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ARTICLE

## Novel Planar Chiral Dopants with High Helical Twisting Power and Structure-Dependent Functions

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Three kinds of novel planar chiral azobenzenophane derivatives for controlling the helical structures of cholesteric liquid crystals were synthesized and found to exhibit excellent chiroptical properties in both chloroform and liquid crystal media. The results of doping experiment showed that all the chiral switches possess high helical twisting power (HTP) values in nematic liquid crystal host ( $> 80 \mu\text{m}^{-1}$ ) so that they can effectively transfer the chirality to the host LC medium resulting in a helical supramolecular structure even at very low doping concentrations ( $< 1.0 \text{ wt}\%$ ). In addition, the dependency of function-structure on various cyclic azobenzenophane scaffolds and flexible chains was also discussed in detail. It shows that introducing ordered segments and flexible long alkyloxy chain in the dopants can increase the cholesteric induction ability of dopants effectively. And the screw direction of the formed chiral nematic liquid crystal was dependent upon the planar chiral configuration of the molecules switch. Moreover, in this mixed system, reversible tuning between orange and green reflection color were achieved when irradiating with alternating UV/Vis light.

### Introduction

As an important member in liquid crystals' family, cholesteric liquid crystals (CLCs) have attracted tremendous interest for their unique layer and helical structures that can be adjusted by different external stimuli, such as temperature,<sup>1, 2</sup> electric field,<sup>3, 4</sup> light<sup>5-7</sup> and solvent.<sup>8</sup> Some CLCs materials have imparted unique advantages in display devices.<sup>9</sup> For a long time, direct tuning of the cholesteric pitch has always been an important issue. Currently, the most popular way to solve this problem is doping photoresponsive chiral dopants into nematic liquid crystals. As a typical photochromic group, azobenzene shows peculiar responsiveness to external light stimulus, whose conformation can change between *trans*- and *cis*- states upon the irradiation of UV or visible light.<sup>10-13</sup> Introducing chiral azobenzene derivatives into the helical supramolecular system can effectively tune the helical pitch and the full-color reflective displays can be achieved without any color filter or polarizer.<sup>14-17</sup>

Helical twisting power (HTP,  $\beta$ ) is a useful parameter to

describe the ability of a chiral dopant to twist a nematic phase,<sup>18</sup> which is usually expressed as the equation shows:  $\beta = (\text{pc})^{-1}$ , where  $p$  is the pitch length of the helical structure, and  $c$  is either weight concentration or molar fraction of the chiral dopant. Simultaneously, it's notable that high HTP can effectively decrease the concentration of chiral dopants, which plays a significant role in optical display addressing. While for many chiral azobenzene dopants, their HTP values are less than  $15 \mu\text{m}^{-1}$ . So they are often used at concentrations of 20 % or higher in nematic liquid crystal (NLC), which might change the physical properties (viscosity, clearing point) of host materials.<sup>19-21</sup> Undoubtedly, high HTP as well as a significant difference in HTP among the various states are the most desirable features of LC dopants. The considerable developments towards high HTP has been obtained from axially chiral binaphthyl or planar chiral azobenzene molecules provided by Li<sup>22-27</sup> and Tamaoki,<sup>28-31</sup> respectively. Then, as we all know, axially chiral binaphthyl possess dihedral angle between the two naphthalene rings, when they were linked to azobenzene moieties, planar chirality of twisted azobenzene structure can be induced by chiral transfer from binaphthyls.<sup>32, 33</sup> However, researches on these new planar chiral azo dopants with high HTP values are still relatively rare. Recently, our group has reported a serial of novel azobenzenophanes with planar chiral azobenzene units for potential applications as chiroptical switches.<sup>34, 35</sup> In this study, we designed and prepared three novel planar chiral azo dopants for nematic liquid crystals by introducing different flexible long ethylene glycol/alkyl chains into the cyclic azobenzenophanes (Scheme 1). Simultaneously, reversible reflection colors tuning of the self-organized chiral nematic

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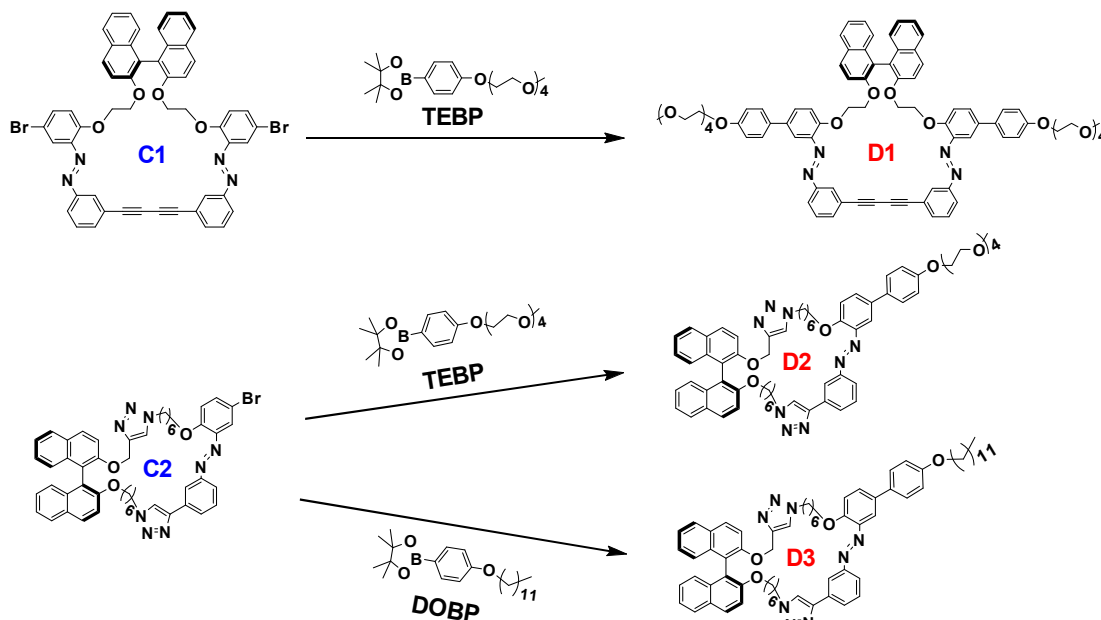
Electronic Supplementary Information (ESI) available: Experimental details for the synthesis of chiral switches and structural characterization data were given. See DOI: 10.1039/x0xx00000x

liquid crystals based on the chiral azo dopants have been investigated systematically.

## Results and discussion

Initially, we attempted to investigate the HTP difference in NLC of cyclic azobenzenes C1 and C2 that we reported early, as shown in Scheme 1.<sup>34, 35</sup> Unfortunately, the experiment failed due to their poor solubility in LC host. Therefore, in order to address this problem, three new chiral dopants with different flexible chains (D1, D2 and D3) were designed and prepared facily via the Suzuki-

Miyaura coupling reaction of C1/C2 with the corresponding phenylboronate derivatives. The detailed synthesis routes are shown in Scheme 1. By comparing the three new compounds, it's easy to find that D1 and D2 bear different core constructions while D2 and D3 contain different tail groups, which allows us to know whether the structure difference affects the formation and pitch variation of CLC mostly. Before further studies, all the intermediates and products were confirmed by <sup>1</sup>H NMR (Figure S1-S5), high-resolution mass spectroscopy (HR-MS) and elemental analysis (EA). Also, they are optically and chemically stable in air.



Scheme 1 Synthesis routes of chiral azobenzene dopants D1, D2 and D3.

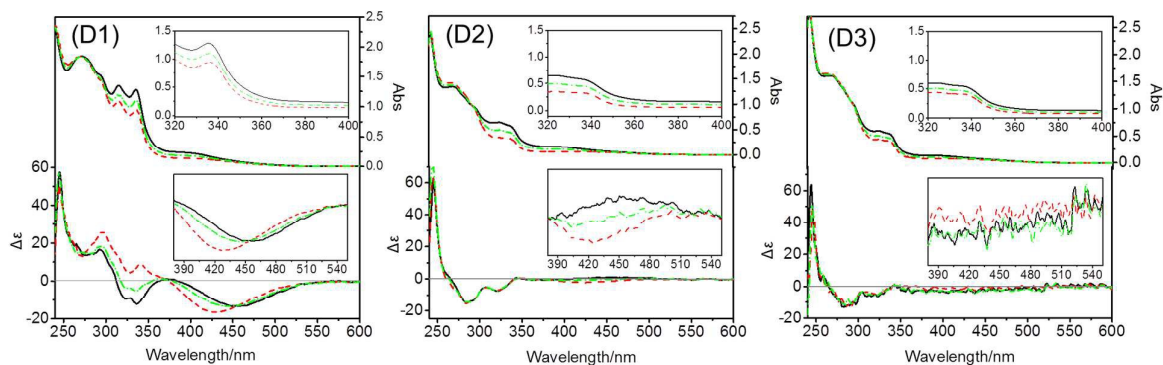


Figure 1 Changes in the absorption spectra (upper) and circular dichroism (CD) spectra (below) of D1-D3 at the initial states (black solid line) and the photostationary states resulting from irradiation at 365 nm light (red dash line) and 530 nm light (green dash-dot line) in chloroform. Conditions: 0.033 mg/mL, 25 °C, irradiation wavelengths = 365 nm (10 mW/cm<sup>2</sup>) and 530 nm (50 mW/cm<sup>2</sup>).

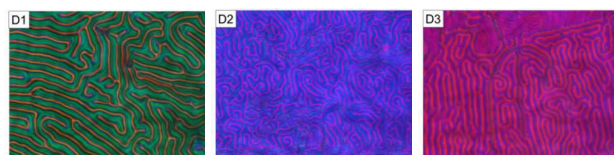
The photoisomerization behaviors of three cyclic azobenzenes in chloroform with same concentration (0.03 mg/mL) were investigated via UV-Vis spectrophotometer. Before this, the all solution was served in dark to maximize the absorption at 367 nm assigned to the *trans*-azobenzene moieties. As shown in Figure 1

(upper), we first characterized the UV/Vis spectra of D1, D2 and D3 at initial states and photostationary states. It is similar to the results of their cyclic precursors reported before, where the typical peak at about 250 nm is belonged the <sup>1</sup>B<sub>u</sub> long axis transition of the binaphthyl moiety.<sup>36</sup> Then, the absorption at 367 nm is the

characteristic  $\pi \rightarrow \pi^*$  transition of *trans* azobenzene moiety.<sup>37</sup> Upon UV irradiation at 365 nm for about 40 s, all the three compounds reached to the photostationary states (PSS<sub>UV</sub>) and additional irradiation did not induce further changes in absorption. However, the variation was not so large because the tension of cyclic scaffold has restricted the isomerization of azobenzene moiety as well as the steric effect of long flexible chains. Furthermore, it's deserved to be noted that, unlike the structures D2 and D3, D1 has two azobenzene linkages. Thus, as shown in the absorption spectra, the initial absorbance value of D1 at 367 nm is 0.33, double that of D2 (0.16). After irradiating under UV light, they turned into 0.14 and 0.06 respectively, showing that D1 has larger initial absorbance value and difference of the value than the other two. Subsequently, when irradiated by visible light, an increase in the absorption value corresponding to the  $\pi \rightarrow \pi^*$  transition accompanied by the absorption decrease at the  $n \rightarrow \pi^*$  transition of azobenzene segment were observed in all compounds. Moreover, an isosbestic point of 280 nm was maintained in the absorption spectra, indicating that none of the switches showed any signals of degradation during the UV/Vis irradiation.

We have also studied the chiroptical behavior during photoisomerization of the three compounds via circular dichroism (CD) spectroscopy at room temperature. Figure 1 shows the change in the CD spectra of D1-D3 upon UV light irradiation at 365 nm and visible light at 530 nm, respectively. We can see that there are obvious exciton couplet signals at 400-500 nm for all the CD spectra, which are typically belonged to the planar chiral azobenzene moieties that is induced by axial chiral binaphthyl segments. And the D1 exhibited the most distinct chirality and change of chirality than the other two because of its shortest linkers between azobenzene and chiral binaphthyl group.<sup>38</sup> Moreover, there are intense positive excitations at about 240 nm, which are likely due to the long-axis-polarized transition of the naphthalene.<sup>39</sup> In overall, there were no larger differences for the three new dopants with their cyclic precursors reported before.

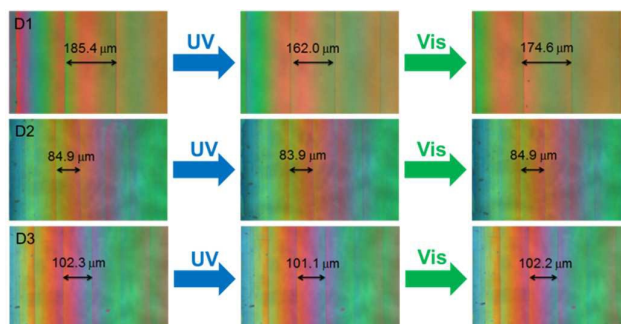
Then, the chirality transfer characteristics of D1-D3 were investigated in a nematic liquid crystal (NLC) medium. As expected, after doping them into a commercially available NLC host E7, the optically tunable helical structures could be induced. For instance, as shown in Figure 2, even when the mixture concentration was 1 wt%, the typical fingerprint textures for CLC phases were observed under a crossed polarized microscope (POM), which indicated that all the cyclic compounds can induce the formation of CLC phases successfully.



**Figure 2** Polarized optical microscope images of the characteristic fingerprint textures of 1 wt% D1, 1 wt% D2 and 1 wt% D3 in nematic liquid crystal E7, respectively.

The screw direction of the LC system mixture induced by the chiral dopants was confirmed by miscibility test.<sup>40,41</sup> The

POM photographs of the mixing area between the measured CLC samples and the S1 or R1 (as described in Supporting Information) as a standard LC were shown in Figure S6. It's clear to see that continuous area existed between sample (D1/E7)  $\cap$  S1 and discontinuous area appeared in the mixing area of (D1/E7)  $\cap$  R1. This indicates that the sample was left-handed. Similarly, we come to conclusions that sample D2/E7 and D3/E7 both showed right-handed screw sense.



**Figure 3** Stripe-wedge Grandjean-Cano cell containing 1 wt% D1, D3 and D2 in E7 and the stripe spacing change under UV or Vis light irradiation.

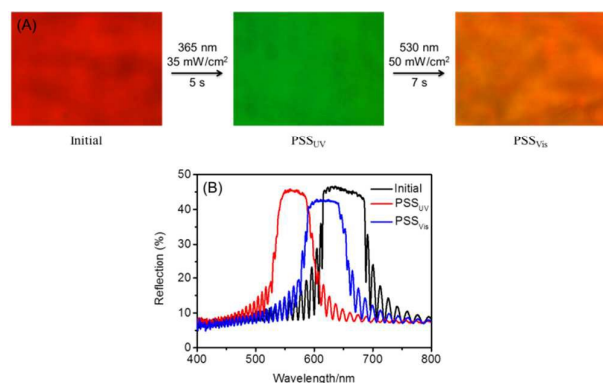
Furthermore, we have determined the HTP of CLCs and the changes in HTP upon light irradiation by Grandjean-Cano method (Figure 3).<sup>42</sup> The measurement of pitch and HTP ( $\beta$ ) are described in Supporting Information. The results are summarized in Table 1, where the positive and the negative signs indicate a right-handed and left-handed screw sense, respectively. The three chiral dopants showed high HTP ( $> 80 \mu\text{m}^{-1}$ ) at all photostationary states (PSS). In addition, we also have found the differences of cyclic matrix or flexible chains in chiral molecular switches display non-ignorable influence on HTP values. For example, D2 had a higher HTP value than D1 at the initial state though they have same flexible chain, which revealed that the cyclic scaffold has an important effect on their cholesteric induction behaviors. It's reported that the molecular regularity can improve high induction ability and stability of chiral dopants effectively,<sup>43</sup> so we tested the structure of the two cyclic matrixes *via* XRD technique, finding the spectrum of C2 shows many sharp peaks while C1 not, indicating the former has a higher degree of crystalline structures than the latter (Figure S7), which can be attributed to C2 has a more ordered molecular packing resulting from its better molecular regularity than C1. Then, it's noted that D2 displays a higher initial HTP value than D3 that has same cyclic scaffold with D2 but the long alkoxy chain was chosen as the solubilizing chain. It is probably because the long alkoxy chain increases the intermolecular association and compatibility between the dopant and the host. As we know, the chirality change of dopant molecule is the key factor in the formation and variation of cholesteric phase during photoisomerization process.<sup>44</sup> Owing to the existence of flexible linkers between the binaphthyl and azobenzene groups, the CD signal changes, especially under 250 nm that reflected on Figure 1 were

relatively weak during the isomerization process of azo moieties, so that the observed HTP value changes were not as obvious as expected. Upon UV irradiation to photostationary state,  $\beta$  of D1 increased from  $-81 \mu\text{m}^{-1}$  to  $-91.6 \mu\text{m}^{-1}$ , while the  $\beta$  of D2 and D3 slightly changed by  $1.4 \mu\text{m}^{-1}$  and  $1.8 \mu\text{m}^{-1}$ , respectively. So, compound D1 has the largest percent change ( $\sim 13\%$ ) in  $\beta$  in initial state and  $\text{PSS}_{365\text{nm}}$  resulting from the co-actuation of double azobenzene segments. And then, the  $\beta$  of the three chiral switches all decreased almost to the value of initial state after irradiation with visible light. The HTP in the *cis*-state is higher than that in its *trans*-state, which is less frequently observed in previous reports on chiral azobenzenes derivatives.<sup>[23,28,29,39]</sup>

**Table 1** Helical twisting power HTP ( $\beta$ ) of chiral dopants at different states in achiral nematic E7<sup>a</sup>.

Dopants	$\beta$ (mol%) $\mu\text{m}^{-1}$			$\Delta\beta/\beta^b$
	Initial	$\text{PSS}_{\text{UV}}$	$\text{PSS}_{\text{Vis}}$	
D1	-81.0	-91.6	-84.4	13.1
D2	107.5	108.9	107.9	1.3
D3	95.1	96.9	95.3	1.9

[a] E7 is an eutectic mixture of LC components commercially designed for display applications. [b] Percent change in  $\beta$  observed between initial state and  $\text{PSS}_{365\text{nm}}$ .



**Figure 4.** Reflection color images (A) and reflective spectra (B) of 4.0 wt% D1 and 19.7 wt% S811 in nematic LC host E7 in a 10  $\mu\text{m}$  thick planar cell at room temperature.

It is also well-known that CLC can reflect light according to Bragg's law. The wavelength  $\lambda$  of the selective reflection is defined by  $\lambda = np$ , where  $p$  is the pitch length of the helical structure and  $n$  is the average refractive index of the LC material. On the basis of the high HTP and good solubility of D1-D3 in E7, we also investigated the reflection color tuning of the self-organized CLC in the visible region. The mixtures of chiral switches and NLC host E7 were injected into a 10  $\mu\text{m}$  thick planar cell. The doping concentrations of three dopants were 4.0 wt%, 8.9 wt% and 8.7 wt%, respectively. And 19.7 wt% S811 was added to the mixture with dopant D1. Testing results showed that the initial reflection colors for all cases were red, and the CLC induced by D1 exhibited the best photocontrol behavior than the other two because of the largest change of

HTP ( $\Delta\beta$ ) that was observed in the D1 as listed in Table 1. For example, it quickly tuned to green upon UV irradiation at 365 nm ( $35 \text{ mW}/\text{cm}^2$ ) within approximately 5 s, reaching a photostationary state  $\text{PSS}_{\text{UV}}$  (Figure 4(A)). Reflective spectra (Figure 4(B)) showed that its reflection central wavelength was around 650 nm at the initial state and blue-shifted to 560 nm at the  $\text{PSS}_{\text{UV}}$  correspondingly. This process was reversed upon visible light irradiation at 530 nm ( $50 \text{ mW}/\text{cm}^2$ ) for 7 s to the  $\text{PSS}_{\text{Vis}}$ . In addition, the reflection central wavelengths of D2 and D3 were 670 nm and 690 nm, respectively. Their reflection colors and the reflection spectra of the CLC remained relatively unchanged during the photoisomerization process because of the little change of HTP value.

## Conclusions

In this work, three novel planar chiral azobenzene dopants with high HTPs ( $> 80 \mu\text{m}^{-1}$ ) were designed and synthesized. Then, the function-dependency on various chiral azobenzenophane matrices and flexible chains were also discussed in detail. It seems that introducing ordered segments and flexible long alkyloxy chain onto the photoresponsive chiral azobenzene molecules can increase the cholesteric induction ability of dopants effectively. In addition, their chiroptical behaviors were investigated and the reversible reflection color tuning between orange and green was demonstrated by using dopant D1. This work has provided new insight into designing and developing novel chiral azobenzene dopants for practical applications in liquid crystals and further research is ongoing in our laboratory.

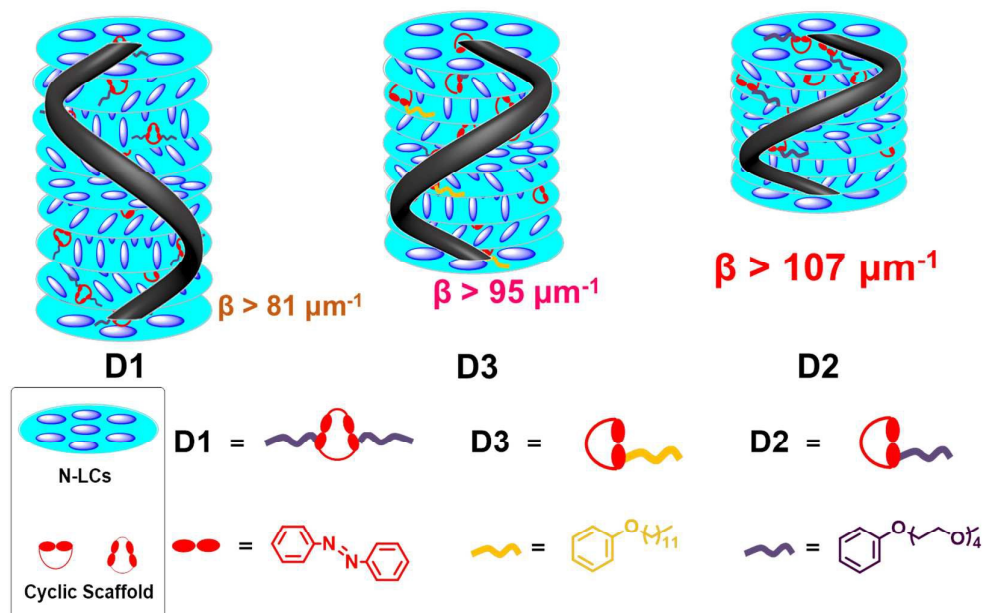
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