Recent progress in research on stimuli-responsive circularly polarized luminescence based on π-conjugated molecules*

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Abstract: This short review article summarizes recent progress in research on various stimuli-responsive circularly polarized luminescence (CPL) properties derived from π-conjugated molecules and related materials. As representative examples, assembled structures of chiral π-conjugated polymers and molecules showed tunable CPL resulting from the enhancement of chirality induction by aggregation. Fascinating CPL-active species, pyrrole-based anion-responsive π-conjugated molecules exhibiting CPL induced by anion binding and ion pairing, are also discussed.

Keywords: chirality; fluorescence; helical structures; molecular recognition; self-assembly; supramolecular chemistry.

INTRODUCTION

Chirality is the state derived from the dissymmetry of molecules and molecular assemblies [1]. Chiral molecules and assemblies can exhibit fascinating chiroptical properties. One representative chiroptical property is circular dichroism (CD), which is evaluated as the difference between left- and right-handed circularly polarized light. CD spectra have been used to examine various molecular behaviors such as host–guest binding, assembly, and molecular folding [2]. Among chiral species, π-conjugated molecules with chiral moieties in their core units and side chains are suitable for investigation by CD because of their high molar extinction coefficient (ε) in the UV and visible regions [3]. On the other hand, emissive chiral species show circularly polarized luminescence (CPL), which attracts significant attention as the basis for cryptographic communication and stereoscopic vision. CPL is correlated with the chirality of a chiral species in its excited state. The anisotropy factor, $g_{\text{lum}}$, of CPL is obtained by $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where $I_L$ and $I_R$ are the intensities of the left- and right-handed circularly polarized emissions, respectively [4]. Theoretically, $g_{\text{lum}}$ is defined as $4|m||\mu|\cos\theta(|m|^2 + |\mu|^2)$, where $m$ and $\mu$ are the magnetic and electric transition dipole moments, respectively, and $\theta$ is the angle between $m$ and $\mu$. The possible $g_{\text{lum}}$ values are within the range of –2 to +2. High $g_{\text{lum}}$ values are only expected for $m$-allowed and $\mu$-forbidden transitions, and low values are derived from $m$-forbidden and $\mu$-allowed transitions.

Among various emissive chiral species, lanthanide complexes often show high $g_{\text{lum}}$ values as observed in Eu(III) complexes exhibiting $g_{\text{lum}} > 1$ [5]. On the other hand, emissive π-conjugated molecules, most of which show fairly low $g_{\text{lum}}$ values, have the advantages of readily tunable emission.
properties according to changes in their electronic states and assembled structures; such properties can be controlled by core modifications and introduction of peripheral substituents.

Furthermore, changes of the electronic states and assembled structures can also be achieved by external stimuli; various factors that change the situations of chiral molecules and molecular assemblies may act as stimuli for enhancing CPL. In this short review article, we focus on π-conjugated molecules and related materials that exhibit CPL properties controllable by physical and chemical stimuli.

**STIMULI-RESPONSIVE CPL PROPERTIES OF π-CONJUGATED POLYMERS**

Emissive polymers possessing chiral substituents are promising CPL-active candidates. For example, Swager et al. reported opposite CPL for spin-cast films of poly(π-phenylene vinylene) 1 possessing chiral alkyl chains depending on the solvents, which are crucial for supramolecular preorganization of the polymers (Fig. 1a) [6]. In nonpolar solvents such as CHCl₃, in which the polymer easily dissolves, the resulting film exhibited no significant CD or CPL. However, upon annealing the film at 45 °C for 30 min in the presence of CHCl₃ vapor, the polymer chains self-assembled from a disordered state to a more thermodynamically favored chiral organization. This resulted in strong bisignate CD spectra derived from exciton coupling between obliquely oriented neighboring chromophores arranged in a predominantly M-type organization. The annealed film exhibited the preferential emission of right CPL with a negative \( g_{\text{lum}} \), suggesting that both absorption and luminescence transitions were derived from the M-type arrangement of polymers. In contrast, spin-casting of 1 from less polar solvent 1,2-dichloroethane (DCE) provided a film exhibiting the CD signals of a P-type organization and predominantly left circularly polarized light with a positive \( g_{\text{lum}} \) (Fig. 1b) [6].

Akagi et al. reported the photoresponsive CPL properties of chiral π-conjugated polymers (R)- and (S)-2,3 [7]. The polymers (R)- and (S)-2,3 contain the fluorescent π-conjugated aromatic unit as the main chain and a photochromic dithienylethene unit linked to a chiral moiety as a side chain (Fig. 2a). In contrast to the solution state, the cast film of (R)-2 with the open form of the dithienylethene moiety showed the Cotton effect in the CD spectrum, presumably derived from the formation of P-helicity with a right-handed (clockwise, CW) π-stacked structure [3b]. In the cast film state, the fluorescence bands of (R)-2,3 with the open form of the dithienylethene moiety drastically decreased in intensity and were quenched by UV irradiation at 254 nm owing to the efficient energy transfer from the excited polymer main chain to the closed form of the dithienylethene moiety and nonradiative transition to its ground state. The open form of (R)-2 showed a negative sign while that of (S)-2 showed a positive sign in the CPL spectra in the film state, suggesting the formation of the right- and left-handed helical structures, respectively (Fig. 2b). The \( g_{\text{lum}} \) values for the films were on the order of \( 10^{-2} \) at 414 nm for 2 and 650 nm for 3, respectively. Furthermore, photoswitching behavior in CPL was observed over 10 cycles. The helical stacking structures in (R)- and (S)-2,3 are so rigid that the chirality is not affected by the photochemical opening and closing isomerization reaction in the film state [7]. Akagi et al. also showed the CPL property of chiral nematic liquid crystals comprising chiral thiophene-based copolymers [8].

Physical chirality of a vortex flow can be transferred to the CPL of a fluorophore-doped polymer gel. Yamashita, Fujiki, and Okano et al. reported a fascinating dye-doped smart gel exhibiting CPL, wherein a reversible change in the positive and negative signs was achieved using vortex flow as an external stimuli [9]. Gelator polymer 4 (1.0 wt % in water, Fig. 3a) formed a very soft gel with the sol–gel transition temperature at 73–75 °C. The addition of emissive Rhodamine B 5 (1.3 × 10⁻⁵ M, Fig. 3a) in an aqueous gel of 4 resulted in the fluorescence of 5 at 580 nm (\( \lambda_{\text{ex}} = 520 \) nm) in the gel state. When the gel was not stirred, almost no CPL signal was observed, whereas a CPL signal was observed upon mechanical stirring at 1500 rpm. The 5-doped gel of 4 gave stirring-induced mirror-image CPL spectra, wherein the signs of the CPL signals were determined by the stirring direction (Fig. 3b). Positive and negative signs were induced with CCW and CW stirring, respectively, with the \( g_{\text{lum}} \) values of \( 6 \times 10^{-2} \) at 577 nm. The stirring-induced chirality in the gel was assumed to transfer to
Fig. 1 (a) Molecular structure of 1 and (b) the $g$ values of absorption (lines) and emission (markers) of the films spin-cast from DCE (green line) and CHCl$_3$ before (red line) and after (blue line) annealing. The $g_{abs}$ values, defined as $\Delta \varepsilon / \varepsilon$, of the DCE film were plotted at 20% of their actual values for easier comparison. Adapted from ref. [6] for (b). Copyright © (2006) American Chemical Society.

Fig. 2 (a) Structures of polymers (R)- and (S)-2,3 and (b) (i) fluorescence and (ii) CPL spectra along with photographs (inset) of (R)- and (S)-2 cast films in open and photostationary states (PSSs). Adapted from ref. [7] for (b). Copyright © (2010) John Wiley.

Fig. 3 (a) Structures of ionic oligomer 4 and Rhodamine B 5 and (b) CPL of the hydrogels of 5 (1.6 × 10$^{-5}$ M) in aqueous solutions of 4 (0.6 wt % in water) prepared with clockwise (CW, red) and counterclockwise (CCW, blue) stirring and without stirring (black). Adapted from ref. [9] for (b). Copyright © (2011) John Wiley.
the helical alignment of 4 on a molecular level. Such CPL behavior was not observed in the solution state above the sol–gel transition temperature [9].

**STIMULI-RESPONSIVE CPL PROPERTIES OF π-CONJUGATED MOLECULES**

CPL properties have been observed in assemblies based on emissive π-conjugated molecules. For example, Kawai et al. reported the concentration-dependent enhancement of the $g_{\text{lum}}$ value in π-conjugated chiral perylenebisimide derivatives ($R$)- and ($S$)-6 (Fig. 4a), which formed aggregated structures with higher optical chirality [10]. By increasing the concentrations of ($R$)- and ($S$)-6 in CHCl$_3$ from $5 \times 10^{-6}$ to $2 \times 10^{-3}$ M, the emission intensity from individual molecules at 555 nm decreased, whereas that at around 630 nm increased owing to the formation of aggregates. The $g_{\text{lum}}$ values of monomer emission stayed constant as $3 \times 10^{-3}$ at 555 nm, whereas those from the aggregates at 630 nm significantly increased at concentrations higher than $3 \times 10^{-4}$ M (Fig. 4b). The fitting function for the concentration-dependent $g_{\text{lum}}$ values provided the absolute $g_{\text{lum}}$ value, which was for the dimer state, of $1.8 \times 10^{-2}$ [10].

Recently, Haino et al. prepared tris(phenylisoxazolyl)benzene derivative ($S$)-7 possessing a perylenebisimide moiety (Fig. 5), whose CPL was triggered by helically stacking self-assembly that was responsive to changes in solvent properties [11]. The concentration-dependent $^1$H NMR spectrum of ($S$)-7 in CDCl$_3$ showed upfield-shifted signals upon increasing the concentration from $2 \times 10^{-4}$ to $2 \times 10^{-2}$ M. This observation suggested the formation of stacking J-like aggregates, which was also supported by changes in the UV/vis absorption spectrum. In dilute CHCl$_3$ solution ($1 \times 10^{-5}$ M), monomeric ($S$)-7 exhibited a fluorescence band at 539 nm with a fluorescence quantum efficiency of $\Phi_F = 0.56$. In contrast, in decalin ($1 \times 10^{-5}$ M), ($S$)-7 showed two emission bands at 525 and 650 nm ($\Phi_F = 0.07$) from monomeric and aggregated states, respectively. Along with the CD spectra with a positive Cotton effect at 545 nm in decalin, the assemblies of ($S$)-7 provided a positive CPL with a $g_{\text{lum}}$ value of 0.007, suggesting the formation of emissive chiral assemblies in the less polar solvent [11].

The correlation between solid-state CPL properties and aggregation-induced emission (AIE) was reported by Wong and Tang et al. [12]. Although silole derivative 8 possessing chiral sugar moieties (Fig. 6a) showed no CD or fluorescence emission in the solution state, the aggregation of 8 simultaneously turned on both CD and fluorescence, showing aggregation-induced CD and emission (AIE) effects. The CD signal of the assembly was related to the formation of right-handed helical nanoribbons and superhelical ropes as observed in scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images. On the other hand, the AIE effect boosted the $\Phi_F$ values by 136-fold as seen in the change of $\Phi_F = 0.006$ in solution to $\Phi_F = 0.813$ in the solid state. The helical assemblies of 8 preferred to show right-handed CPL with large $g_{\text{lum}}$ values of 0.08–0.32 (Fig. 6b). The solid-state assemblies showed excellent spectral stability, as observed in the CPL performance in the fluorescent pattern, which was preserved after storage for over half a year under ambient conditions [12].

Very recently, Ajayaghosh et al. reported the photoresponsive CPL of supramolecular assemblies comprising azobenzene-linked phenylene ethynylene derivatives ($S$)- and ($R$)-9 (Fig. 7a) [13]. In the ($E,E$) forms before isomerization, ($S$)- and ($R$)-9, which formed aggregates in methycyclohexane ($1 \times 10^{-4}$ M), showed positive and negative CPL with $g_{\text{lum}}$ values of +0.008 and −0.01, respectively, at 503 nm (Fig. 7b). Interestingly, after photoisomerization, the signs of CPL in the photostationary states (PSSs) including the ($E,Z$) and ($Z,Z$) forms along with the ($E,E$) forms were reversed with decreases in the $g_{\text{lum}}$ values at −0.002 and +0.002, respectively, at 503 nm. The CPL observed in this study is associated with the respective helicity of the assembled structures. The result suggested that the assembly of the ($E,E$) form alone and that consisting of all the isomers exhibited opposite chirality [13].

In addition to the supramolecular assemblies discussed above, monomers or discrete oligomeric assemblies of emissive π-conjugated molecules can also exhibit CPL properties. Takeuchi et al. prepared phthalhydrazide-functionalized helicene ($M$)-10 (Fig. 8a), which formed trimeric disks by hydro-
gen-bonding interactions in nonpolar solvents such as CHCl₃ [14]. The CPL properties of (M)-10 were observed in CHCl₃ and methanol, wherein (M)-10 forms monomers by disruption of hydrogen-bonding interactions. The $g_{\text{lum}}$ values were $-3.5 \times 10^{-2}$ at 476 nm in CHCl₃ (4 × 10⁻⁴ M) and $-2.1 \times 10^{-2}$ in methanol [14].

Fig. 4 (a) Structures of (R)- and (S)-6 and (b) concentration-dependent CPL spectral changes of (S)-6 (blue) and (R)-6 (red) in CHCl₃ with the concentrations of $1 \times 10^{-4}$, $3 \times 10^{-4}$, $5 \times 10^{-4}$, $1 \times 10^{-3}$, and $2 \times 10^{-3}$ M and the representative photographs (inset). Adapted from ref. [10] for (b). Copyright © (2010) American Chemical Society.

Fig. 5 Molecular structure of (S)-7.

Fig. 6 (a) Molecular structure of 8 and (b) normalized CPL intensities ($\lambda_{\text{ex}} = 325$ nm) vs. wavelengths for 8 in different forms: CH₂Cl₂ solution (2 × 10⁻⁴ M), CH₂Cl₂/hexane (1:9 (v/v), 2 × 10⁻⁴ M) suspension, neat cast film from DCE solution (2 mg/mL), dispersion in polymer matrix (10 wt % in PMMA), and fabricated micropattern by evaporation of DCE solution in microfluidic channels. Adapted from ref. [12] for (b). Copyright © (2012) Royal Society of Chemistry.
ANION-RESPONSIVE AND ION-PAIRING-RESPONSIVE CPL PROPERTIES OF PYRROLE-BASED π-CONJUGATED MOLECULES

In the previous section, the stimuli-responsive CPL behaviors of chiral π-conjugated molecules are limited to those based on the formation of chiral assembled structures. However, appropriate design and synthesis of emissive π-conjugated molecules that are responsive to chemical stimuli are crucial for inducing CPL properties that can be controlled by the recognition of guest species. The control of CPL
by intermolecular interactions would enable the emissive π-conjugated systems to achieve more facile on-off switching of CPL.

Fascinating guest species to be bound by π-conjugated molecules are anions, which often interact with polarized hydrogen-bonding donating sites [15]. Promising candidates for emissive anion-responsive molecules are BF₂ complexes of 1,3-dipyrrolyl-1,3-propanedione such as 11 (Fig. 9), wherein pyrrole rings are stabilized by the neighboring electron-withdrawing carbonyl unit [16,17]. The center boron-bridged 1,3-propanedione moiety between the two pyrrole rings is effective in affording suitable electronic states that exhibit UV/vis absorption and emission maxima in the visible region at 432 and 451 nm, respectively, in CH₂Cl₂. Therefore, its skeleton structure could be appropriate for various uses such as anion sensors and ion-based assemblies and materials. The modification of 11 by substitution at the pyrrole α- and β-positions provided various derivatives of the anion receptor [18–22]. The two pyrrole NH moieties of 11 are located at the side of the carbonyl oxygen, which results in a less preorganized conformation for anion binding. Therefore, upon the addition of anions, receptor 11 exhibits inversion of the two pyrrole rings and binds the anions using the pyrrole NH and the bridging CH to form a planar receptor–anion complex (Fig. 9). The N–H⋯X– and bridging C–H⋯X– interactions are implicated by the ¹H NMR chemical shifts of a series of anion receptors upon the addition of anions as tetrabutylammonium (TBA) salts. Furthermore, the UV/vis absorption and emission spectra of 11 change in the presence of anions as TBA salts, which suggest its potential as a colorimetric and fluorescent anion sensor. The Kₐ values of 11 in CH₂Cl₂ were estimated as 15000, 2100, 930000, and 270000 M⁻¹ upon binding with Cl⁻, Br⁻, CH₃CO₂⁻, and H₂PO₄⁻, respectively [18b].

![Fig. 9 Pyrrole-based acyclic anion receptor 11 and its anion-binding mode.](image)

The modification of the anion receptors is not restricted to the pyrrole rings, as it can also be achieved at the boron moiety of the central six-membered ring [23]. In particular, substitution of the diol moieties on boron was found to provide various receptor molecules with useful functionalities. Along with achiral BF₂ receptors 12a–15a and catechol-boron receptors 12b–15b, chiral (R)-(−)-1,1’-bi-2-naphtholboron receptors 12c–15c and (R)-(−)-3,3’-diphenyl-1,1’-bi-2-naphtholboron receptors 12d–15d (Fig. 10a) were obtained from the reactions of the precursory diketone derivatives, BCl₃, and chiral diols. The CD spectra of chiral molecules 12c–15c and 12d–15d in CH₂Cl₂ exhibited negative Cotton effects derived from the core π-planes, which suggested that enantiomerically distorted M-like conformations were induced by the substituents at boron. On the basis of a steady state, the induction of chirality of π-conjugated molecules in the excited state by anion binding was examined using CPL measurements. Anion-responsive CPL was observed for 15d upon complexation with anions such as Cl⁻ as TBA salts (Fig. 10b). For example, 15d exhibited a CPL g lum value of 2 × 10⁻³ in the presence of Cl⁻, but showed a negligibly small CPL in the absence of Cl⁻. The enhancement of g lum of 15d by anion binding is greater than that of g abs by Cl⁻ binding, which suggests that the anion-driven chiral induction, which is mainly due to conformation changes in the π-conjugated system, is more pronounced in the excited state than in the steady state. Such an on/off switching of g lum was not observed in receptors 12c,d, 13c,d, 14c,d, and 15c, some for which exact g lum values could not be determined owing to their smaller CPL intensities [23c].

Although helical π-conjugated molecules can effectively exhibit chiroptical properties, it is challenging to induce the chirality with a unidirectional helical structure. In order to form anion-driven helical structures, the oligomeric systems of pyrrole-based anion-responsive molecules have been studied. Thorough examination of chirality induction in the anion-driven helices has revealed fascinating observations in the ion pairing of the helices with chiral counter cations.

Recently, meta-phenylene-bridged anion receptor dimers 16a, b and tetramer 17 (Fig. 11) were synthesized by iodination of the pyrrole α-position(s) of the receptors, followed by cross-coupling reactions [21a,d]. The UV/vis absorption maxima (λ_max) of the oligomers in CH_2Cl_2 are 489 nm for 16a, 514 nm for 16b, and 478 nm for 17, suggesting that there is no significant π-extension relative to monomer 18 (499 nm) because of the cross-conjugated meta-phenylene spacer(s) along with the distortion of planarity. In particular, the broad absorption band of 17 with a shoulder at 515 nm suggests the formation of partially folded structures. The formation of anion-driven helical structures was initially elucidated by single-crystal X-ray analysis of anion complexes of receptor oligomers that were prepared by treatment with a TPA salt of Cl\(^{-}\) as a TBA salt (50 equiv for UV/vis and 200 equiv for the other measurements as sufficient amounts for almost complete complexation; 15d: black line, 15dCl\(^{-}\): red line) and corresponding solution photographs (inset).

![Fig. 10](a) Boron-modified anion receptors 12a–d, 13a–d, 14a–d, and 15a–d and (b) spectral changes of 15d (1.0 × 10^{-5} M in CH_2Cl_2) in (i) UV/vis absorption (bottom) and CD (top) and (ii) fluorescence (bottom) and CPL (top) excited at the isosbestic point of the UV/vis absorption spectrum upon the addition of Cl\(^{-}\) as a TBA salt (50 equiv for UV/vis and 200 equiv for the other measurements as sufficient amounts for almost complete complexation; 15d: black line, 15dCl\(^{-}\): red line) and corresponding solution photographs (inset).

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Table 1 Binding constants (K, M⁻¹) of 16a,b, 17, and 18 for halide anions in CH₂Cl₂.

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Anion complexes of the receptor oligomers could be formed in an enantiomerically enriched state in solution through ion pairing with optically active cations such as chiral binaphthylammonium salts of Cl⁻ and Br⁻ [24], RR·X (X = Cl and Br) [Fig. 12a(i)]. In fact, when Cl⁻ was added in the form of its RR·Cl⁻ salt that appeared at 535 nm (negative peak) and 480 nm (positive peak) were larger when the CD spectrum was acquired at −70 °C than when it was acquired at 20 °C [Fig. 12b(i)], which suggests the asymmetric formation of helical structures through diastereoselective ion-pair formation [Fig. 12a(ii)] [21g]. The Cotton effects in the CD spectra, which are consistent with the formation of a helical structure, are associated with an excitonic interaction between the two receptor monomer units. Time-dependent density functional theory (TD-DFT) calculations suggest that in the presence of RR⁺, 16b·Cl⁻ should exist predominantly as an M-type helical structure. The two sets of ¹H NMR signals of 16b in the presence of 1.5 equiv of RR⁺·Cl in CD₂Cl₂ at −50 °C are consistent with the presence of two types of 1:1 complexes in a ratio of 1:0.62, which represents the diastereomeric excess (d.e.) of 24 % between the M- and P-type helical structures. The chemical shifts associated with each set of signals represent an average of the shifts of the respective ion pairs (16b⁺·Cl⁻·RR⁺ and 16b⁺·Cl⁻·RR⁺) and the corresponding free ions (16b⁺·Cl⁻ and 16b⁺·Cl⁻). When 16b in CD₂Cl₂/octane-d₁₈ (1:1, 1 × 10⁻³ M) was treated with 1.5 equiv of the chiral salt at −70 °C, the resulting ion pairs, 16b⁺·Cl⁻·RR⁺ and 16b⁺·Br⁻·RR⁺, were formed with higher d.e. values of 70 %. This increase in d.e. is presumably due to increased stabilization of the ion pairs in a less polar solvent. Furthermore, when a solution of either 16b⁺·Cl⁻ or 16b⁺·Br⁻ in the presence of RR⁺ (1.5 equiv) in CH₂Cl₂ (1 × 10⁻³ M) at −70 °C was excited at the isosbestic point in the corresponding UV/vis absorption spectrum, the resulting fluorescence spectrum exhibited an emission maximum (λₑm) of 559 nm [Fig. 12b(ii), bottom]. The ion pairs formed from 16b⁺·X⁻ (X = Cl and Br) and the chiral cations exhibit CPL [Fig. 12b(ii), top] under the conditions described above with the gₘ values of 8.4 × 10⁻³ and 1.3 × 10⁻², respectively. The gₘ values increased to 1.8 × 10⁻² and 2.1 × 10⁻², respectively, when the ion pairs were formed in CH₂Cl₂/octane (1:1, 1 × 10⁻³ M) at −70 °C. Notably, CPL has been found to be induced through ion-pair formation involving helical charged species and counter ions in solution [21g].
CONCLUDING REMARKS

In this review article, various examples of stimuli-responsive CPL of π-conjugated species were summarized. Among the various chiral emissive species, pyrrole-based π-conjugated anion receptors exhibit attractive chiroptical properties such as anion-driven CPL of chiral receptors and ion-pairing-driven CPL in helical anion complexes. Designing chiral molecules that show efficient and tunable CPL is a significant challenging because the chirality in the excited state cannot be easily predicted. However, innovative design and synthesis of π-conjugated molecules by considering their geometries, assembling behaviors, and electronic and optical properties will make it possible to induce attractive CPL properties in the near future.

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