

Dynamic Switching of the Circularly Polarized Luminescence of Disubstituted Polyacetylene by Selective Transmission through a Thermotropic Chiral Nematic Liquid Crystal**

Benedict A. San Jose, Jialin Yan, and Kazuo Akagi*

Abstract: The circularly polarized luminescence (CPL) of chiral disubstituted liquid-crystalline polyacetylene (di-LCPA) can be dynamically switched and amplified from left- to right-handed CPL and vice versa through the selective transmission of CPL across a thermotropic chiral nematic liquid crystal (N*-LC) phase. By combining a chiral di-LCPA CPL-emitting film with an N*-LC cell and tuning the selective reflection band of the N*-LC phase to coincide with the CPL emission band, a CPL-switchable cell was constructed. The phase change induced by the thermotropic N*-LC cell by varying the temperature leads to a change in the selective transmission of CPL, which enables the dynamic switching and amplification of CPL. It is anticipated that CPL-switchable devices might find applications in switchable low-threshold lasers and optical memory devices.

The circularly polarized luminescence (CPL) of organic and polymeric materials has attracted considerable interest, and this property has been used for the development of photonic devices, such as light-emitting diodes, optical amplifiers, and for optical information storage.^[1,2] Various chiral liquid-crystalline fluorescent conjugated polymers that exhibit CPL have been reported.^[2–5] The well-defined chiral packing of the liquid-crystalline main chain as well as chiral interchain interactions have led to emission dissymmetry factors (g_{em}) on the order of up to 10^{-1} . Recently, we reported the synthesis of chiral disubstituted liquid-crystalline polyacetylene derivatives (di-LCPA), and a highly ordered lyotropic chiral nematic liquid crystal (N*-LC) phase with g_{em} values of up to -2.3×10^{-1} was observed.^[6]

One unique and important optical property of the N*-LC helical structure is the selective reflection of circularly polarized light, which was employed to achieve high degrees of CPL.^[7] When N*-LCs are sandwiched between a pair of substrates with anchoring surfaces, the helical axis is spontaneously oriented perpendicular to the substrate surface. In this alignment, the N*-LCs show an intrinsic optical texture, the so-called planar or Grandjean texture.^[8] When CPL propagates into a planarly aligned N*-LC cell along the

helical axis, the N*-LC molecules can reflect CPL with the same helical handedness as the N*-LC phase centered at λ_{max} . In contrast, CPL with the opposite helical handedness to the N*-LC phase is transmitted through the planar N*-LC cell without light reflection. The center of the CPL reflection band, λ_{max} , is related to the helical pitch, p , of the N*-LC phase according to $\lambda_{max} = np$, where n is the refraction index of the LCs.^[9]

A common method for preparing an N*-LC phase involves the addition of a chiral dopant to a nematic LC (N-LC) host. Upon the addition of a chiral dopant, chirality is induced in the N-LC hosts, thereby forming an N*-LC phase. To construct an N*-LC phase that selectively reflects in the visible-light range, a helical pitch on the order of several hundred nanometers is necessary. Tetra-LC-substituted binaphthyl derivatives, which are chiral dopants with a large helical twisting power (β_M), induce an N*-LC phase with selective reflection in the visible-light range.^[9]

The selective reflection properties of N*-LCs have been utilized in various areas, such as the preparation of glassy N*-LC films embedded with chromophores having high degrees of CPL,^[10] photonic crystals with low-threshold lasing,^[11] and N*-LC mixtures with photochemically tunable CPL.^[12]

Recently, CPL-switching properties have been reported for a variety of materials, such as poly(*para*-phenylene ethynylene) aggregates, which exhibit chiral inversion of CPL on changing the solvent.^[13] Furthermore, dynamic switching between fluorescence and quenching of CPL from poly(bithienylene phenylene)s with photoresponsive diarylethene moieties has also been described.^[14] Moreover, there have been reports of the dynamic switching of the handedness of CPL using N*-LCs with photoswitchable chiral dopants,^[15] such as azobenzenophanes,^[15a] diarylethenes,^[15b] and azoarenes.^[15c] To further develop the concept of dynamic CPL switching, we utilized the selective reflection properties and thermotropic liquid crystallinity of N*-LCs as thermally responsive materials to enable the dynamic chiral switching of CPL that is emitted by chiral di-LCPA.

Herein, a CPL-switchable cell was prepared that consists of a CPL-emitting film and chiral di-LCPA combined with a thermoresponsive N*-LC cell. The N*-LC cell was prepared by tuning the amount of the chiral dopant additive so that the selective reflection range of the N*-LC coincided with the CPL wavelength of the di-LCPA film. Through the phase change of the thermotropic N*-LC cell at different temperatures, dynamic CPL switching was achieved. Furthermore, the selective transmission of CPL across the N*-LC phase enabled the amplification of CPL emitted from di-LCPA to achieve high g_{em} values.

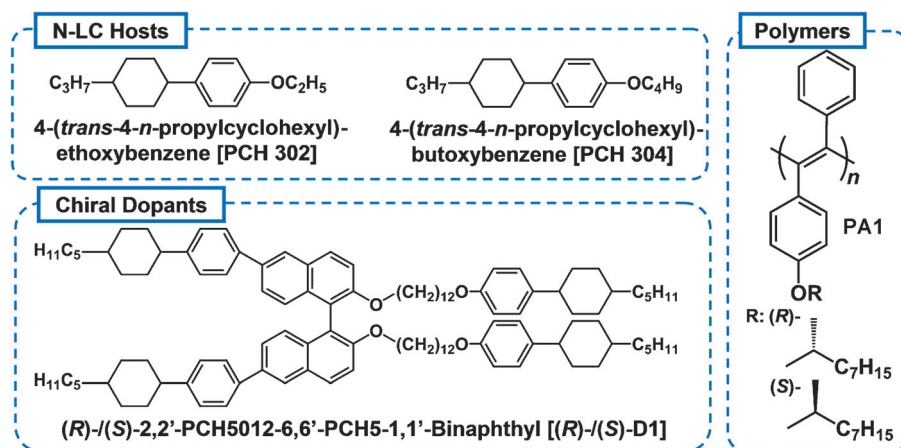
[*] Dr. B. A. San Jose, J. Yan, Prof. K. Akagi
Department of Polymer Chemistry, Kyoto University
Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
E-mail: akagi@fps.polym.kyoto-u.ac.jp

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We synthesized the room-temperature N-LC hosts PCH302 and PCH304, which consist of phenylcyclohexyl mesogen cores and *n*-ethyloxy or *n*-butyloxy tails, respectively. The tetra-LC-substituted binaphthyl derivatives (*R*)- and (*S*)-2,2'-PCH5012-6,6'-PCH5-1,1'-binaphthyl ((*R*)-**D1** and (*S*)-**D1**) with high β_M values were used as chiral dopants to prepare an N*-LC phase with the selective reflection band within the visible-light range. The syntheses of the N-LC hosts and of (*R*)-**D1** and (*S*)-**D1** were described in a previous report.^[9] Two chiral di-LCPA derivatives, (*R*)-**PA1** and (*S*)-**PA1**, with a poly(diphenylpolyacetylene) main chain and 4-nonyloxy phenyl groups with either *R* or *S* chirality as their side chains were polymerized using a WCl_6 catalyst in a metathesis polymerization reaction, as previously described.^[6] The structures of the synthesized N-LC hosts, chiral dopants, and chiral di-LCPAs are shown in Scheme 1.

An N*-LC phase that consists of PCH302, PCH304, and (*S*)-**D1** in a 100:100:2.2 molar ratio was prepared and injected into a cell consisting of two sandwiched quartz slides with



Scheme 1. Structures of the nematic LC (N-LC) hosts PCH 302 and PCH 304, the chiral dopants (*R*)-**D1** and (*S*)-**D1**, and the disubstituted liquid-crystalline polyacetylenes (*R*)-**PA1** and (*S*)-**PA1**.

a 35 μ m polyimide spacer.^[16] (*R*)-**PA1** was dissolved in toluene at 10 wt% to form a lyotropic N*-LC solution, which was cast on a quartz slide to prepare a CPL-emitting layer. The left-handed (*S*)-N*-LC cell was placed together with the (*R*)-**PA1** CPL-emitting layer to form a CPL-switchable cell (Figure 1a). A CPL-switchable cell with opposite handedness, consisting of an (*R*)-N*-LC cell with an (*S*)-**PA1** CPL-emitting layer, was also prepared.

Polarizing optical microscopy (POM) images of the prepared (*S*)-N*-LC cell at room temperature revealed a Grandjean texture, which is characteristic of an N*-LC phase with the helical axis aligned perpendicularly to the substrate. (Figure 1b).^[8] Upon heating to 36 °C, the N*-LC phase transformed into an isotropic phase. Cholesteryl oleyl carbonate is an N*-LC molecule known to have a left-handed helical sense of chirality and was utilized as an LC standard for a miscibility test with the prepared N*-LCs.^[17] The miscibility test is based on determining the mixing area between the N*-LC phase and an LC standard by POM; the helical sense of the LC standard is known. As shown in

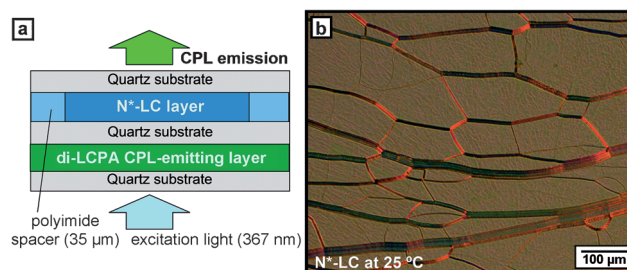


Figure 1. a) Schematic representation of the CPL-switchable cell. b) POM image of the (*S*)-N*-LC cell at 25 °C showing a planar Grandjean texture.

Figure S1a in the Supporting Information, the mixture of (*R*)-N*-LC and cholesteryl oleyl carbonate revealed a discontinuity in the mixing area of the two N*-LC phases. In the contact region of the two N*-LC phases, the striation characteristics of the N*-LC phase were lost, yielding an LC texture corresponding to an N-LC phase. In contrast, the mixture of (*S*)-N*-LC and cholesteryl oleyl carbonate showed no change in optical texture, and the N*-LC phase was maintained in the mixing area (Figure S1b). Furthermore, the circular dichroism (CD) spectra of the N*-LCs revealed that (*R*)-N*-LC selectively reflected right-handed CPL, whereas (*S*)-N*-LC selectively reflected left-handed CPL (Figure S1c). The results of the LC miscibility test and the CD spectra confirm that (*R*)-N*-LC and (*S*)-N*-LC have right- and left-handed helical senses of chirality, respectively.

After verifying the helical sense of the prepared N*-LC cells through the miscibility test and the CD spectra, the selective reflection bands of the prepared N*-LC cells were determined from their transmission spectra. The photoluminescence (PL) spectra of the di-LCPA CPL-emitting film were also measured to verify the overlap between the CPL emission band of di-LCPA and the selective reflection band of the prepared N*-LC cells. The PL spectra of (*R*)-**PA1** showed a green-colored PL band centered at 515 nm, whereas the transmission spectra of the (*S*)-N*-LC cell showed a selective reflection band from 460 to 530 nm centered at 505 nm, coinciding with the PL band of the CPL-emitting film (Figure 2). The PL and transmission spectra of (*S*)-**PA1** and the prepared (*R*)-N*-LC cell were also measured (Figure S2).

The CPL spectra of the CPL-switchable cell made from (*R*)-**PA1**/*S*)-N*-LC were recorded. A schematic representation of the CPL-switching mechanism is shown in Figure 3. Upon excitation with monochromatic light at 367 nm, the (*R*)-**PA1** CPL-emitting film emitted both left- and right-handed CPL, but it was predominantly left-handed CPL (i). At room temperature, the (*S*)-N*-LC cell selectively reflected left-

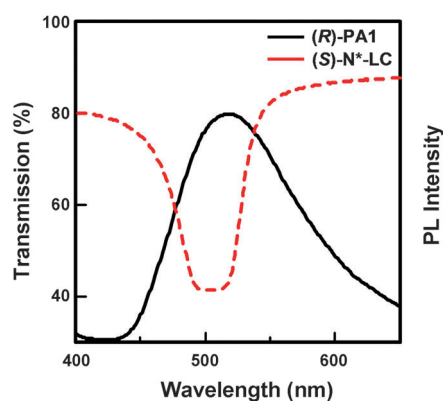


Figure 2. Photoluminescence (PL) emission (black) of the (R)-PA1 film upon excitation at 367 nm and transmission spectrum (red) of the (S)-N*-LC cell showing the selective reflection band.

handed CPL (ii), and only right-handed CPL was transmitted (iii; Figure 3a). The transmitted right-handed CPL signal was observed in the CPL spectra (Figure 3c).

At 40 °C, the helical arrangement of the N*-LC phase was lost, and it was turned into a disordered isotropic phase where the selective reflection of left-handed CPL does not occur (iv). In this state, the predominantly left-handed CPL from the (R)-PA1 CPL-emitting film is transmitted (v; Figure 3b). The transmitted left-handed CPL signal was observed by CPL spectroscopy (Figure 3c).

The degree of CPL was evaluated by the emission dissymmetry factor, g_{em} . The emission dissymmetry factor is defined as $g_{em} = (I_L - I_R) / [(I_L + I_R) / 2] = \Delta I / I$, where $|g_{em}| < 2$. I_L

and I_R are defined as the intensities of left- and right-handed polarized light, respectively. At room temperature, we observed a remarkable amplification by more than one order of magnitude for the right-handed CPL originating from the di-LCPA film through the selective transmission of right-handed CPL through the (S)-N*-LC phase. The amplified right-handed CPL showed g_{em} values of nearly pure CPL with values of up to -1.79 . At 40 °C, the predominantly left-handed CPL showed a g_{em} value of $+1.25 \times 10^{-1}$, which is an order of magnitude smaller than the value at room temperature.

The CPL spectra of the CPL-switchable cell that consists of an (S)-PA1 CPL-emitting layer with an (R)-N*-LC cell were also measured and gave similar results. The CPL spectra of the (S)-PA1/(R)-N*-LC CPL-switchable cell showed a handedness opposite to that of the (R)-PA1/(S)-N*-LC CPL-switchable cell (Figure S3). At room temperature, the amplified left-handed CPL showed g_{em} values of up to $+1.77$, whereas at 40 °C, the predominantly right-handed CPL from the (S)-PA1 film had a g_{em} value of -1.46×10^{-1} . The g_{em} values, wavelengths, and handedness of the CPLs in the switchable cells are summarized in Table 1.

Another CPL-switchable cell was prepared with Teflon anchoring surfaces.^[18] Then, after cooling back to room temperature from the isotropic phase, CPL measurements were performed to check the performance and recovery of the N*-LC phase of this CPL-switchable cell (Figure S4). After cooling from its isotropic phase, the CPL-switchable cell (R)-PA1/(S)-N*-LC, showed a right-handed CPL signal with a g_{em} value of -1.47×10^{-1} , which is an order of magnitude lower than at 465 nm. The handedness of the CPL signal

suggests that selective transmission of right-handed CPL occurred at room temperature because of the recovery of the N*-LC phase. The decrease of the g_{em} value may have occurred because the N*-LC phase was not completely planarly aligned after cooling from the isotropic phase. An optimization of the preparation of the anchoring surfaces may improve the performance of the CPL-switchable cell even after successive heating and cooling cycles and will be performed in future studies.

It was confirmed that thermotropic N*-LCs are excellent materials for the switching and amplification of CPL originating from a chiral di-LCPA film. The emission of CPL originating from a di-LCPA film within

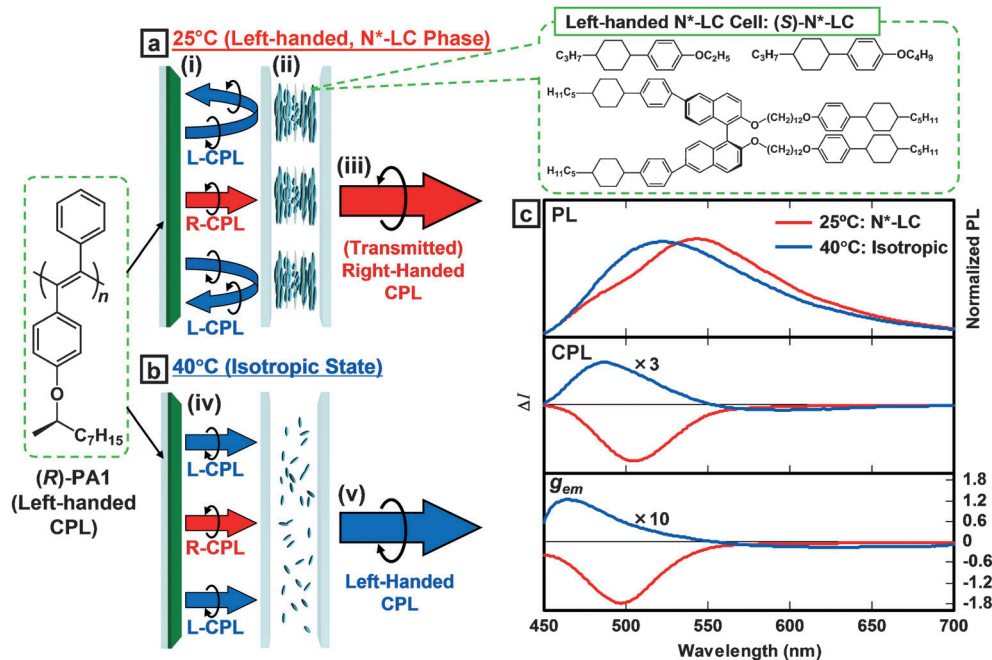


Figure 3. a) Schematic representation of the (R)-PA1/(S)-N*-LC CPL-switchable cell. a) At 25 °C, i) the (R)-PA1 film emits predominantly left-handed CPL, ii) the (S)-N*-LC cell selectively reflects left-handed CPL, and iii) only right-handed CPL is transmitted, leading to the amplification of right-handed CPL. b) At 40 °C, iv) the (S)-N*-LC cell turns into an isotropic phase, and selective reflection of CPL does not occur; therefore, v) predominantly left-handed CPL is transmitted. c) The PL (upper), CPL (middle), and g_{em} (lower) spectra of the (R)-PA1/(S)-N*-LC CPL-switchable cell at 25 °C (red) and 40 °C (blue).

Table 1: Emission dissymmetry factors (g_{em}), wavelengths, and handedness of CPLs in switchable cells.

Polymer/N*-LC	T [°C]	g_{em} (λ [nm]) ^[a]	Handedness (CPL)
(R)-PA1/(S)-N*-LC	25	−1.79 (497)	right
	40	+1.25 × 10 ^{−1} (464)	left
(S)-PA1/(R)-N*-LC	25	+1.77 (510)	left
	40	−1.46 × 10 ^{−1} (460)	right

[a] Wavelength (λ) at which the g_{em} value was determined.

the selective reflection band of the N*-LC cell enabled the selective reflection of CPL, leading to CPL switching and amplification upon a change in the phase of the thermotropic N*-LC cell. We anticipate that this concept could be extended further to other liquid-crystal systems that exhibit selective reflection, such as ferroelectric liquid crystals and blue liquid-crystal phases, to achieve faster dynamic switching and selective reflection of CPL in three dimensions. The synergistic incorporation of chiral fluorescent conjugated polymers as CPL materials with the dynamic switching functionality of liquid crystals might lead to the emergence of next-generation switchable low-threshold lasers and optical memory devices.

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