

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_{lum} , of CPL is obtained by $g_{\text{lum}} = 2(I_{\text{L}} - I_{\text{R}})/(I_{\text{L}} + I_{\text{R}})$, where I_{L} and I_{R} are the intensities of the left- and right-handed circularly polarized emissions, respectively [4]. Theoretically, g_{lum} is defined as $4|m||\mu|\cos\theta/(|m|^2 + |\mu|^2)$, where m and μ are the magnetic and electric transition dipole moments, respectively, and θ is the angle between m and μ . The possible g_{lum} values are within the range of -2 to $+2$. High g_{lum} values are only expected for m -allowed and μ -forbidden transitions, and low values are derived from m -forbidden and μ -allowed transitions.

Among various emissive chiral species, lanthanide complexes often show high g_{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_{lum} values, have the advantages of readily tunable emission

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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(*p*-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 CHCl_3 , 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 CHCl_3 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_{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_{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_{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_{lum} values of 6×10^{-2} at 577 nm. The stirring-induced chirality in the gel was assumed to transfer to

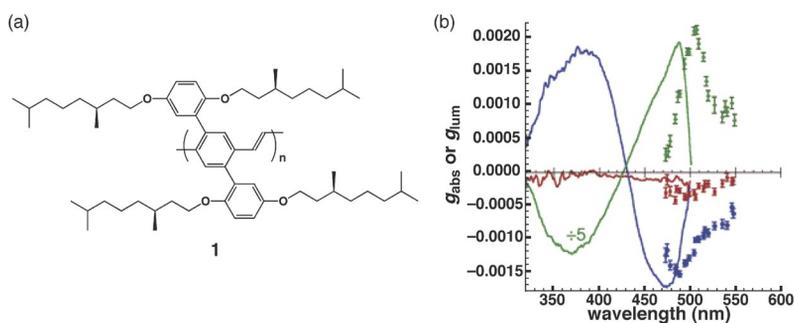


Fig. 1 (a) Molecular structure of **1** and (b) the g values of absorption (lines) and emission (markers) of the films spin-cast from DCE (green line) and CHCl_3 before (red line) and after (blue line) annealing. The g_{abs} values, defined as $\Delta\epsilon/\epsilon$, of the DCE film were plotted at 20 % of their actual values for easier comparison. Adapted from ref. [6] for (b). Copyright © (2006) American Chemical Society.

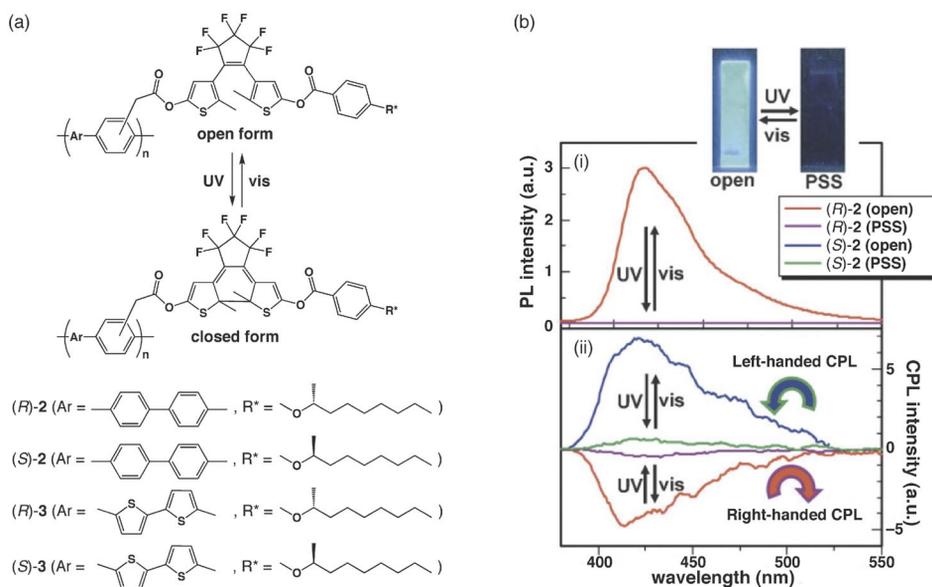


Fig. 2 (a) Structures of polymers (*R*)- and (*S*)-**2,3** and (b) (i) fluorescence and (ii) CPL spectra along with photographs (inset) of (*R*)- and (*S*)-**2** cast films in open and photostationary states (PSSs). Adapted from ref. [7] for (b). Copyright © (2010) John Wiley.

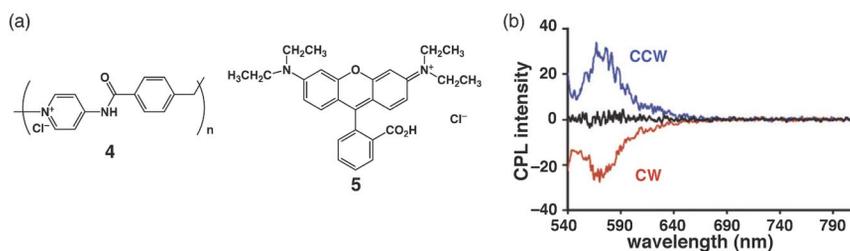


Fig. 3 (a) Structures of ionic oligomer **4** and Rhodamine B **5** and (b) CPL of the hydrogels of **5** (1.6×10^{-5} M) in aqueous solutions of **4** (0.6 wt % in water) prepared with clockwise (CW, red) and counterclockwise (CCW, blue) stirring and without stirring (black). Adapted from ref. [9] for (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_{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 5×10^{-6} to 2×10^{-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_{lum} values of monomer emission stayed constant as 3×10^{-3} at 555 nm, whereas those from the aggregates at 630 nm significantly increased at concentrations higher than 3×10^{-4} M (Fig. 4b). The fitting function for the concentration-dependent g_{lum} values provided the absolute g_{lum} value, which was for the dimer state, of 1.8×10^{-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 ^1H NMR spectrum of (*S*)-**7** in CDCl_3 showed upfield-shifted signals upon increasing the concentration from 2×10^{-4} to 2×10^{-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 (1×10^{-5} M), monomeric (*S*)-**7** exhibited a fluorescence band at 539 nm with a fluorescence quantum efficiency of $\Phi_{\text{F}} = 0.56$. In contrast, in decalin (1×10^{-5} M), (*S*)-**7** showed two emission bands at 525 and 650 nm ($\Phi_{\text{F}} = 0.07$) 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_{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 Φ_{F} values by 136-fold as seen in the change of $\Phi_{\text{F}} = 0.006$ in solution to $\Phi_{\text{F}} = 0.813$ in the solid state. The helical assemblies of **8** preferred to show right-handed CPL with large g_{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 methylcyclohexane (1×10^{-4} M), showed positive and negative CPL with g_{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_{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-

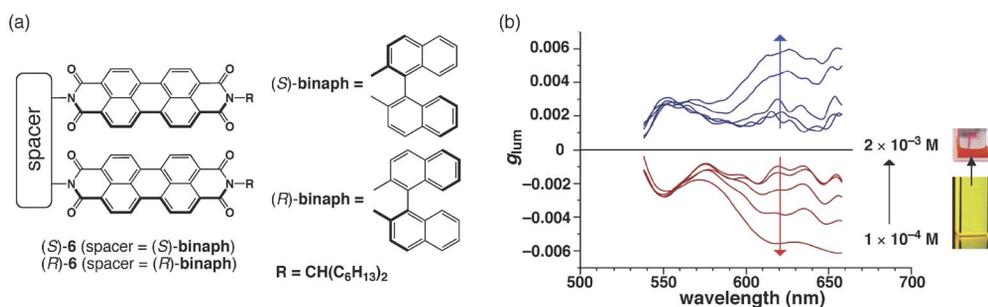


Fig. 4 (a) Structures of (*R*)- and (*S*)-**6** and (b) concentration-dependent CPL spectral changes of (*S*)-**6** (blue) and (*R*)-**6** (red) in CHCl_3 with the concentrations of 1×10^{-4} , 3×10^{-4} , 5×10^{-4} , 1×10^{-3} , and 2×10^{-3} M and the representative photographs (inset). Adapted from ref. [10] for (b). Copyright © (2010) American Chemical Society.

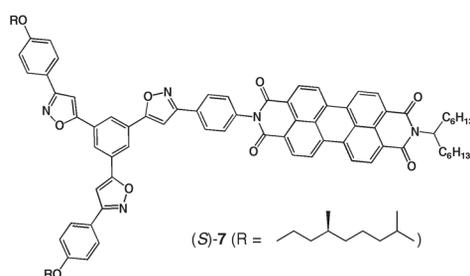


Fig. 5 Molecular structure of (*S*)-**7**.

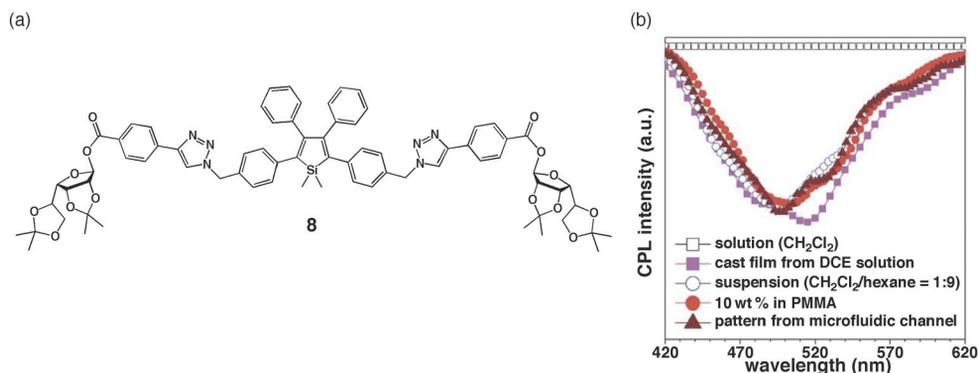


Fig. 6 (a) Molecular structure of **8** and (b) normalized CPL intensities ($\lambda_{\text{ex}} = 325$ nm) vs. wavelengths for **8** in different forms: CH_2Cl_2 solution (2×10^{-4} M), CH_2Cl_2 /hexane (1:9 (v/v), 2×10^{-4} M) suspension, neat cast film from DCE solution (2 mg/mL), dispersion in polymer 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.

gen-bonding interactions in nonpolar solvents such as CHCl_3 [14]. The CPL properties of (*M*)-**10** were observed in CHCl_3 and methanol, wherein (*M*)-**10** forms monomers by disruption of hydrogen-bonding interactions. The g_{lum} values were -3.5×10^{-2} at 476 nm in CHCl_3 (4×10^{-4} M) and -2.1×10^{-2} in methanol [14].

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 BF_2 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 CH_2Cl_2 . 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 $\text{N-H}\cdots\text{X}^-$ and bridging $\text{C-H}\cdots\text{X}^-$ 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 K_a values of **11** in CH_2Cl_2 were estimated as 15000, 2100, 930000, and 270000 M^{-1} upon binding with Cl^- , Br^- , CH_3CO_2^- , and H_2PO_4^- , respectively [18b].

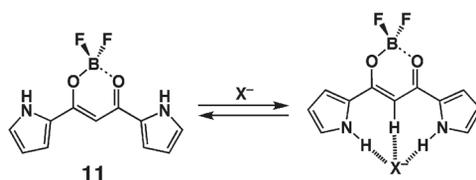


Fig. 9 Pyrrole-based acyclic anion receptor **11** and its anion-binding mode.

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 BF_2 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, BCl_3 , and chiral diols. The CD spectra of chiral molecules **12c–15c** and **12d–15d** in CH_2Cl_2 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].

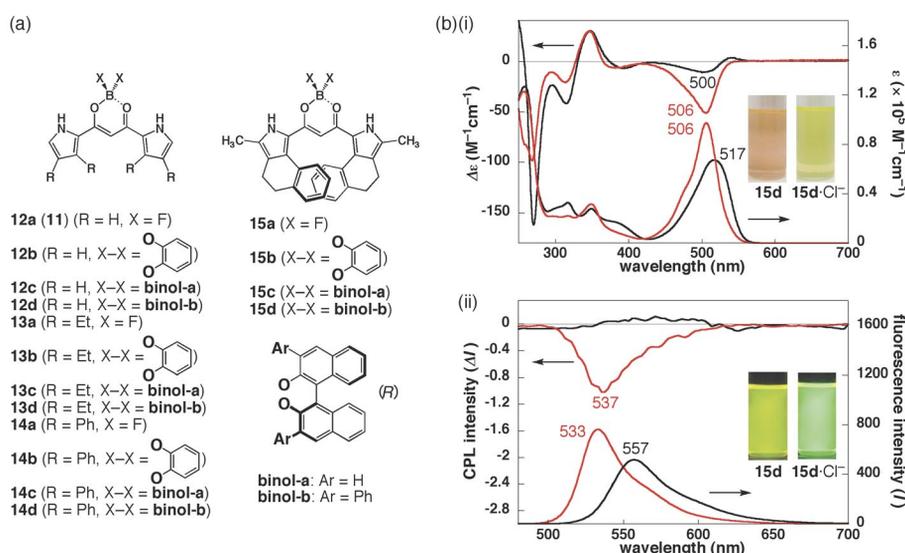


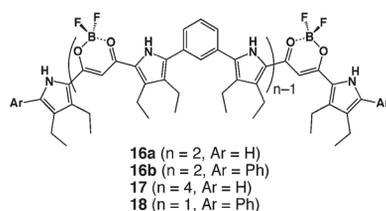
Fig. 10 (a) Boron-modified anion receptors **12a–d**, **13a–d**, **14a–d**, and **15a–d** and (b) spectral changes of **15d** (1.0×10^{-5} M in CH_2Cl_2) in (i) UV/vis absorption (bottom) and CD (top) and (ii) fluorescence (bottom) and CPL (top) excited at the isosbestic point of the UV/vis absorption 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, **15d**· Cl^- : red line) and corresponding solution photographs (inset).

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^- . In the solid state, driven by Cl^- complexation, **16a** and **17** form single helices, whereas **16b** forms a double helical structure. On the other hand, in the solution state, dimers **16a,b** showed the formation of [1 + 1]-type single helices, whereas, for the tetramer **17**, [1 + 2]-type single helices formed in the solution state at millimolar concentration and stepwise spectral changes from [1 + 1] to [1 + 2] were observed at a micromolar concentration. The anion-binding constants (K_a) of oligomers **16a,b** and **17** along with a reference monomer **18**, as estimated by UV/vis absorption spectral changes, are summarized in Table 1. The receptor oligomers exhibit significantly augmented K_a values in CH_2Cl_2 owing to formation of multiple hydrogen bonding. For example, the K_a values of **16a**, **16b**, and **17** in the [1 + 1] complexation with Cl^- are 5.9×10^7 , 1.2×10^7 , and 1.2×10^8 M^{-1} , respectively, which are much higher than that of **18** (2700 M^{-1}) [21d].

Table 1 Binding constants (K_a , M^{-1}) of **16a,b**, **17**, and **18** for halide anions in CH_2Cl_2 .

	16a	16b	17	18
Cl^-	59 000 000	12 000 000	K_1 : 120 000 000 K_2 : 3200	2700
Br^-	4 800 000	24 000	K_1 : 23 000 000 K_2 : 1600	300
I^-	58 000	6800	K_1 : 88 000 K_2 : 33	17

**Fig. 11** Anion receptor dimers **16a,b** and tetramer **17** along with reference monomer **18**.

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^+ salt, the CD signals associated with $16b \cdot Cl^-$ that appeared at 535 nm (negative peak) and 480 nm (positive peak) were larger when the CD spectrum was acquired at $-70^\circ C$ than when it was acquired at $20^\circ C$ [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^+ , $16b \cdot Cl^-$ 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 CD_2Cl_2 at $-50^\circ C$ 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 ($16b^M \cdot Cl^- \cdot RR^+$ and $16b^P \cdot Cl^- \cdot RR^+$) and the corresponding free ions ($16b^M \cdot Cl^-$ and $16b^P \cdot Cl^-$). When **16b** in CD_2Cl_2 /octane- d_{18} (1:1, 1×10^{-3} M) was treated with 1.5 equiv of the chiral salt at $-70^\circ C$, the resulting ion pairs, $16b \cdot Cl^- \cdots RR^+$ and $16b \cdot Br^- \cdots RR^+$, 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 $16b \cdot Cl^-$ or $16b \cdot Br^-$ in the presence of RR^+ (1.5 equiv) in CH_2Cl_2 (1×10^{-3} M) at $-70^\circ C$ was excited at the isosbestic point in the corresponding UV/vis absorption spectrum, the resulting fluorescence spectrum exhibited an emission maximum (λ_{em}) of 559 nm [Fig. 12b(ii), bottom]. The ion pairs formed from $16b \cdot X^-$ ($X = Cl$ and Br) and the chiral cations exhibit CPL [Fig. 12b(ii), top] under the conditions described above with the g_{lum} values of 8.4×10^{-3} and 1.3×10^{-2} , respectively. The g_{lum} values increased to 1.8×10^{-2} and 2.1×10^{-2} , respectively, when the ion pairs were formed in CH_2Cl_2 /octane (1:1, 1×10^{-3} M) at $-70^\circ C$. Notably, CPL has been found to be induced through ion-pair formation involving helical charged species and counter ions in solution [21g].

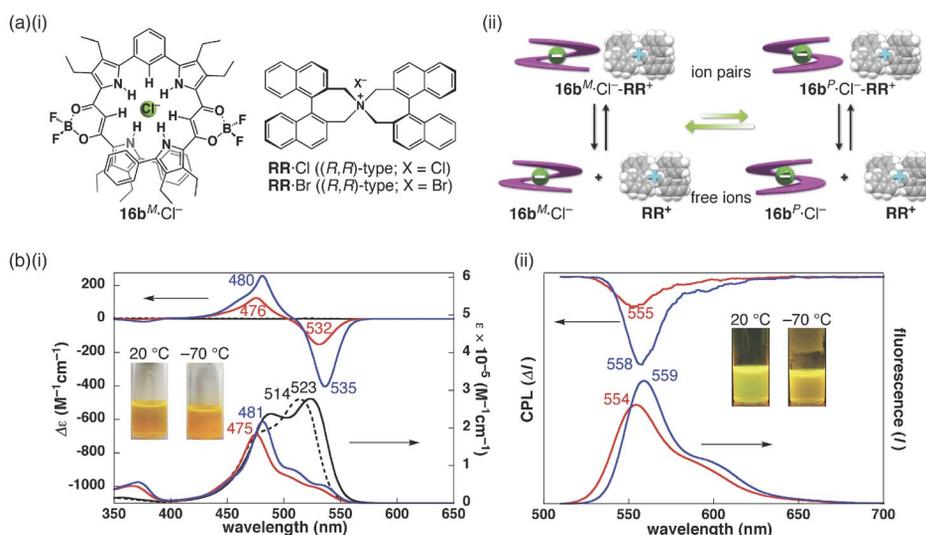


Fig. 12 (a) (i) Schematic representations of the Cl^- complex of **16b** with *M*-helicity (left) and binaphthylammonium halides $\text{RR}\cdot\text{X}$ ($\text{X} = \text{Cl}$ and Br) (right) and (ii) schematic models illustrating the interconversion between *M*- and *P*-type helices (horizontal equilibria), wherein ion pairs dissociate to give free ions (vertical equilibria), and (b) (i) CD spectra (top) and UV/vis spectra (bottom) and (ii) CPL (top) and fluorescence (bottom) spectra (excited at 483 nm) of **16b** in CH_2Cl_2 (1×10^{-3} M) with $\text{RR}\cdot\text{Cl}$ salt (1.5 equiv) at 20 (red) and -70 °C (blue), along with photographs of $\text{16b}\cdot\text{Cl}^- \cdots \text{RR}^+$ at 20 and -70 °C under visible and $\text{UV}_{365\text{nm}}$ light (inset). These spectra, which were measured under their respective optimized conditions, are represented using arbitrary units.

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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REFERENCES

1. (a) W. J. Lough, I. W. Wainer. *Chirality in Natural and Applied Science*, Blackwell/CRC, Oxford (2002); (b) D. B. Amabilino (Ed.). *Chirality at the Nanoscale*, Wiley-VCH, Weinheim (2009).
2. M. Crego-Calama, D. N. Reinhoudt (Eds.). *Supramolecular Chirality, Topics in Current Chemistry*, **265**, pp. 1–312, Springer-Verlag, Berlin (2006).
3. (a) N. Berova, K. Nakanishi, R. W. Woody (Eds.). *Circular Dichroism: Principal and Applications*, Wiley-VCH, New York (2000); (b) N. Berova, L. D. Bari, G. Pescitelli. *Chem. Soc. Rev.* **36**, 914 (2007); (c) G. A. Hembury, V. V. Borovkov, Y. Inoue. *Chem. Rev.* **108**, 1 (2008).
4. (a) J. P. Riehl, F. S. Richardson. *Chem. Rev.* **86**, 1 (1986); (b) P. M. L. Blok, H. P. J. M. Dekkers. *Chem. Phys. Lett.* **161**, 188 (1989); (c) T. Nakanishi, M. Naito, Y. Takeoka, K. Matsuura. *Curr. Opin. Coll. Int. Sci.* **16**, 482 (2011).
5. As an example of CPL-active lanthanide complexes: L. L. Jamie, D. Shirotani, K. Yamanari, S. Kaizaki, G. Muller. *J. Am. Chem. Soc.* **130**, 13814 (2008).
6. A. Satrijo, S. C. J. Meskers, T. M. Swager. *J. Am. Chem. Soc.* **128**, 9030 (2006).
7. H. Hayasaka, T. Miyashita, K. Tamura, K. Akagi. *Adv. Funct. Mater.* **20**, 1243 (2010).
8. K. Watanabe, I. Osaka, S. Yorozuya, K. Akagi. *Chem. Mater.* **24**, 1011 (2012).
9. K. Okano, M. Taguchi, M. Fujiki, T. Yamashita. *Angew. Chem., Int. Ed.* **50**, 12474 (2011).
10. H. Tsumatori, T. Nakashima, T. Kawai. *Org. Lett.* **12**, 2362 (2010).
11. T. Ikeda, T. Masuda, T. Hirao, J. Yuasa, H. Tsumatori, T. Kawai, T. Haino. *Chem. Commun.* **48**, 6025 (2012).
12. J. Liu, H. Su, L. Meng, Y. Zhao, C. Deng, J. C. Y. Ng, P. Lu, M. Faisal, J. W. Y. Lam, X. Huang, H. Wu, K. S. Wong, B. Z. Tang. *Chem. Sci.* **3**, 2737 (2012).
13. A. Gopal, M. Hifsudheen, S. Furumi, M. Takeuchi, A. Ajayaghosh. *Angew. Chem., Int. Ed.* **51**, 10505 (2012).
14. T. Kaseyama, S. Furumi, X. Zhang, K. Tanaka, M. Takeuchi. *Angew. Chem., Int. Ed.* **50**, 3684 (2011).
15. (a) R. Vilar (Ed.). *Recognition of Anions, Structure and Bonding*, **129**, pp. 1–252, Springer-Verlag, Berlin (2008); (b) P. A. Gale, W. Dehaen (Eds.). *Anion Recognition in Supramolecular Chemistry, Topics in Heterocyclic Chemistry*, **24**, pp. 1–370, Springer-Verlag, Berlin (2010).
16. H. Maeda, Y. Kusunose. *Chem.—Eur. J.* **11**, 5661 (2005).
17. Reviews and book chapters: (a) H. Maeda. *Eur. J. Org. Chem.* 5313 (2007); (b) H. Maeda. *Chem.—Eur. J.* **14**, 11274 (2008); (c) H. Maeda. *J. Incl. Phenom. Macrocycl. Chem.* **64**, 193 (2009); (d) H. Maeda. In *Handbook of Porphyrin Science*, **8**, p. 205, K. M. Kadish, K. M. Smith, R. Guilard (Eds.), World Scientific, New Jersey (2010); (e) H. Maeda. In *Anion Recognition in Supramolecular Chemistry, Topics in Heterocyclic Chemistry*, P. A. Gale, W. Dehaen (Eds.), **24**, p. 103, Springer-Verlag, Berlin (2010); (f) H. Maeda. In *Supramolecular Soft Matter: Applications in Materials and Organic Electronics*, T. Nakanishi (Ed.), p. 97, John Wiley, New Jersey (2011); (g) H. Maeda, Y. Haketa. *Pure Appl. Chem.* **83**, 189 (2011); (h) H. Maeda, B. Dong. *Chem. Commun.* **49**, 4085 (2013); (i) H. Maeda, Y. Bando. *Chem. Commun.* **49**, 4100 (2013); (j) H. Maeda. In *Intelligent Stimuli Responsive Materials: Well-defined Nanostructures to Applications*, Q. Li (Ed.), John Wiley, New Jersey, in press.
18. (a) C. Fujimoto, Y. Kusunose, H. Maeda. *J. Org. Chem.* **71**, 2389 (2006); (b) H. Maeda, M. Terasaki, Y. Haketa, Y. Mihashi, Y. Kusunose. *Org. Biomol. Chem.* **6**, 433 (2008).
19. (a) H. Maeda, Y. Haketa, T. Nakanishi. *J. Am. Chem. Soc.* **129**, 13661 (2007); (b) H. Maeda, N. Eifuku. *Chem. Lett.* **38**, 208 (2009); (c) H. Maeda, Y. Ito, Y. Haketa, N. Eifuku, E. Lee, M. Lee, T. Hashishin, K. Kaneko. *Chem.—Eur. J.* **15**, 3706 (2009); (d) H. Maeda, Y. Terashima, Y. Haketa, A. Asano, Y. Honsho, S. Seki, M. Shimizu, H. Mukai, K. Ohta. *Chem. Commun.* **46**, 4559 (2010); (e) H. Maeda, N. Eifuku, Y. Haketa, Y. Ito, E. Lee, M. Lee. *Phys. Chem. Phys. Chem.* **13**, 3843

- (2011); (f) H. Maeda, Y. Terashima. *Chem. Commun.* **47**, 7620 (2011); (g) H. Maeda, K. Kinoshita, K. Naritani, Y. Bando. *Chem. Commun.* **47**, 8241 (2011).
20. (a) H. Maeda, Y. Ito. *Inorg. Chem.* **45**, 8205 (2006); (b) H. Maeda, Y. Kusunose, Y. Mihashi, T. Mizoguchi. *J. Org. Chem.* **72**, 2612 (2007); (c) H. Maeda, Y. Haketa, Y. Bando, S. Sakamoto. *Synth. Met.* **159**, 792 (2009); (d) H. Maeda, Y. Bando, Y. Haketa, Y. Honsho, S. Seki, H. Nakajima, N. Tohnai. *Chem.—Eur. J.* **16**, 10994 (2010); (e) Y. Bando, S. Sakamoto, I. Yamada, Y. Haketa, H. Maeda. *Chem. Commun.* **48**, 2301 (2012); (f) Y. Bando, T. Sakurai, S. Seki, H. Maeda. *Chem. Asian J.* **8**, in press (<http://dx.doi.org/10.1002/asia.201300635>) (2013).
21. (a) H. Maeda, Y. Haketa. *Org. Biomol. Chem.* **6**, 3091 (2008); (b) H. Maeda, Y. Mihashi, Y. Haketa. *Org. Lett.* **10**, 3179 (2008); (c) H. Maeda, R. Fujii, Y. Haketa. *Eur. J. Org. Chem.* 1469 (2010); (d) Y. Haketa, H. Maeda. *Chem.—Eur. J.* **17**, 1485 (2011); (e) H. Maeda, K. Kitaguchi, Y. Haketa. *Chem. Commun.* **47**, 9342 (2011); (f) Y. Haketa, S. Sakamoto, K. Chigusa, T. Nakanishi, H. Maeda. *J. Org. Chem.* **76**, 5177 (2011); (g) Y. Haketa, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, M. Naito, H. Shibaguchi, T. Kawai, H. Maeda. *Angew. Chem., Int. Ed.* **51**, 7967 (2012); (h) H. Maeda, T. Shirai, S. Uemura. *Chem. Commun.* **49**, 5310 (2013).
22. (a) Y. Haketa, S. Sasaki, N. Ohta, H. Masunaga, H. Ogawa, N. Mizuno, F. Araoka, H. Takezoe, H. Maeda. *Angew. Chem., Int. Ed.* **49**, 10079 (2010); (b) H. Maeda, K. Naritani, Y. Honsho, S. Seki. *J. Am. Chem. Soc.* **133**, 8896 (2011); (c) B. Dong, Y. Terashima, Y. Haketa, H. Maeda. *Chem.—Eur. J.* **18**, 3460 (2012); (d) Y. Haketa, M. Takayama, H. Maeda. *Org. Biomol. Chem.* **10**, 2603 (2012); (e) Y. Haketa, Y. Honsho, S. Seki, H. Maeda. *Chem.—Eur. J.* **18**, 7016 (2012); (f) B. Dong, T. Sakurai, Y. Honsho, S. Seki, H. Maeda. *J. Am. Chem. Soc.* **135**, 1284 (2013).
23. (a) H. Maeda, Y. Fujii, Y. Mihashi. *Chem. Commun.* 4285 (2008); (b) H. Maeda, M. Takayama, K. Kobayashi, H. Shinmori. *Org. Biomol. Chem.* **8**, 4308 (2010); (c) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori, T. Kawai. *J. Am. Chem. Soc.* **133**, 9266 (2011); (d) Y. Terashima, M. Takayama, K. Isozaki, H. Maeda. *Chem. Commun.* **49**, 2506 (2013).
24. (a) T. Ooi, M. Kameda, K. Maruoka. *J. Am. Chem. Soc.* **121**, 6519 (1999); (b) T. Ooi, M. Kameda, K. Maruoka. *J. Am. Chem. Soc.* **125**, 5139 (2003).