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Reactivity differences of $Sc_3N@C_{2n}$ ($2n$ = 68 and 80). Synthesis of the first methanofullerene derivatives of $Sc_3N@D_{5h}$-C_{80}

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(*R*)-Binaphthyl Derivatives as Chiral Dopants: Substituent Position Controlled Circularly Polarized Luminescence in Liquid Crystals

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A series of nonbridged axially chiral binaphthyl derivatives were synthesized and used as chiral dopants for chiral nematic liquid crystals (N*-LCs). It was found that binaphthyl derivatives substituted at 3,3' positions or 2,2' positions of binaphthyl rings, could induce N*-LCs to show opposite circularly polarized luminescence (CPL) signals, despite having the same configuration. Additionally, CPL switch could be constructed in these N*-LCs regulated by applied electric field.

In recent decades, the chiroptical materials with circularly polarized luminescence have attracted considerable attention due to their promising applications in 3D imaging[1], high-security systems[2], CPL laser[3], biological probe[4], enantio-selective CPL sensors[5] or electro-optic display[6]. Besides, CPL provides a probe of configuration and conformation in the emitting state of chiral luminescence systems. The magnitude of circular polarization in the excited state is quantified by the dissymmetry factor $g_{lum}=2(I_L-I_R)/(I_L+I_R)$, where I_L and I_R denote the intensities of the left and right circularly polarized light, respectively. However, the level of CPL for most chiral organic molecules are much smaller in solvents or in aggregation state ($|g_{lum}| = 10^{-5}–10^{-2}$)[7]. To develop CPL-active materials with high g_{lum}, doping chiral chromophores into achiral nematic liquid crystals is one of the most effective approaches[8]. Akagi's group have reported one kind of chiral liquid crystal polyacetylene devitatives, which exhibited CPL activity with high g_{lum}[9]. Recently Cheng et al. have reported chiral liquid crystals, which showed aggregation-induced circularly polarized luminescence (AI-CPL) with an extremely large g_{lum} value up to 0.41[10].

So far, it has been elucidated that binaphthyl derivatives have a good miscibility towards N-LCs as well as large helical twisting power which can control the screw sense (helical sense) and strength of N*-LCs[11]. On the other hand, binaphthyl derivatives are ease of synthesis, easy to modify and low cost[12]. Therefore, they are not only useful for asymmetric reaction solvents to produce chiral conducting polymers, but also are used as dopants of achiral liquid crystals[13]. By modifying the chemical structures of binaphthyl derivatives to control the screw sense of N*-LCs have been reported before. For example, the mono-and di-substituted binaphthyl derivatives with the same configuration gave opposite screw senses in N*-LCs, though they both had the bridged structures[8a]. Another example is that nonbridged and bridged binaphthyl derivatives added into N-LCs leading to opposite screw senses, though they had the same configuration[14]. However, by changing the positions of substituents of binaphthyl derivatives with the same configuration to control the CPL signals in liquid crystal has never been involved. In addition, chirality switching bestows much potential applications in CPL-active materials and electro-optic displays.

Herein, according to rational molecule design, a kind of aggregation-induced emission (AIE) chiral binaphthyl derivatives were synthesized, where substituents were introduced at 3,3' positions or 2,2' positions at binaphthyl rings, abbreviated as *R*/*S*-1 and *R*/*S*-2, and used as chiral dopants for N*-LCs. The commercially available liquid crystal medium 5CB (4-Cyano-4'-n-pentylbiphenyl), shows a N-LC phase within the range of 24-35 °C, which was used as host liquid crystalline compound. The N*-LCs samples were prepared by adding a small amount of chiral dopant into liquid crystal. We took insight into the chiroptical properties of the N*-LCs. It was found that, as chiral dopants, *R*-1 and *R*-2 could induce N*-LCs with left-handed and right-handed CPL, respectively, though having the same (*R*)-configuration (Fig. 1). We inferred that the opposite CPL signals of N*-LCs should be assigned to the different dihedral angle of binaphthyl derivatives, which could be explained in terms of substituent positions modifying the molecule structures. Additionally, the

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effect of direct current (DC) electric field on the N*-LCs was also investigated. Finally, CPL switch could be achieved in the induced N*-LCs by applying with a DC electric field.

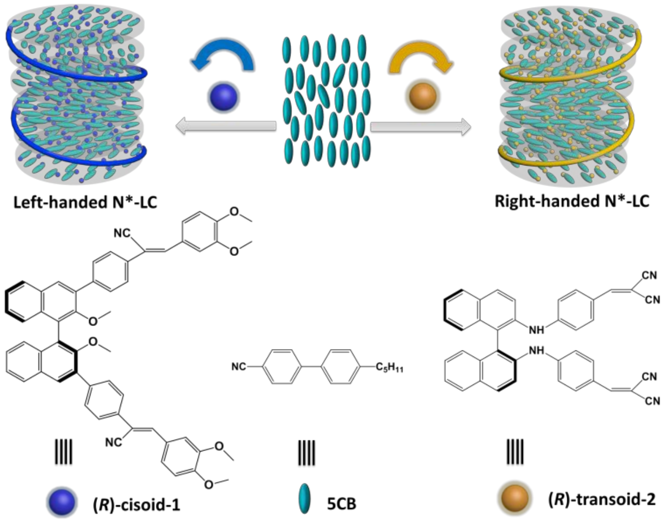

Fig. 1 Illustration of the helical structures of N*-LCs including each chiral dopant with the same (*R*)-configuration. The molecular structures of binaphthyl derivatives used as dopants and the used liquid crystal.

The synthesis procedures of *R*/*S*-binaphthyl derivatives where the substituents were introduced at 3,3' positions or 2,2' positions of binaphthyl rings, were synthesized via the Suzuki-Miyaura cross-coupling and Knoevenagel reactions according to the reported literatures[15]. The chemical structures, detailed synthesis processes and characterizations were described in the electronic supplementary information (Fig.S1, ESI†). First, the photo-physical properties of binaphthyl derivatives were investigated. The fluorescent emission spectra of *R*-1 and *R*-2 were carried out in THF/H_2O mixed solution, which showed typical AIE phenomena (Fig.S2, ESI†). It is well known that Tang's group demonstrated that AIE molecules are weakly fluorescent or non-fluorescent in the solution state because of the intramolecular rotation consuming energy from the excited state[16]. The CPL signals of *R*-1 and *R*-2 were silent in the polar solvents. The chiral nematic liquid crystals consisting of a host nematic liquid crystal (5CB) and each chiral dopant in different concentrations were prepared. The fluorescence intensities of N*-LCs samples showed enhancement as the concentration increased. Meanwhile, the CPL level of N*-LCs decreased slightly (Fig.S3, ESI†). These results indicated that the AIE effect played a key role not only on the emission intensity but also on the CPL degree of N*-LCs. The fluorescent emission spectra and CPL spectra of N*-LC doped with 0.5 wt% *R*-1 and N*-LC doped with 0.5 wt% *R*-2 in liquid crystal cells at room temperature, were also measured (Fig. 2). The stop band of N*-LCs induced by *R*-1 and *R*-2 couldn't be detected in visible light region, and N*-LCs were almost transparent outside the stop band (inset pictures in Fig. 2). At the same time, *R*-1 was found to induce N*-LC exhibited positive CPL signal with blue emission (450 nm) (Fig. 2c). However, *R*-2 induced N*-LC showed negative CPL signal with yellow light (560 nm) (Fig. 2d). Moreover, *S*-1 exhibited a mirror image of CPL spectrum of *R*-1 and gave Cotton effects with opposite sign to that of *S*-2. The opposite CPL signals implied the different screw direction of N*-LCs. The chirality was also confirmed via circular dichroism (CD) spectra, which measures the differential absorption of left-handed and right-handed circularly polarized light[17]. Moreover, the signal of the CD spectra is related to the dihedral angle (θ) of binaphthyl rings. The *R*-1 and *R*-2 displayed negative Cotton effects either dissolved in CH_2Cl_2 or formed thin films, indicating they had the same conformation in isotropic solvent or at the film state (Fig.S4, ESI†). Unfortunately, CPL signals of the thin films couldn't be detected yet, which might be due to the amorphous phases. As shown in Fig. 2e and 2f, N*-LC doped with *R*-1 showed a distinct Cotton effect with a positive signal. *R*-2 was found to induce N*-LC with a negative Cotton effect. These results demonstrated that *R*-1 and *R*-2 had different conformations in liquid crystal. To further investigate the origins of opposite CPL signals, the screw senses of N*-LCs films were investigated under polarized optical microscopy (POM). As described in Fig. 3, N*-LC induced by 0.5 wt% *R*-1 and 0.5 wt% *R*-2 showed a clockwise screw direction and counterclockwise screw direction in LC, respectively. The screw senses of N*-LCs were coincided with the signals of CPL and CD. It is clear that the screw sense of N*-LCs is determined by the

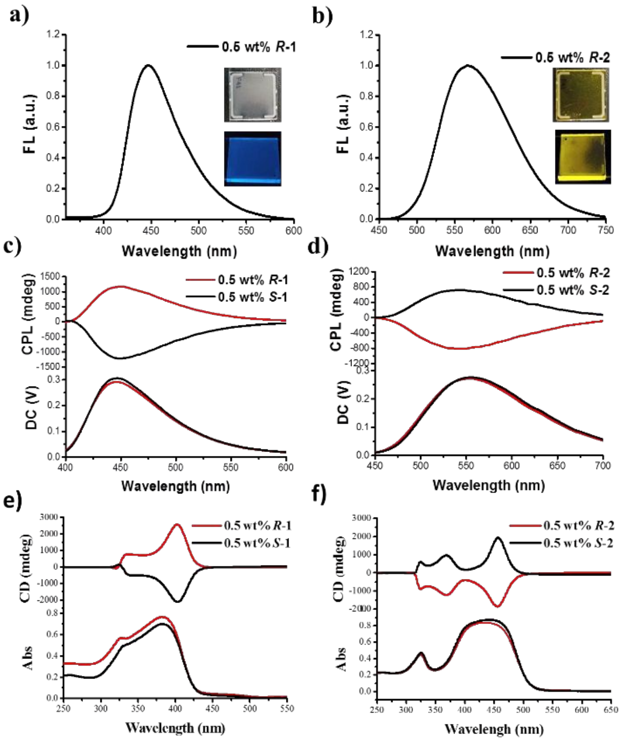

Fig. 2 (a) Fluorescence spectra of N*-LC doped 0.5 wt% *R*-1 excited at 340 nm; (b) Fluorescence spectra of N*-LC doped 0.5 wt% *R*-2 excited at 360 nm; (c) CPL spectra of N*-LC doped 0.5 wt% *R*/*S*-1 excited at 340 nm; (d) CPL spectra of N*-LC doped 0.5 wt% *R*/*S*-2 excited at 360 nm. (e) CD spectra of the N*-LC doped 0.5 wt% *R*/*S*-1; (f) CD spectra of N*-LC doped 0.5 wt% *R*/*S*-2.

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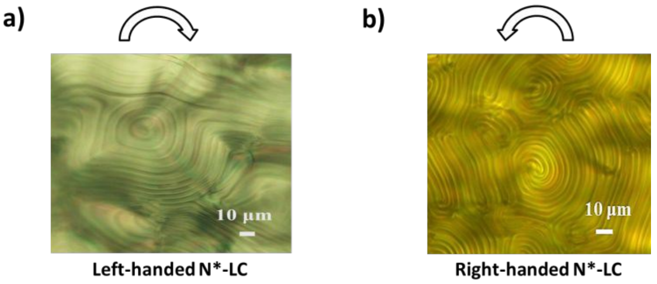
stereospecific intermolecular interactions between the binaphthyl moieties of chiral dopants and the surrounding N-LC molecules. The former reports have demonstrated that the helicity of binaphthyl derivatives depend on the dihedral angle (θ) of binaphthyl rings. (*R*)-binaphthyl derivatives have (*R*)-cisoid conformation (0°< θ < 90°) and (*R*)-transoid conformation (90° < θ < 180°) corresponding to (M)-helicity and (P)-helicity, respectively[18]. As the dopants, the *R*-1 and *R*-2 took an *M*-helicity and *P*-helicity in N-LCs, respectively, which leading to oppositely screwed N*-LCs. Therefore, the reason of the opposite CPL signals of the induced N*-LCs were caused by the difference in dihedral angle[19].



Left-handed N*-LC

Right-handed N*-LC

Fig. 3 Polarized optical micrograph (POM) images of N*-LC films including (a) 0.5 wt% *R*-1 , (b) 0.5 wt% *R*-2 at room temperature.

The helical pitch and the helical twisting power (β_w) of N*-LCs doped with each dopant were evaluated via the Grandjean-Cano method[20] and were summarized in table S1. The Grandjean-Cano lines could be observed in the POM images which indicated the formation of thermotropic chiral N*-LCs phases (Fig.S5, ESI†). The helical twisting power of *R*-1 and *R*-2 were calculated to be around 26.0 um^{-1} and 15.6 um^{-1}, respectively. The twisting power of *R*-1 was about 1.7 times larger than that of *R*-2, which might be owing to the difference in the conformation.

The finger-printed textures of N*-LCs and high g_{lum} values of CPL were owing to the intermolecular interactions, including the π-π interactions between binaphthyl derivatives and surrounding liquid crystal molecules and dipolar interaction from cyano groups. As demonstrated above, N*-LCs induced by *R*-1 and *R*-2 showed opposite screw senses. The structural difference between *R*-1 and *R*-2 was that the substituents were linked at the 3,3′ positions and 2,2′ positions of binaphthyl rings, respectively. In order to clarify the relationship between the screw directions of N*-LCs and the substituents positions of non-bridged binaphthyl derivatives, we have particularly synthesized *R*/*S*-3 molecules which have the same substituent position for comparison (Scheme S3). The result of N*-LCs induced by *R*-3 was in accordance with that of N*LCs induced by *R*-1 (Fig.S6, ESI†). This further indicated that the screw direction of N*-LCs was dominated by the substituent position of non-bridged binaphthyl derivatives. It has been reported that the chirality of non-bridged binaphthyl derivative depends on the change of the dihedral angle between two binaphthyl rings. It is expected that the substituents were directly linked at 3,3′ positions at binaphthyl rings leading to more rigid structure and *R*-2 had larger steric effect at 2,2′ positions leading a restriction in the internal rotation of binaphthyl rings. Therefore, the opposite CPL signals of N*-LCs arose from the difference of dihedral angle.

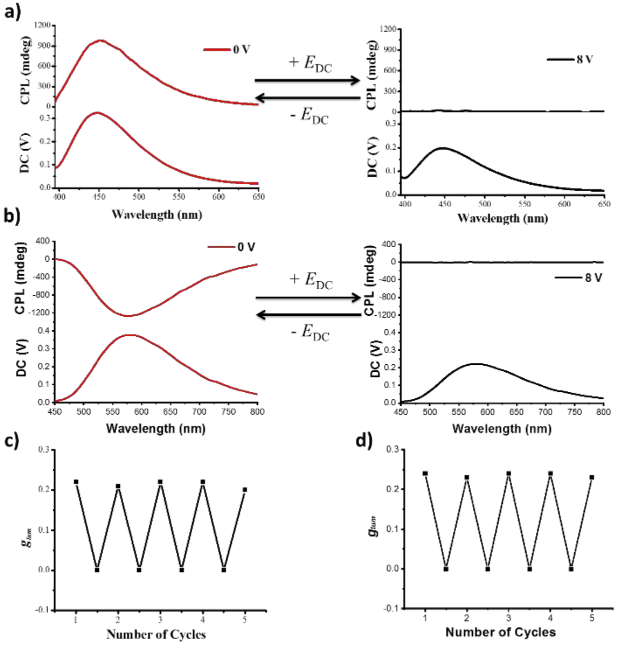


Fig.4 (a) and (b) CPL spectra of N*-LCs including 0.5 wt% *R*-1 and 0.5 wt% *R*-2 under the electric field “off” and “on”, respectively; (c) and (d) intensity of the CPL g_{lum} value of N*-LC including 0.5 wt% *R*-1 and 0.5 wt% *R*-2, respectively, against the repeated electric field “off” and “on” cycles.

Recent research interests have focused on the optoelectronics luminescent devices where the CPL is involved[21]. To further take insight into the CPL-active materials applications, a liquid crystal (LC) device was constructed on a conductive ITO glass substrate. It was found that CPL signals of the N*-LCs induced by this kind of AIE-active dye molecules could be detected when a DC electric field was turned off, which would represent the ‘‘on-state’’ of the system (Fig. 4a). When a DC electric field (8 V) was applied to the LC cell, there was no CPL signal, which would represent the ‘‘off-state’’ of the system described in Fig. 4b. Interestingly, N*-LCs exhibited almost the same degree of CPL when the DC electric field was turned off again. The calculated value of the dissymmetry factor ($|g_{lum}|$) of the N*-LCs doped with 0.5 wt% *R*-1 and 0.5 wt% *R*-2 were around 0.25 and 0.27, respectively. Meanwhile, the g_{lum} values showed stable repeatability after several cycle treatments (Fig. 4c and 4d). Therefore, we successfully achieved an electric-field induced CPL switch that was reversible and repeatable over multiple cycles. The POM images of N*-LCs with electric field “ off” and “on” were examined. As a result, the characteristic Grandjean texture of N*-LC phases were observed without applied electric field. Applying a DC electric field (8V), the characteristic of nematic phases disappeared (Fig.S7, ESI†). This indicated that the

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planar orientation of the LC molecules changed to the homeotropic orientation[22]. Therefore, a CPL switch of N*-LCs doped with AIE-active fluorescence dyes were fabricated by applying an exceedingly lower electric voltage. This will facilitate the application of AIE-active molecules in electro-optic displays and CPL field.

Conclusions

In summary, we have prepared N*-LCs samples by doping with a small amount of AIE-active binaphthyl derivatives. It is interesting to note that N*-LCs induced by *R*-1 exhibited negative CPL signals and that induced by *R*-2 showed positive CPL signals, despite having the same (*R*)-configuration. The results of CD spectra and POM images confirmed that *R*-1 and *R*-2 had different conformations in liquid crystal and the induced N*-LCs showed opposite screw directions. The opposite chirality of the N*-LCs was actually attributed to the difference in the dihedral angle of non-bridge binaphthyl derivatives as dopants. We also achieved a DC electric-field-induced reversible CPL switching. This work provides promising prospects to chiroptical material and devices.

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Conflicts of interest

The authors declare no conflict of interest.

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