 C. Ruslim and K. Ichimura, *Adv. Mater.*, 2001, **13**, 37.

13 M. Tsukamoto, T. Ohtsuka, K. Morimoto and Y. Murakami, *Jpn. J. Appl. Phys.*, 1975, **14**, 1307.

14 C. Ruslim and K. Ichimura, *J. Mater. Chem.*, 1999, **9**, 673.

15 The glass substrates were treated with n-octadecyltriethoxysilane to provide homeotropic anchoring of LCs.