Simulation of Circular Dichroism by Chromophores Coupled with Selective Reflection by Cholesteric Stacks

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ABSTRACT: The Good–Karali theory is extended to simulate composite circular dichroism (CD) through a cholesteric stack by incorporating chromophore’s selective absorption (SA) and cholesteric stack’s selective reflection (SR). Based on the independently evaluated anisotropic refractive indices and absorption coefficients, helical sense and pitch length, and film thickness, the theory is capable of describing transmission, reflection, and absorption through spin-cast cholesteric glassy liquid crystal films of nonafluorene. The resulting composite CD spectra agree quite well with experimental observations. The theory informs that SA plays a dominant role over SR in the composite CD. Specifically, the right-handed stack of the chrophore with its absorption dipole aligned with the local director in the cholesteric stack preferentially absorbs the left-handed over the right-handed circularly polarized light. The algebraic sign of the predicted composite CD flips by reversing the cholesteric host film’s handedness without altering other parameter values. The established theory and computation constitute a solid foundation for optimizing circular polarizers by exploring the readily accessible parameter space targeting various potential applications.

INTRODUCTION

Supramolecular assemblies of chiral and achiral molecules and polymers present fertile grounds for theoretical and experimental explorations. In particular, circularly polarized light generation, propagation, and absorption through films of supramolecular chiral assemblies have been actively pursued in recent years. As an essential class of polarization control device, circular polarizers can be readily constructed by combining a linear polarizer with a quarter-wave plate. For the sake of device compactness and spectral versatility from the near ultraviolet through visible to the short-wave infrared ranges, device compactness and spectral versatility from the near ultraviolet through visible to the short-wave infrared ranges, micro-thick cholesteric liquid crystal fluid films offer a viable alternative by resolving incident unpolarized light at normal incidence into forward and backward circularly polarized beams with opposite handedness based on the property of selective wavelength reflection. The present work is motivated to cultivate a new idea of one-way circular polarizers, that is, forward transmission predominating over backward reflection, made possible by doped or functionalized chromophores in cholesteric glassy liquid crystal (Ch-GLC) films to exploit their physical robustness and environmental durability on top of the advantages inherent to cholesteric liquid crystal films.

The doped or functionalized material system is expected to result in composite circular dichroism (CD), consisting of selective absorption (SA) by the helically stacked chromophores and selective reflection (SR) by light propagation through a Ch-GLC film. This problem was first undertaken by Sackmann and Voss using a left-handed cholesteric liquid crystal film doped with a chromophore having its absorption dipole along the local director within the cholesteric liquid crystal host film. Their experimental results can be summed up in two conclusive statements that SR alone contributes to a positive CD value and that SA plus SR results in a negative CD value. The second statement amounts to the chrophore in a left-handed stack preferentially absorbing right-handed over left-handed circularly polarized light propagating through a left-handed cholesteric liquid crystal film.

In the present study, a comprehensive theory is formulated by adding SA to the classical Good–Karali theory exclusively for SR for validation against the observed composite CD spectra for a series of monodomain Ch-GLC films of nonafluorenes with independently characterized anisotropic absorption coefficients and refractive indices, helical sense and pitch length, and film thickness. The goal is to gain original insight into the contributions by SA and SR to the composite CD serving as a sound basis for material design targeting specific applications.

MODEL EQUATIONS FOR COMPUTATION

Light propagating through a planar cholesteric structure undergoes SA by helically stacked chromophores and SR originating in optical birefringence. The observed composite CD is treated herein by generalizing the Good–Karali theory originally formulated for light propagation through a cholesteric stack without light absorption. Let incident light
enter the CLC film at \( z = 0 \) and exit at \( z = b \) as depicted in Figure 1.

![Figure 1. Depiction of incident, reflection, and transmission of light through a cholesteric stack.](image)

In Figure 1, \( K \) and \( L \) represent the \( E^\perp \) and \( E^\parallel \) as the electric fields of the incident light propagating in the positive \( z \) direction; \( F \) and \( G \) the \( E^\perp \) and \( E^\parallel \) of the transmitted light; \( K \) and \( F \) are right-handed circularly polarized component; \( L \) and \( G \) are left-handed circularly polarized component. In addition, \( H \) and \( I \) represent the \( E^\perp \) and \( E^\parallel \) of the incident light propagating in the negative \( z \) direction; \( M \) and \( N \) represent \( E^\perp \) and \( E^\parallel \) of the reflected light. In the problem set up in Figure 1, let both \( H \) and \( I \) vanish to mesh the experimental characterization of composite CD using RCP incident described by \( K = 1 \) and \( L = 0 \), as well as LCP incident by \( K = 0 \) and \( L = 1 \). Moreover, \( M \) and \( N \) are the reflected left-handed and right-handed circularly polarized component; respectively.

The wave equations for light propagating along the helical axis \( z \) are

\[
\frac{\partial^2 E_x}{\partial z^2} = \frac{1}{\omega^2} \left( \varepsilon_{xx} \frac{\partial^2 E_x}{\partial t^2} + \varepsilon_{xy} \frac{\partial^2 E_y}{\partial t^2} \right)
\]
\[
\frac{\partial^2 E_y}{\partial z^2} = \frac{1}{\omega^2} \left( \varepsilon_{xy} \frac{\partial^2 E_x}{\partial t^2} + \varepsilon_{yy} \frac{\partial^2 E_y}{\partial t^2} \right)
\]

in which \( E^\perp = E_x \pm iE_y \) express the oscillating electric fields with coefficients \( \varepsilon_{xy} \)'s as the elements in the dielectric tensor, and \( \omega \) is the speed of light in a given medium. Furthermore

\[
\varepsilon_{xx} = \varepsilon(1 + \delta \cos 2\theta), \quad \varepsilon_{yy} = \varepsilon(1 - \delta \cos 2\theta),
\]
\[
\varepsilon_{xy} = \varepsilon \delta \sin 2\theta, \quad \delta = \frac{\varepsilon_{ll} - \varepsilon_{ll}}{\varepsilon_{ll} + \varepsilon_{ll}},
\]
\[
\varepsilon = \frac{\varepsilon_{ll} + \varepsilon_{ll}}{2}, \quad \theta = qz, \quad q = \frac{2\pi}{\Lambda}
\]
\[
e_x = (n_l + i\kappa)^2
\]

where \( n \) and \( \kappa \) are the refractive index and extinction index; subscripts \( \parallel \) and \( \perp \) represent the direction parallel and perpendicular to the long and short molecular axis, respectively; \( \Lambda \) is the helical pitch length; \( q \) is the rotation angle of the long molecular axis per unit length along the helical axis; \( z \) is the depth into the film; and \( \theta \) is the cumulative rotation angle up to \( z \).

The generalized Good–Karali theory is applied to assess the contributions of both SA and SR by propagating light. The general solutions of eq 1 for all the nonvanishing electric fields identified in Figure 1 are as follows

\[
K_{gen} = (1 - \rho)(1 + \beta + \beta\lambda)A \quad (3a)
\]
\[
L_{gen} = (1 + \rho)(1 - \beta + \beta\lambda)A \quad (3b)
\]
\[
M_{gen} = (1 - \rho)(1 - \beta - \beta\lambda)A \quad (3c)
\]
\[
N_{gen} = (1 + \rho)(1 + \beta - \beta\lambda)A \quad (3d)
\]
\[
F_{gen} = (1 - \rho)(1 + \beta + \beta\lambda) \exp \left( i \frac{1 - \frac{1}{\beta}}{\rho^2} qz \right) A \quad (3e)
\]
\[
G_{gen} = (1 + \rho)(1 - \beta + \beta\lambda) \exp \left( i \frac{1 + \frac{1}{\beta}}{\rho^2} qz \right) A \quad (3f)
\]
\[
H_{gen} = (1 - \rho)(1 - \beta - \beta\lambda) \exp \left( i \frac{1 + \frac{1}{\beta}}{\rho^2} qz \right) A \quad (3g)
\]
\[
I_{gen} = (1 + \rho)(1 + \beta - \beta\lambda) \exp \left( i \frac{1 - \frac{1}{\beta}}{\rho^2} qz \right) A \quad (3h)
\]

For each of eq 3, there are four \( l \) and \( \rho \) values identified as follows

\[
l_j = \pm \sqrt{1 + y^2 + y^2\delta^2}, \quad y = \frac{\omega}{qu} v,
\]
\[
\omega = \frac{2\pi c}{\lambda}, \quad \rho_j = \frac{2l_j}{l_j^2 + 1 - y + \delta^2},
\]
\[
\beta = \frac{uq}{\omega}, \quad j = 1 \text{ to } 4
\]

The general solutions, eq 3, are reduced to particular solutions, eq 5

\[
H = \sum_{j=1}^{4} H_j = \sum_{j=1}^{4} (1 - \rho_j)(1 - \beta - \beta\lambda_j) \exp \left( i \frac{1 - \frac{1}{\beta}}{\rho_j^2} qz \right) A_j = 0 \quad (5a)
\]
\[
I = \sum_{j=1}^{4} I_j = \sum_{j=1}^{4} (1 + \rho_j)(1 + \beta - \beta\lambda_j) \exp \left( i \frac{1 - \frac{1}{\beta}}{\rho_j^2} qz \right) A_j = 0 \quad (5b)
\]
\[
K = \sum_{j=1}^{4} K_j = \sum_{j=1}^{4} (1 - \rho_j)(1 + \beta + \beta\lambda_j) A_j \quad (5c)
\]
\[
L = \sum_{j=1}^{4} L_j = \sum_{j=1}^{4} (1 + \rho_j)(1 - \beta + \beta\lambda_j) A_j \quad (5d)
\]

For right-handed circularly polarized incident, \( K = 1 \) and \( L = 0 \), and left-handed circularly polarized incident, \( K = 0 \) and \( L = 1 \), are inserted in eq 5c and 5d, respectively. The implementation of separate LCP and RCP incidents is consistent with the way CD is experimentally characterized.11

Equation 5 is solved simultaneously for \( A_1 \) through \( A_4 \) to turn the general solutions eq 3 into particular solutions \( F, G, M, \) and \( N \) for both RCP and LCP incidents. Using \( T_R = |F_R|^2 + |F_L|^2 \) and \( T_L = |G_R|^2 + |G_L|^2 \) with subscripts \( R \) and \( L \) representing the RCP and LCP incident, respectively, one arrives at \( \text{CD} = 32.982\log_{10}(T_R/T_L) \) in degrees. Similarly, the \( M \) and \( N \) fields
characterize the SR, as depicted in Figure 1. The balance of the total incident energy is ascribed to absorption. Conversely, all three elements sum up to unpolarized light, thus describing its resolution into the three components via propagation through a cholesteric stack. A computer code is provided in the Supporting Information.

RESULTS AND DISCUSSION

Ch-GLC films comprising monodisperse nonafluorenes can be described as a helical stack of rigid rods, for which the composite CD is successfully modeled by eliminating fluorescence from the circularly polarized fluorescence theory. Alternatively, the classical Good–Karali theory is extended by adding light absorption to light propagation through a cholesteric stack. Upon the stated modifications, these two theories are equivalent as both consider light propagation with simultaneous absorption through a cholesteric stack. Furthermore, according to Yang and Li’s analysis, the extents of selective wavelength reflection and the resulting apparent CD are elevated by increasing the $\frac{h\Delta n}{p n_{\text{avg}}}$ value, in which $h$ and $p$ are the film thickness and cholesteric pitch length, respectively. In addition, optical birefringence, $\Delta n = n_\perp - n_\parallel$, and average refractive index, $n_{\text{avg}} = \left(\left(n_\perp^2 + 2n_\parallel^2\right)/3\right)^{1/2}$, with subscripts $\parallel$ and $\perp$ denote the long and short nonafluorene axes in the quasinematic sublayers comprising the cholesteric stack. Note that the minor error in Yang and Li’s Figure 10 3b is corrected in Figure 2 below.

Figures 3c and 4a specifically for LCP incident through a right-handed 90 nm thick Ch-GLC film with $p = 252$ nm, 4% reflection from $|M|^2 + |L|^2$, and 12% transmission from $|L|^2 + |I|^2$ are achieved at the absorption peak at 375 nm. This transmission-to-reflection ratio at 3 is the minimum across the absorption peak. At the same absorption maximum, LCP incident through a right-handed Ch-GLC film with $p = 1151$ nm, 5% reflection, and 31% transmission can be achieved, namely, the minimum transmission-to-reflection ratio at 6 across the absorption peak. While decreasing the film thickness to 30 nm under otherwise

For the calculation of composite CD spectra, all the model parameters including anisotropic absorption coefficients and refractive indices, film thickness, helical sense and pitch length, are determined by spectroscopic ellipsometry. In the case of the nonafluorene film with $p = 252$ nm for the film thickness of 90 nm, two local extrema appear at 335 and 412 nm in Figure 3a. The intensity of selective wavelength reflection traverses maxima shown in Figure 3b because of the augmented $h\Delta n/n_{\text{avg}}$ values by $\Delta n/n_{\text{avg}}$ in which $\alpha_l = \alpha_r = 0$, where $\alpha_l$ and $\alpha_r$ are the anisotropic light absorption coefficients parallel and perpendicular to nonafluorene. Spin-cast films of all four monodomain nonafluorenes films possess the same anisotropic absorption and refractive index profiles at 90 nm film thickness. The same interpretation offered for $p = 252$ nm applies to the other three nonafluorene films characterized by $p = 346, 501$, and 1151 nm for adjusting the $h\Delta n/n_{\text{avg}}$ values. In principle, there are two contributors to the composite CD, that is, SA and SR broached in the Introduction section. The composite CD is characterized as $32.982\left(A_L - A_R\right)$, in which $A_L$ and $A_R$ are the absorbances with left- and right-handed circularly polarized incidents, noting that $A_L - A_R = \log_{10}\left(T_L/T_R\right)$ by definitions. The SA and SR effects are quantified in Figure 10 b,c to reveal the dominant role of the former over the latter in the ultimate composite CD, whereas a 90 nm thick nonafluorene film serves both as the chromophore and the cholesteric host as illustrated herein; the analysis is also applicable to doped guest–host systems.

With the formula for the nominal stopband’s center wavelength at normal incidence, $\Delta k = p n_{\text{avg}}$ as well as the dispersion of $n_{\text{avg}}(\lambda)$ and the $p$ values independently measured by spectroscopic ellipsometry, $\Delta k$ values turn out to be 1860, 809, 571, and 446 nm for $p = 1151, 501, 346$, and 252 nm, respectively. The nominal stopband is physically meaningful in that the peak at 412 nm identified in Figure 3b, $h\Delta n/n_{\text{avg}} = 0.177$ with $h$ and $p = 90$ and 252 nm, respectively, corresponds to a reflection of 0.255 according to Figure 1, giving rise to the maximum SR effect across the 300–500 nm spectral range. As a comparison, the peak reflection of 0.082 arises from the minimum $\Delta n/n_{\text{avg}}$ at 335 nm. The fact that films of an order-of-magnitude thinner than the pitch length are capable of selective wavelength reflection decreasing monotonically with thickness across the stopband has been conclusively demonstrated for a Ch-GLC film of chiral alternating fluorene copolymer. The calculated spectra presented in Figure 3d are in excellent agreement with the experimental results compiled in Figure 5b of ref 10, thus inspiring our confidence in uncovering how the identified parameters affect the observed composite CD in what follows. As displayed in Figure 3d, the composite CD value increases as the nominal stopband approaches the absorption peak at 375 nm.

In view of the maximum composite CD value presented in Figure 3d, the transmission of the RCP component is favored over the LCP counterpart by a factor of 2, hereby defined as the circular polarization ratio in transmission, through the 90 nm-thick Ch-GLC film. With the optical model reported here, an increase of the film thickness to 900 nm enhances the circular polarization ratio to 30 under otherwise identical conditions. The positive composite CD values surrounding the absorption peak indicates that LCP is lost more than RCP to the circular polarization ratio in transmission, through the 90 nm-thick Ch-GLC copolymer. The calculated spectra presented in Figure 3d are consistent with Sackmann and Voss’ observation that the opposite is true with the left-handed stacked chromophores. It is understood that the circular polarization ratio is subject to maximization via a host of system parameters, including the spectral separation between the absorption peak and the stopband.

In addition to the total transmission contributed by SA and SR shown in Figure 3c, the total reflection is computed for presentation in Figure 4a. Displayed in Figure 4b is absorption evaluated as $100 - \text{total transmission} - \text{total reflection}$ %, signifying the major portion of propagating light being absorbed. Based on the spectra presented in Figures 3c and 4a specifically for LCP incident through a right-handed 90 nm thick Ch-GLC film with $p = 252$ nm, 4% reflection from $|M|^2 + |N|^2$, and 12% transmission from $|L|^2 + |I|^2$ are achieved at the absorption peak at 375 nm. This transmission-to-reflection ratio at 3 is the minimum across the absorption peak. At the same absorption maximum, LCP incident through a right-handed Ch-GLC film with $p = 1151$ nm, 5% reflection, and 31% transmission can be achieved, namely, the minimum transmission-to-reflection ratio at 6 across the absorption peak. While decreasing the film thickness to 30 nm under otherwise...
identical conditions, reflection increases slightly to 6% while transmission doubles to 60%, yielding the minimum transmission-to-reflection ratio at 10 across the absorption peak. The presently formulated theory with computation is instrumental to the exploration of rich parameter space for the optimization of device performance. It is worth noting that the algebraic sign of the predicted composite CD flips upon reversing the cholesteric host film’s handedness while keeping other parameter values the same.

**CONCLUSIONS**

The salient points emerging from this study are summarized as follows:

1. Using independently evaluated anisotropic absorption coefficients and refractive indices, film thickness, helical sense, and pitch length by spectroscopic ellipsometry, the extended Good–Karali theory is capable of quantifying SR and transmission through a Ch-GLC film of nonafluorene. Furthermore, the calculated composite CD spectra are in excellent agreement with experimental results.

2. With chromophore’s absorption dipole parallel to the long molecular axis of nonafluorene, the chromophore in RH Ch-GLC film absorbs left-handed circularly polarized component preferentially over the right-handed component, which is instrumental to one-way circular polarization with an overwhelming transmission intensity over reflection.
The one-way circular polarization demands minimum reflection by limiting $h\Delta n/pn_{avg} < 0.10$ to yield a peak reflection <0.10. The presently formulated theory for computation provides a framework for exploring the sizable parameter space for optimization of device performance.

**ASSOCIATED CONTENT**

**Supporting Information**
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.9b09321.

Computer program for the calculation of reflection and transmission spectra as well as the composite CD (PDF)

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