

Chapter 9

Circularly Polarized Luminescence of Chirally Arranged Achiral Organic Luminophores by Covalent and Supramolecular Methods



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Abstract Circularly polarized luminescence (CPL) produced by achiral organic luminophores is described. Achiral organic luminophores can exhibit CPL by the chiral arrangement of the achiral luminophores. Chiral arrangement of achiral luminophores can be constructed through a covalently linked chiral spacer like a binaphthyl moiety. A helical supramolecular assembly also provides chiral environment on an achiral luminophore. The helically stacked assemblies of achiral luminophores are excellent for realizing CPL of the achiral luminophore since the highly assembled structure in the helical assembly provides good CPL activity. The stimuli-responsivity of supramolecular systems provides stimuli-responsive CPL.

9.1 Introduction

In the field of circularly polarized luminescence (CPL), chiral lanthanide complexes have been dominant due to their large CPL dissymmetry factor, g_{lum} [1]. In recent years, CPL-active organic compounds have attracted growing interest toward their potential applications in optoelectronic devices [2, 3]. The early research on CPL-active organic molecules started with chiral ketones in the 1960s [4]. After that, various CPL-active organic compounds were developed, and some of them exhibit large g_{lum} values comparable to those of chiral lanthanide complexes.

A key issue for constructing CPL-active materials is how to prepare an asymmetric environment on luminophores. A straightforward strategy for realizing CPL-active materials is the direct introduction of chirality on the luminophore. Actually, many lanthanide complexes possessing chiral ligands have been reported

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to exhibit CPL with the luminescence of the metal center [1]. In the same manner, chiral organic dyes such as helicenes also exhibit CPL [3]. In the field of polymers, chiral polymers are reported as CPL-active materials [5–7]. The alternative way to achieve CPL-active organic compounds is the chiral arrangement of achiral luminophores. If two or more luminophores take a chiral orientation, the luminophores chirally interact each other. Then, the electronic state of the luminophore is chirally perturbed. Thus, the emission of the luminophore gets circularly polarized despite the luminophore being achiral. Such chiral orientation can be constructed through a covalently linked chiral spacer. Another way to achieve chiral orientation of achiral luminophores is the use of a chiral supramolecular assembly. In this chapter, CPL properties of small organic compounds and their supramolecular assemblies are described (Fig. 9.1).

9.2 CPL of Chiral Organic Luminophores

The early CPL of organic compounds was produced by fluorescence based on the $\pi^* \rightarrow n$ transition of the carbonyl group of chiral ketones (Fig. 9.2) [4, 8–11]. However, the $\pi^* \rightarrow n$ transition of the carbonyl group is weak and limited at short

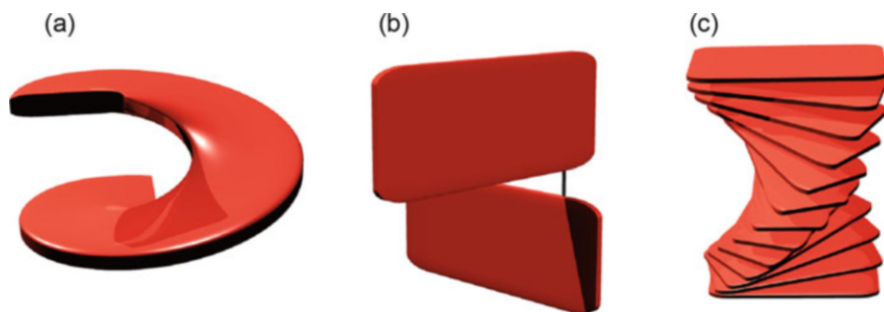


Fig. 9.1 CPL-active organic compounds: (a) chiral luminophore, (b) chirally arranged achiral luminophore, and (c) supramolecular helical assembly

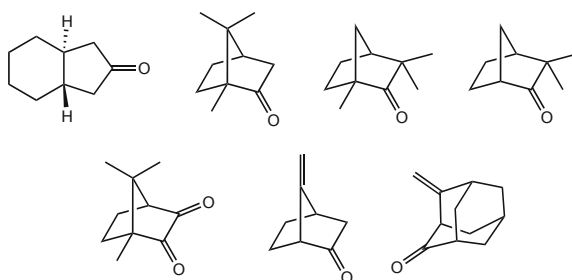


Fig. 9.2 CPL-active chiral ketones

wavelengths (~ 360 nm). The use of chiral π -conjugated luminophores that exhibit fluorescence by the $\pi^* \rightarrow \pi$ transition as CPL-active organic compounds is desirable due to their emission in the visible region with a high emission quantum yield. The most popular chiral π -conjugated molecule is a helicene. A helicene is an ortho-ring-fused polycyclic aromatic compound, in which aromatic rings are angularly annulated to give a helical structure. Helicenes have been widely investigated from the 1950s, and the CPL of a helicene was reported by Katz and coworkers in 2001 [12]. They synthesized [7]helicene-like compound **1** (Fig. 9.3). The molecule exhibited polarized fluorescence at 440 nm in diluted dodecane solution (2×10^{-6} mol L $^{-1}$), but CPL was not reported under these conditions. However, **1** displayed CPL in the condensed dodecane solution ($>1 \times 10^{-3}$ mol L $^{-1}$). The authors considered that the formation of aggregated species triggers the CPL.

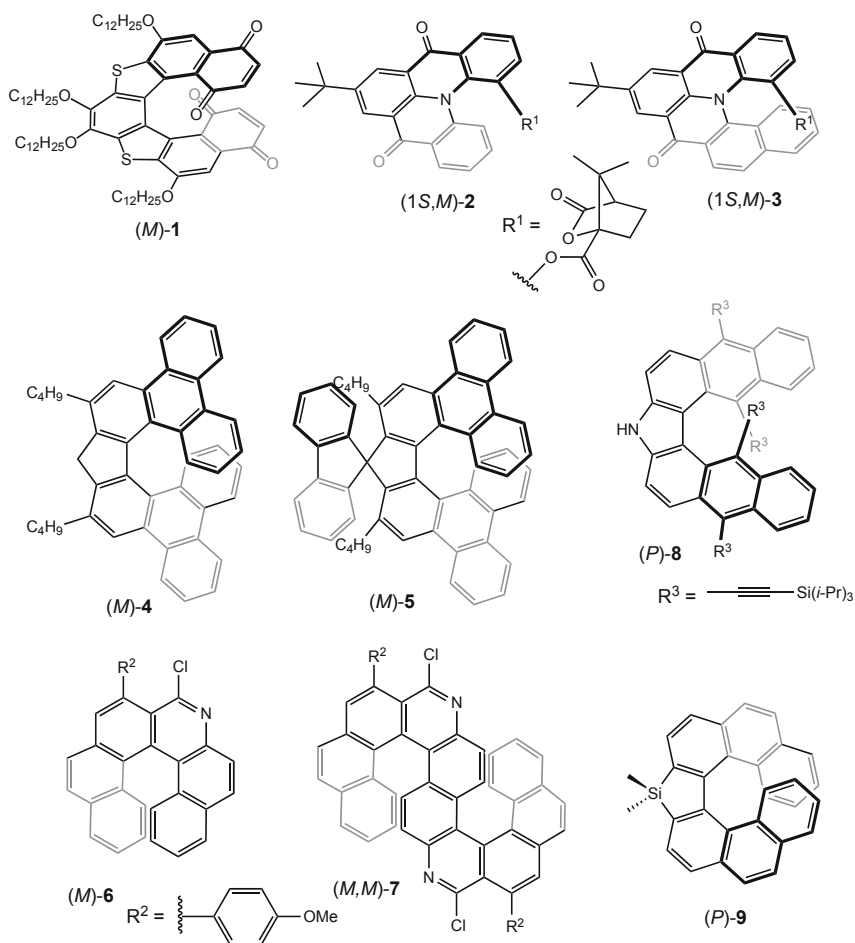


Fig. 9.3 CPL-active helicenes

The first observation of CPL of a nonaggregated helicene was reported by Venkataraman and coworkers in 2003. They synthesized a racemic pair of a helicene, and then, the helicene was reacted with (1*S*)-camphanate to give a corresponding diastereomeric pair of the helicene ((1*S*,*M*)- and (1*S*,*P*)-**2**, Fig. 9.3) [13]. Both of the diastereomers exhibited CPL on the monomeric fluorescence with a g_{lum} of ca. 1×10^{-3} . Interestingly, the CPL spectrum of (1*S*,*M*)-**2** was a mirror-image of that of (1*S*,*P*)-**2** in spite of a diastereomer, indicating that the (1*S*)-camphanate attached on the helicene core does not perturb the CPL of the helicene. They also synthesized the more extended [5]helicene-like compounds (1*S*,*M*)- and (1*S*,*P*)-**3** that display CPL too.

After the pioneering work by Venkataraman and coworkers, various chiral helicenes exhibiting CPL have been investigated. Tanaka and coworkers have developed several [7]helicene-like compounds displaying CPL since 2012 (Fig. 9.3) [14, 15]. For example, (*M*)-**4** and (*M*)-**5** exhibited CPL on its monomeric fluorescence in CHCl_3 with a g_{lum} of ca. 3×10^{-2} , which is a high value for an organic compound [15]. Tanaka and coworkers have also developed the CPL of aza[6]helicene-like compounds [14]. They synthesized aza[6]helicene (*M*)-**6** and S-shaped double aza[6]helicene-like compound (*M*,*M*)-**7**. Interestingly, the CPL of (*M*,*M*)-**7** ($g_{\text{lum}} = 1.1 \times 10^{-2}$) was enhanced compared to that of (*M*)-**6** ($g_{\text{lum}} < 1 \times 10^{-3}$). Shinokubo and coworkers reported the CPL of aza[7]helicenes (*M*)- and (*P*)-**8** in 2012 (Fig. 9.3) [16]. They exhibited CPL with a g_{lum} of 3×10^{-3} in CH_2Cl_2 . Nozaki and coworkers have developed CPL-active sila[7]helicenes (*M*)- and (*P*)-**9** that exhibited CPL with a g_{lum} of 3.5×10^{-3} in CH_2Cl_2 (Fig. 9.3) [17].

Takeuchi and coworkers have reported an interesting CPL behavior of a phthalhydrazide-functionalized [7]helicene-like compound **10** (Fig. 9.4) [18]. **10** formed a trimeric disk in chloroform via the hydrogen-bonding interaction of a phthalhydrazide moiety. Further aggregation of the trimeric disk resulted in the formation of a one-dimensional fiber-like assembly. The CPL property of **10** was found in chloroform, but not in methanol, which suggests that the trimeric disk was dissociated by breaking the hydrogen bonds. The g_{lum} values of (*M*)-**10** were estimated to be -3.5×10^{-2} in chloroform and -2.1×10^{-2} in methanol ($4 \times 10^{-4} \text{ mol L}^{-1}$), respectively. The formation of the trimeric disk and one-dimensional fiber-like assembly may increase the g_{lum} value of (*M*)-**10** in chloroform compared to that in methanol.

Thus, various CPL-active helicene-like compounds have been reported. However, the fluorescence quantum yields of CPL-active helicenes are moderate (32% for **4**, 36% for **8**, and 23% for **9**, respectively). The distortion of the π -plane may decrease the effective fluorescence of planar π -conjugated luminophores.

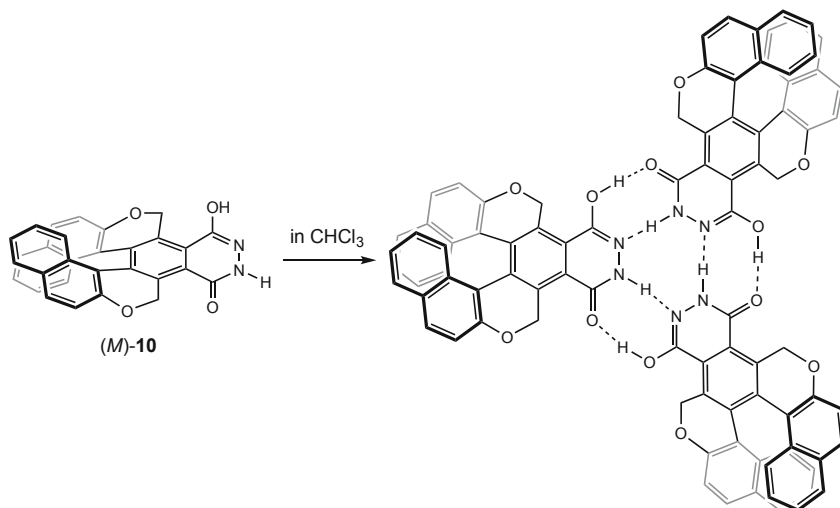


Fig. 9.4 CPL-active trimeric disk of the phthalhydrazide-functionalized [7]helicene-like compound (*M*)-**10**

9.3 CPL of Chirally Arranged Achiral Luminophores Through Chiral Spacers

An achiral luminophore has an advantage with regard to the fluorescence efficiency compared to a chirally distorted luminophore such as a helicene. A strategy to provide a chiral environment on an achiral luminophore is the chiral arrangement of two or more luminophores. When two luminophores are linked through a chiral spacer, the luminophores take a chiral orientation. Then, the luminophores interact each other, and the electronic state of a luminophore is chirally perturbed by the other luminophore. Various skeletons providing chiral orientation have been developed in the field of asymmetric catalysts. The most famous one is a chiral binaphthyl moiety. A binaphthyl has axial chirality since the free rotation about the bond linking the naphthyl rings is restricted due to the steric effect of hydrogen atoms at the 8 and 8' positions. Thus, each naphthalene takes a chiral orientation. Fujiki, Imai, and coworkers have developed CPL of simple and extended binaphthyls **11–18** (Fig. 9.5) [19–27]. The CPL properties of the binaphthyl derivatives depend on the dihedral angle of binaphthyl, the topology of the neighboring groups, the position of binaphthyl linkage, and the π -extension of the binaphthyl unit. The binaphthyl derivatives other than **14** (nonfluorescent) and **17** (CPL-inactive) exhibited CPL with g_{lum} values within the range of $(1.5\text{--}0.8) \times 10^{-3}$ and with fluorescent quantum yields within the range of 15–25%.

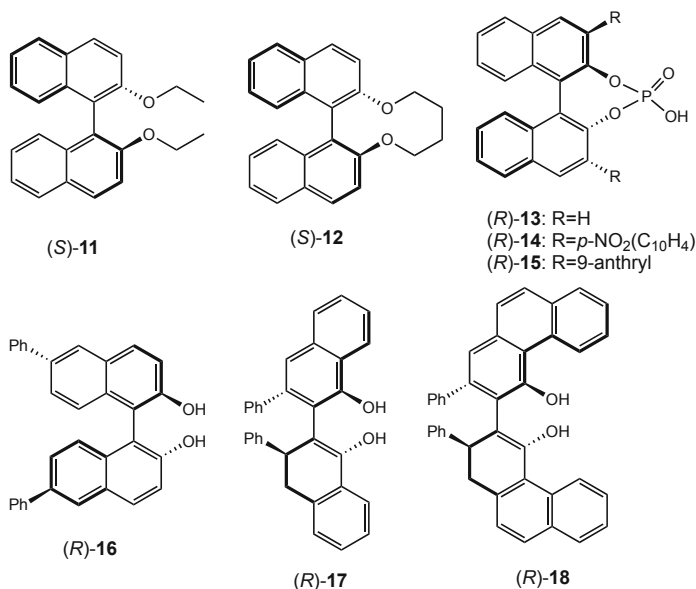


Fig. 9.5 CPL-active chiral binaphthyls

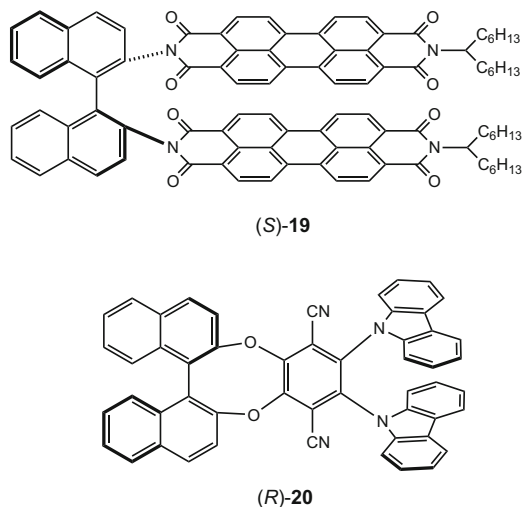


Fig. 9.6 CPL-active achiral luminophores attached onto binaphthyls

The introduction of two luminophores onto binaphthyl is effective for inducing the CPL of the achiral luminophore. The luminophores substituted on each naphthalene take a chiral orientation reflecting the axial chirality of binaphthyl. Kawai and coworkers reported the CPL of perylene bisimide (PBI) linked by a binaphthyl unit (Fig. 9.6) [28]. PBI is one of the most known organic luminophores

that exhibits its fluorescence at approximately 550 nm with a high emission quantum yield. They synthesized (*R*)- and (*S*)-**19**, with two PBI moieties attached to the 2 and 2' positions of the binaphthyl. (*R*)- and (*S*)-**19** exhibited characteristic π - π^* absorption and emission for the pair of PBI units. Chiroptical dissymmetry was observed in the circular dichroism (CD) spectrum, indicating that the two PBI moieties take a chiral orientation. (*S*)-**19** displayed CPL with a g_{lum} of 2×10^{-3} in their diluted solution (1×10^{-3} mol L⁻¹). The g_{lum} value increased as the concentration of (*S*)-**19** increased and reached 6×10^{-3} at the concentration of 1×10^{-3} mol L⁻¹, where (*S*)-**19** formed an opaque colloidal solution. The authors suggest that the formation of the aggregate in the condensed solution results in an increase in the g_{lum} value.

Pieters and coworkers developed a CPL-active delayed fluorescence system [29]. In thermally activated delayed fluorescence (TADF) emitters, the energy gap between their singlet and triplet states is so small that reverse intersystem crossing processes easily occur. Thus, both singlet and triplet excitons can be harvested for their fluorescence from the singlet excited state. This property has an advantage in developing motivated organic light emitting diodes (OLEDs) because of the possibility to overcome the theoretical maximum efficiency. They synthesized TADF emitter **20** possessing two achiral carbazoles as luminophores and a binaphthyl (Fig. 9.6). The TADF character of **20** was demonstrated using time-resolved fluorescence analysis. **20** exhibited CPL with a g_{lum} of 1.3×10^{-3} . The combination of CPL and TADF may provide a remarkable CPL-OLED material.

The use of a chiral cyclophane is also effective for creating CPL-active organic materials. A cyclophane is a cyclic compound that includes aromatic moieties as an integral part of its structure. [2.2]Paracyclophane has two benzene rings linked by two ethylenes at the 1,1' and 4,4' positions. The orientations of two benzene rings of a [2.2]paracyclophane are fixed since the benzene rings cannot invert. Thus, chirally substituted [2.2]paracyclophanes provide a chiral arrangement of luminophores that exhibit chiroptical properties. Recently, CPL-active [2.2]paracyclophanes have been developed by Morisaki, Chujo, and coworkers (Fig. 9.7) [30]. They synthesized propeller-shaped [2.2]paracyclophane derivatives (*R*)- and (*S*)-**21** and their precursors (*R*)- and (*S*)-**22**. (*S*)-**21** exhibited CPL with a g_{lum} of 1.1×10^{-2} and fluorescence quantum yield of 45%. These values are quite good compared to ordinary chiral organic luminophores. Interestingly, the g_{lum} value of (*S*)-**21** is approximately ten-fold higher than that of (*S*)-**22** ($g_{\text{lum}} = 1.1 \times 10^{-3}$). The good CPL activity of (*S*)-**21** comes from its highly extended and crisscrossed delocalized structure. The distortion of the π -conjugated plane in (*S*)-**21** may hinder its fluorescence efficiency, but it is clear that the distortion causes the high g_{lum} value of (*S*)-**21** compared to that of (*S*)-**22**. Morisaki, Chujo, and coworkers also synthesized planar chiral tetra-substituted [2.2]paracyclophanes (*R*)- and (*S*)-**23** and **24** [31]. **23** and **24** have a chirally orientated two *para*-phenylene-ethynylene luminophore that is not distorted. **24** has a more extended π -conjugated structure compared to **23**. **23** and **24** displayed optical dissymmetry in their emissions with good fluorescence quantum yields (65% for **23** and 87% for **24**) in diluted chloroform solution (1×10^{-6} mol L⁻¹). The g_{lum} values of (*R*)-**23** and (*R*)-**24** in the diluted solution were -1.7×10^{-3} and -1.2×10^{-3} , respectively. Interestingly,

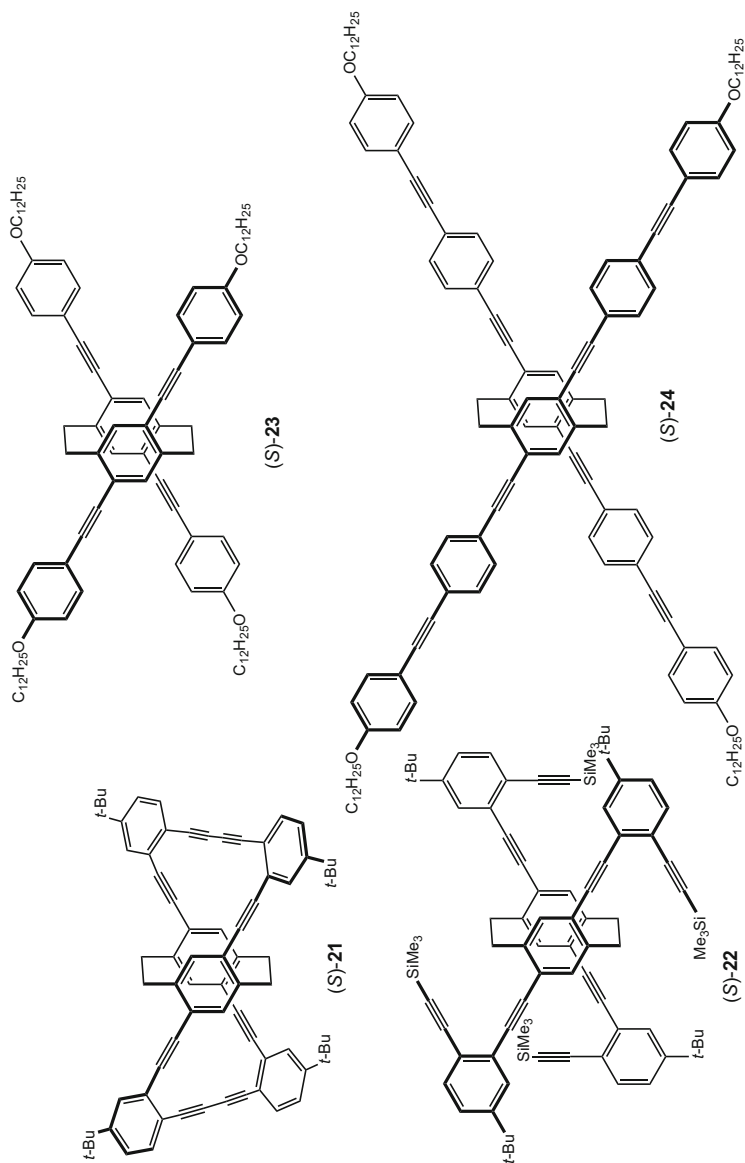
**Fig. 9.7** CPL-active chiral cyclophanes

Table 9.1 CPL properties of the films of **23** and **24**

Film state	Spin-coated film		Drop-casted thin film		Drop-casted thick film	
	Before annealing	After annealing	Before annealing	After annealing	Before annealing	After annealing
(<i>R</i>)- 23	-0.0061	-0.0087	-0.012	-0.026	-0.075	-0.0043
(<i>S</i>)- 23	+0.0056	+0.010	+0.0096	+0.034	+0.056	+0.0015
(<i>R</i>)- 24	+0.021	-0.12	-0.0086	-0.17	-0.030	-0.25
(<i>S</i>)- 24	-0.014	+0.13	+0.016	+0.13	+0.011	+0.27

the CPL activities of **23** and **24** drastically changed when the molecules formed films. They made spin-coated thin films, drop-casted thin films, and drop-casted thick films of **23** and **24**. The films were annealed at 65 °C (for **23**) and 90 °C (for **24**) for 3 h. The CPL properties of the films are summarized in Table 9.1. The g_{lum} values of **24** were increased after annealing, whereas those of **23** were not increased as much. For example, the g_{lum} value of the drop-casted thick film of (*R*)-**24** was -3.0×10^{-2} before annealing and -2.5×10^{-1} after annealing. The value after annealing is quite large for organic compounds. The authors proposed that the self-assembly of (*R*)-**24** in the annealed film results in the increase of the g_{lum} .

Thus far, the CPL properties of chiral organic luminophores and chirally arranged achiral luminophores through covalently linked spacers have been summarized. Three important findings are obtained from the results: (1) the distortion of the π -plane is effective for CPL activity, but it hinders the fluorescence efficiency of the planar π -conjugated luminophore; (2) a chiral arrangement of an achiral luminophore is effective for CPL activity; and (3) the aggregation of CPL-active organic compounds often increases their CPL activity. These findings encourage the use of the supramolecular assembly of achiral luminophores as CPL-active materials.

9.4 CPL Produced by Helical Supramolecular Assemblies

A supramolecular assembly is a well-defined molecular assembly held by noncovalent bonds such as hydrogen-bonding, π - π stacking, dipole-dipole, and hydrophilic/hydrophobic interactions. A finely designed supramolecular system provides a highly ordered structure of the assembly like the double helix of DNA. Recently, various highly ordered supramolecular assemblies have been developed [32–34]. Among them, supramolecular assemblies equipped with chirality have attracted attention due to their potential applications in the fields of asymmetric catalysts, chiral sensors, and chiroptical materials. Here, it is important to remember that the CPL properties of some chiral organic compounds increase in the condensed conditions compared to in the diluted solutions as mentioned above [12, 28, 35]. The increase would result from the formation of aggregates in the condensed conditions. Then, the idea to use supramolecular methods for constructing CPL-active organic materials is attractive since the luminophores form highly

assembled structures in highly ordered supramolecular assemblies [2]. The helix is one of the most frequently appearing motifs in chiral supramolecular systems. The right-handed helix is a mirror-image of the left-handed one, and thus, the helix is chiral. Various types of helical assemblies have been developed: chiral and achiral small molecules, oligomers, and polymers form helical assemblies [36]. Considering the CPL properties, helically stacked assemblies of planar π -conjugated luminophores are optimal to balance the highly assembled structure with the chiral orientation of a luminophore.

To form an assembly of a small π -conjugated molecule, the appropriate molecular design is indispensable. If a π -conjugated molecule forms a helical stacked assembly, a racemic mixture of *P*-helix and *M*-helix would be obtained without any chiral source. However, the introduction of a chiral source makes the *P*-helix and *M*-helix diastereomers. The diastereomers have differences in their Gibbs free-energy, and thus one (*P* or *M*) is more stable than the other (*M* or *P*) (Fig. 9.8). Therefore, the chiral source, a chiral alkyl side-chain in many cases, must be introduced into the molecule.

The assembled structure of a small π -conjugated molecule is stabilized by π - π stacking interactions, but other intermolecular interactions are needed to form a stable stacked assembly. The hydrogen-bonding interactions of amide moieties are often employed to form stacked assemblies. The hydrogen bonds are formed between hydrogen atoms attached to nitrogen and carbonyl oxygen. The consecutive hydrogen bonds of amide moieties form a one-dimensional network of hydrogen bonds (Fig. 9.9). When the amide moiety is attached to the aromatic rings of a π -conjugated luminophore, the amide moiety takes a twisted conformation to the π -conjugated plane of the aromatic ring. Thus, one-dimensional consecutive

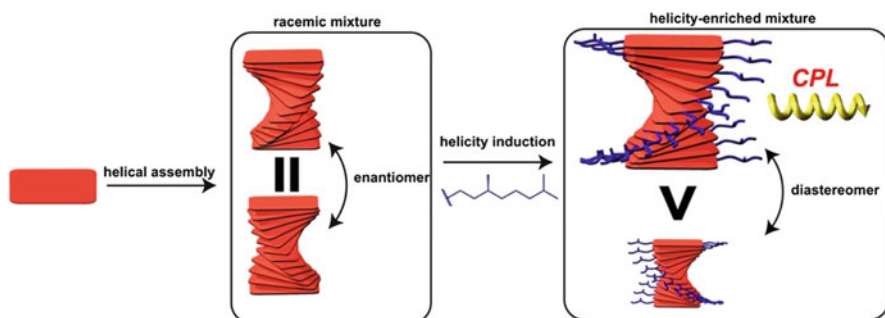


Fig. 9.8 CPL produced by a helical supramolecular assembly of an achiral luminophore

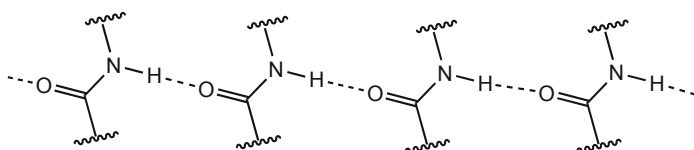


Fig. 9.9 One-dimensional hydrogen bond network of amide moieties

hydrogen bonds are formed to stabilize the stacked assembly of the π -conjugated molecules.

Various helical stacked assemblies via hydrogen-bonding interactions have been reported, and some of them exhibited CPL activity. Ajayaghosh and coworkers reported the self-assembly behavior as well as optical and chiroptical properties of **25**, an oligo-*p*-phenylene-ethynylene derivative possessing an amide moiety and chiral side-chains (Fig. 9.10) [37]. The molecule mostly existed as a monomer in tetrahydrofuran (THF) solution (1×10^{-5} mol L $^{-1}$), whereas **25** formed stacked assemblies in methylcyclohexane (MCH) solution (1×10^{-5} mol L $^{-1}$). **25** is equipped with an azobenzene moiety that exhibits photo-induced isomerization. In fact, photoisomerization from the (*E,E*)-isomer to (*Z,E*)- and (*Z,Z*)-isomers was observed with the irradiation of ultraviolet (UV) light. The formation of a helical assembly was confirmed by using CD spectroscopy. The assembly of the (*E,E*)-isomer of (*S*)-**25** exhibited a positive CD signal at 464 nm with two negative CD signals at 407 nm and 322 nm, corresponding to the $\pi \rightarrow \pi^*$ transition of the oligo-*p*-phenylene-ethynylene moiety. Interestingly, the CD signals inverted in the CD spectrum of the assembly of the (*Z,Z*)-isomer of (*S*)-**25**. This suggests that the helical sense of the assembly inverted during the photoisomerization of **25**. The helical assembly of the (*E,E*)-isomer of (*S*)-**25** exhibited CPL on its emission at 503 nm with a g_{lum} of 8×10^{-3} . The photoisomerization of (*S*)-**25** inverted the CPL as in the case of the CD. The helical assembly of the (*Z,Z*)-isomer displayed a negative CPL signal with a g_{lum} of -2×10^{-3} . (*R*)-**25** gives a mirror-image CD and CPL of (*S*)-**25**.

Recently, Takeda, Akutagawa, and coworkers reported a CPL-active assembly of a pyrene derivative **26** (Fig. 9.11) [38]. They synthesized a pyrene possessing four amide moieties, and a chiral side-chain was introduced onto the amides. The simple molecule formed a helical assembly in chloroform, THF, and MCH through the one-dimensional hydrogen-bonding interactions of the amide moieties, which was confirmed by UV-vis and CD spectroscopy techniques. The helical assembly exhibited CPL on its excimer emission band at 500 nm in chloroform, THF, and MCH (1.0×10^{-4} mol L $^{-1}$). The g_{lum} value of the assembly in MCH (3.0×10^{-2}) was one order of magnitude higher than those in chloroform and THF (ca. 2×10^{-3}). Furthermore, the CPL signal of the helical assembly in chloroform was inverted

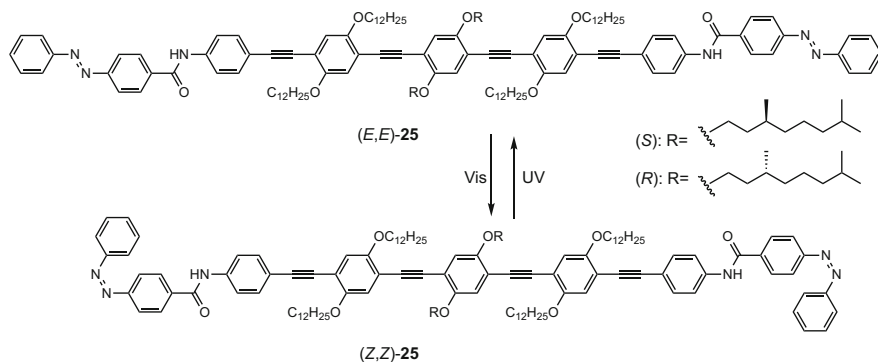
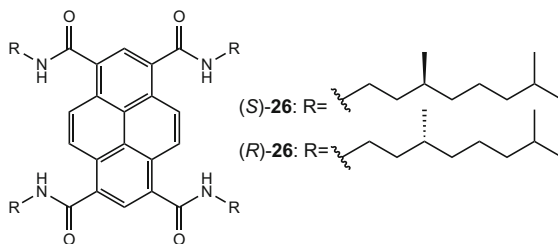


Fig. 9.10 CPL-active helical assembly of a photoresponsive oligo-*p*-phenylene-ethynylene derivative

Fig. 9.11 CPL-active helical assembly of pyrene derivatives



compared to those in THF and MCH. The assemblies in chloroform, THF, and MCH exhibited good fluorescence quantum yields (42%, 31%, and 29%, respectively).

A helical assembly can be formed via intermolecular interactions other than hydrogen-bonding interactions. Dipole–dipole interactions are fruitful to form a helical assembly since C_3 symmetrically arranged dipole moments tend to form a helical stacked assembly [39]. Haino and coworkers have reported the helical assembly behavior of C_3 symmetric 1,3,5-tris(4-alkoxyphenylisoxazolyl)benzene **27**, which possesses three isoxazoles that provide the local dipole moment (Fig. 9.12) [40, 41]. The directional circular arrangement of the isoxazole rings is directed by the head-to-tail dipole–dipole interaction of the local dipole of isoxazoles. Molecular modeling studies for the hexameric assemblies of 1,3,5-tris(phenylisoxazolyl)benzene revealed that the hexameric assembly has two major geometries, helical and eclipsed. In the former geometry, the local dipoles of isoxazole align in a head-to-tail fashion, whereas they take an antiparallel conformation in the latter geometry. The optical and chiroptical properties of **27** in MCH were considered by using UV-vis and CD spectroscopy techniques. Monomeric **27** in the diluted MCH solution exhibited a monomeric absorption band at 278 nm, whereas the assembly of **27** in the concentrated MCH solution displayed the absorption maximum at 310 nm. The redshift of the absorption suggests the formation of the *J*-type aggregate. The monomeric **27** displayed no CD signals, indicating that the chiral side-chain of **27** does not perturb the $\pi \rightarrow \pi^*$ transition. On the other hand, the assembly of (*S*)- and (*R*)-**27** formed in the concentrated MCH solution exhibited CD spectra that have a mirror-image relationship. This suggests that not an antiparallel but helical assembly is formed, and the helicity was determined by the chirality of the side-chain. By using exciton coupling theory, the helical sense of the assembly of (*S*)-**27** was determined to be right-handedness. From these results, the dipole–dipole interaction of the isoxazole rings drives the helical assembly of small molecules. Unfortunately, the CPL properties of **27** were not reported, but the authors have reported the CPL properties of some luminophores possessing phenylisoxazoles.

Haino and coworkers have reported the helical assembly of PBI possessing phenylisoxazoles **28** and their optical and chiroptical properties (Fig. 9.13) [42]. The formation of the supramolecular assembly of PBI perturbs its $\pi \rightarrow \pi^*$ absorption and $\pi^* \rightarrow \pi$ emission. The introduction of tris(phenylisoxazolyl)benzene onto a nitrogen atom of PBI resulted in the formation of a helical assembly, in which the $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi$ transitions are chirally perturbed to give chiroptical

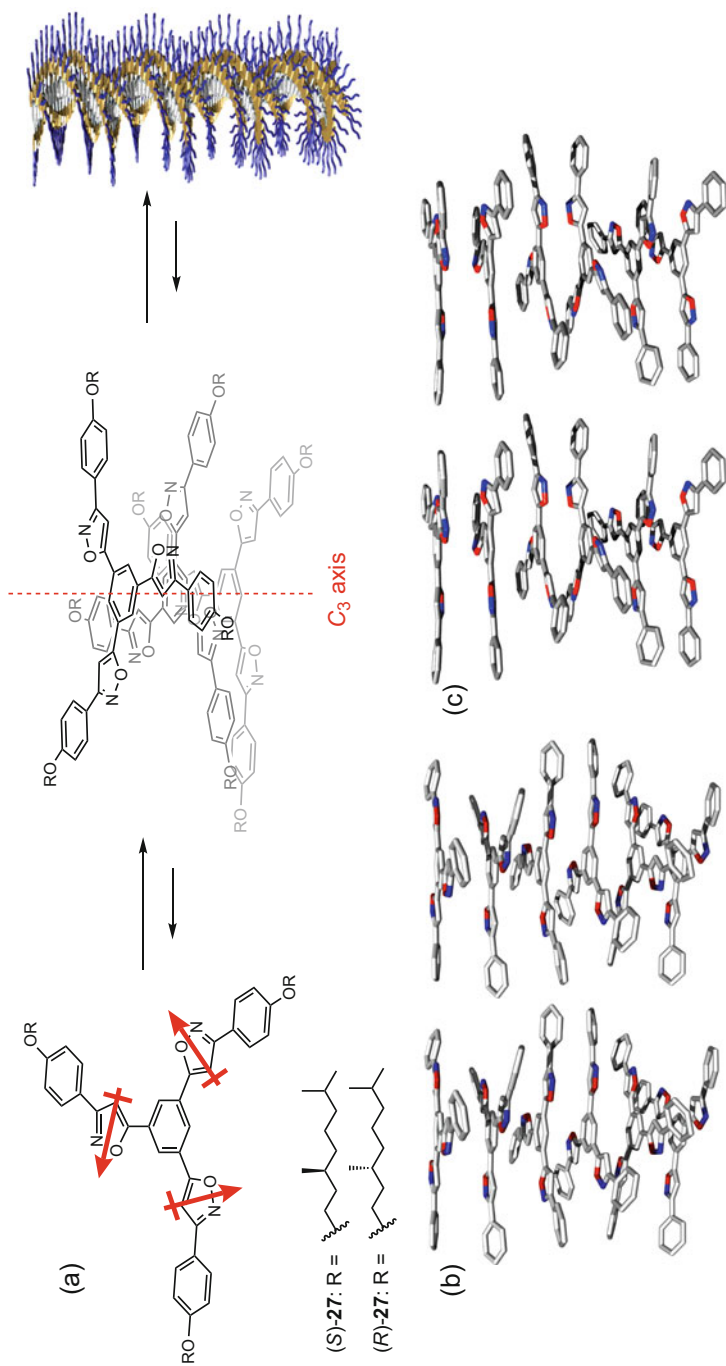


Fig. 9.12 (a) Helical assembly of tris(phenylisoxazolyl)benzene derivatives **27**. (b, c) Stereoplots of two local minimum geometries for the hexamers obtained from a conformation search by the MacroModel program: (a) helical arrangement of the local dipoles and (b) antiparallel arrangement of them. Adapted with permission from Sato et al. [35]. Copyright 2011 American Chemical Society

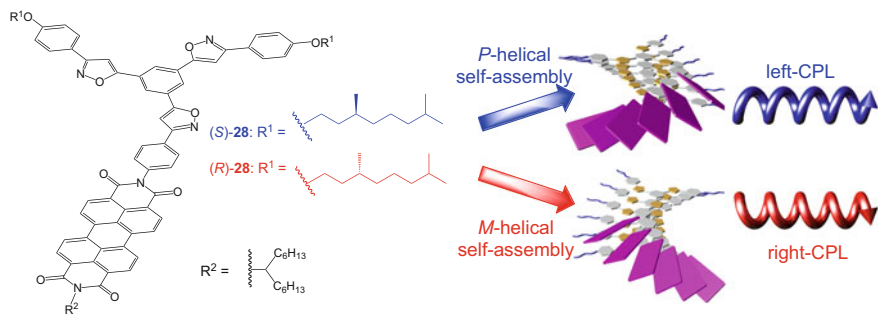


Fig. 9.13 CPL-active helical assembly of PBI derivatives possessing tris(phenylisoxazoly)benzene **28**. Adapted with permission from Satrijo et al. [5]. Copyright 2012 The Royal Society of Chemistry

properties. The self-assembly behavior of **28** was considered by using 1H NMR, UV-vis, and CD spectroscopy techniques. **28** formed a *J*-type assembly that was confirmed by the redshift of the absorption band of the assembly. The assembly of **28** in decalin solution displayed strong CD with a g_{abs} of 1.4×10^{-3} . The right-handedness of the helix was assigned by the plus-to-minus patterns observed in the ascending energy in the CD spectrum of **27**. In the emission spectrum of the assembly of **28** in decalin, a broad and redshifted band of the assembly was observed in addition to the sharp emission band of the monomeric species. CPL was observed on the emission of the assembly with a g_{lum} of 7×10^{-3} , but no CPL was observed on the emission of **28** in chloroform, in which most **28** does not form an assembly. (S) - and (R) -**28** displayed mirror-image CPL spectra. These results clearly suggest that the formation of a helical assembly leads to the CPL activity of **28**.

A square planar Pt(II) complex tends to form a stacked assembly creating a one-dimensional metal array through metallophilic (Pt–Pt) interactions [43]. The Pt(II) phenylbipyridine complex is known as a luminophore exhibiting phosphorescence that comes from a triplet metal-to-ligand charge transfer (3MLCT) transition. The phosphorescence property of the Pt(II) phenylbipyridine complex is perturbed by the formation of a stacked assembly via Pt–Pt interactions to exhibit a triplet metal-metal-to-ligand charge transfer (3MMLCT) transition [44]. The Pt(II) phenylbipyridine complex does not form a helical assembly without any assistance of other intermolecular interactions, but the complex formed a helical assembly when the phenylisoxazole moiety was introduced onto the ligand. Haino and coworkers have reported the optical and chiroptical properties of a Pt(II) phenylbipyridine complex possessing a 3,5-bis(phenylisoxazoly)phenylethynyl ligand ((S) - and (R) -**29**, Fig. 9.14) [45]. **29** effectively formed a stacked assembly via Pt–Pt, dipole–dipole, and π – π stacking interactions. Interestingly, the self-assembly behavior of **29** drastically changed depending on the solvent effect. In chloroform, **29** formed a stacked assembly exhibiting 3MMLCT absorption and emission bands, but the assembly displayed no CD and CPL. It turns out that the assembly of **29** formed in chloroform is not helical, most likely due to the strong solvation that prevents the

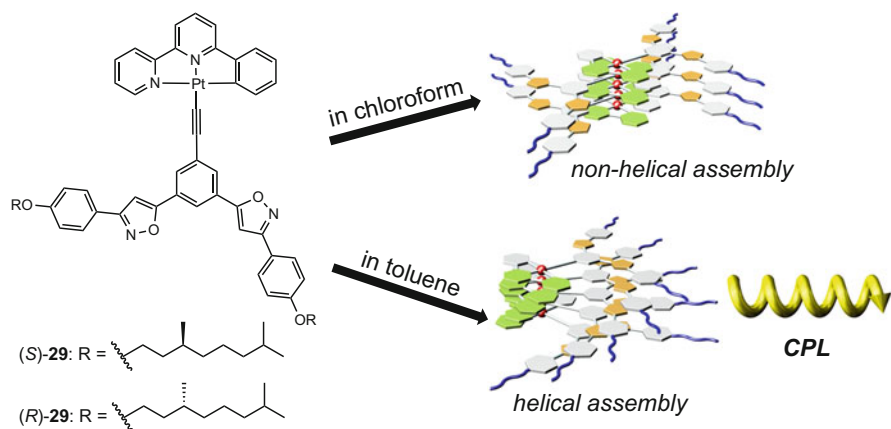


Fig. 9.14 CPL-active helical assembly of **29**, a Pt(II)phenylbipyridine complex possessing phenylisoxazoles. Adapted with permission from Schippers et al. [10]. Copyright 2015 The Royal Society of Chemistry

dipole–dipole interaction between the isoxazole rings. On the other hand, the assembly of **29** formed in toluene displayed completely different characteristics compared to that in chloroform. The assembly formed in toluene was CD active, and mirror-image CD signals were observed upon the assembly of (S)- and (R)-**29**. Thus, helical assemblies are formed, and the helical senses were directed by the chiral side-chains. The assembly in toluene exhibited aggregation-induced emission enhancement (AIEE); the emission is strongly enhanced in the assembled form compared to that of the monomeric species. The molecular motion, presumably the rotation of the triple bond, is prevented through the formation of the assembly to reduce the nonradiative decay of the excited state, which results in the increase in the emission. The monomeric **29** did not display any CD and CPL even in toluene, but the assembly formed in toluene exhibited CPL with a g_{lum} of 1.0×10^{-2} .

Spano, Meskers, and coworkers have developed the self-assembly and chiroptical properties of oligo-*p*-phenylene-vinylene derivative **30** (Fig. 9.15) [46]. **30** dimerized through the complementary quadruple hydrogen bond of the triazine group, and then, the dimer assembled to form a helical stacked assembly via π - π stacking. The helical assembly exhibited CPL on its fluorescence with a g_{lum} on the order of 10^{-3} . Wong, Tang, and coworkers have developed the CPL of tetraphenylsilole derivatives. Tetraphenylsiloles are known as good aggregation-induced emission (AIE) active luminophores; the luminophore is not emissive in its monomeric form, but the aggregate of the luminophore is highly emissive. For example, **31**, a tetraphenylsilole derivative possessing chiral sugar pendants, formed a helical assembly displaying CPL in its suspension and solid state (Fig. 9.15) [47]. The g_{lum} values of **31** depend on the state of the assembly. In a heterogeneous suspension, a neat static cast film, and 10 wt.% Poly(methyl methacrylate) (PMMA) matrix, the g_{lum} values were ca. -0.12 , -0.08 , and -0.17 , respectively. Interestingly, the fabricated pattern obtained by the evaporation of a dichloromethane/toluene solution of **31** in Teflon-based microfluidic channels

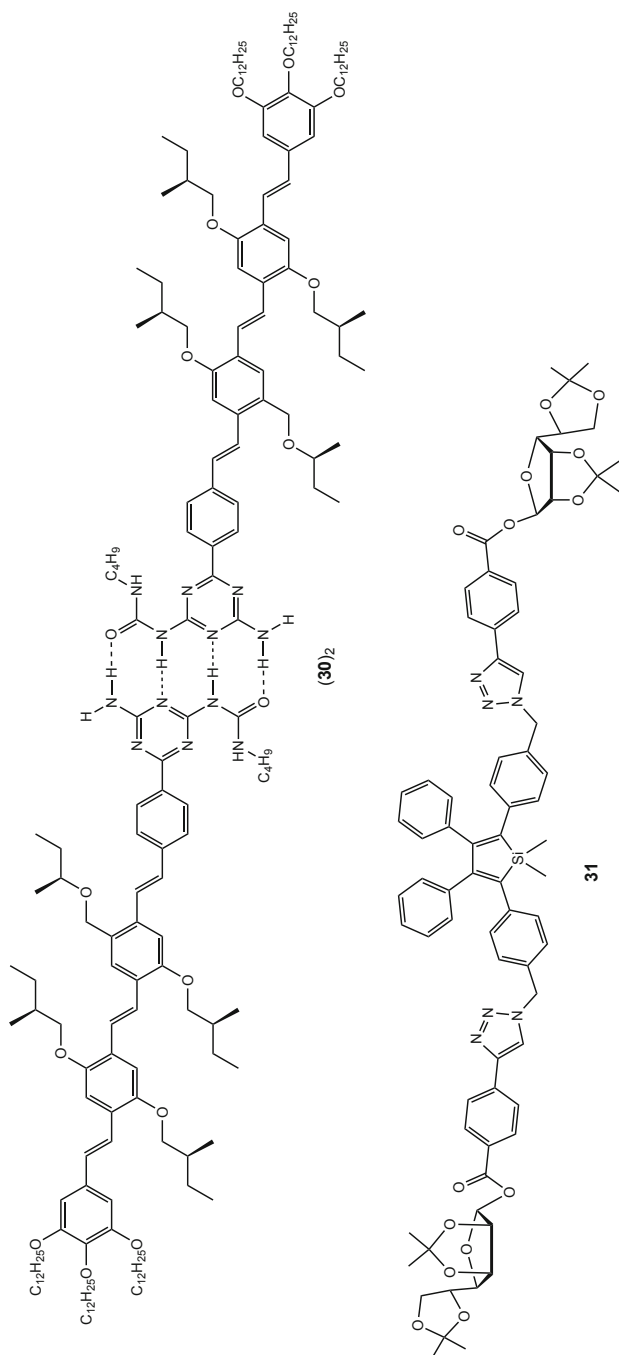


Fig. 9.15 CPL-active helical assemblies of an achiral luminophore

exhibited CPL with a g_{lum} value of -0.32 , which is quite higher than those of other solid samples.

As described herein, supramolecular assemblies that have chirality, especially the helical assemblies, exhibited excellent CPL properties. Highly assembled structures of the luminophore bring about high g_{lum} values [2].

9.5 Stimuli-Responsive CPL Using a Supramolecular Assembly

A notable feature of CPL-active organic compounds is the stimuli-responsiveness of CPL. Organic compounds that exhibit stimuli-responsivity have been widely developed since organic compounds have flexible conformations. For example, **32** and **33**, photoresponsive CPL-active polymers possessing the photochromic dithienylethene moiety, have been developed by Akagi and coworkers (Fig. 9.16) [48]. A supramolecular assembly is constructed by reversible intermolecular interactions, and thus, one can control the assembly and disassembly of the supramolecular system by external stimuli. Therefore,

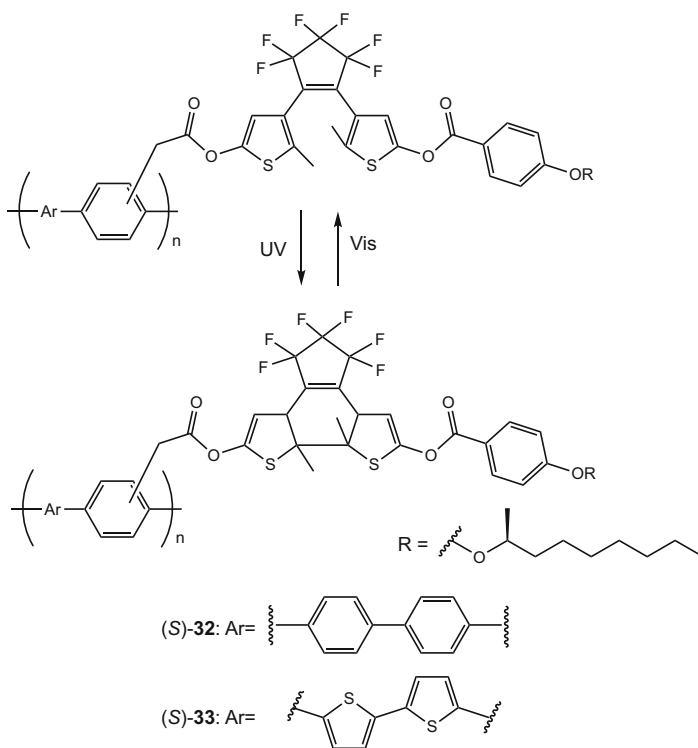


Fig. 9.16 Photoresponsive CPL-active polymer

stimuli-responsive supramolecular assemblies have been widely investigated so far [49]. Many of the CPL-active supramolecular assemblies mentioned above exhibited concentration- and temperature-dependent CPL; the monomeric form of the luminophore that exists in the low concentration or high temperature shows no CPL, whereas the helical assembly formed in the high concentration or low temperature exhibits CPL [38, 42, 45–47]. The CPL signal of compound **25** is photoresponsive, reflecting the photoisomerization of the azobenzene unit [37]. Here, other stimuli-responsive CPL of organic luminophores is described.

Haino and coworkers reported the gelation-induced CPL of Pt(II) phenylbipyridine complex **34** (Fig. 9.17) [50]. The complex has a similar structure to complex **29** mentioned above, but **34** possesses multiple long alkyl side-chains. **34** formed a stacked assembly as **29** did, but the assembly formed in MCH did not display any CD and CPL. The long alkyl side-chains provide the interassembly interaction to afford a three-dimensional network of the one-dimensional stacked assembly. The three-dimensional network holds the solvent molecules in its vacancies to form organogel. **34** formed luminescent organogel in 1-decanol at the concentration of $9.2 \times 10^{-3} \text{ mol L}^{-1}$ with decreasing temperature from 50 to 10 °C. At 50 °C, no CPL signal was observed, but the CPL signals appeared at 500 nm with the gelation. The g_{lum} value at 10 °C was 1.1×10^{-2} . It is noteworthy that the gelation of **34** also triggered the AIEE; the emission intensity increased ca. 50-fold from 50 to 10 °C.

Maeda and coworkers have developed pyrrole-based anion receptors, BF_2 complexes of 1,3-dipyrrolyl-1,3-propanedione [51]. The two pyrrole NH are located at the side of the carbonyl oxygen without any anion, whereas the molecule forms an anion complex through the $\text{N-H}\cdots\text{X}^-$ interaction of the flipped pyrroles and the $\text{C-H}\cdots\text{X}^-$ interaction. The structural change of the luminophore before and after anion-binding can be applied for the anion-responsive CPL system (Fig. 9.18). Anion-responsive CPL was observed for chiral anion-receptor **35** upon complexation with anions such as Cl^- and tetrabutylammonium (TBA) salts [52]. **35** possesses a chiral 1,1'-bi-2-naphthol (BINOL) moiety as the ligand of boron. **35** displayed CPL with a

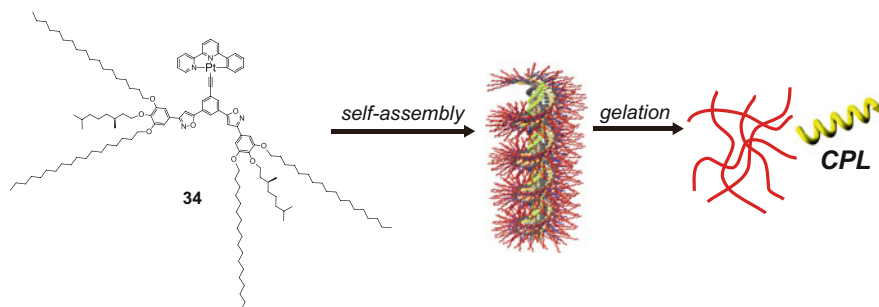


Fig. 9.17 Gelation-induced CPL of **34**, a Pt(II)phenylbipyridine complex possessing phenylisoxazoles. Adapted with permission from Wilson et al. [6]. Copyright 2018 The Royal Society of Chemistry

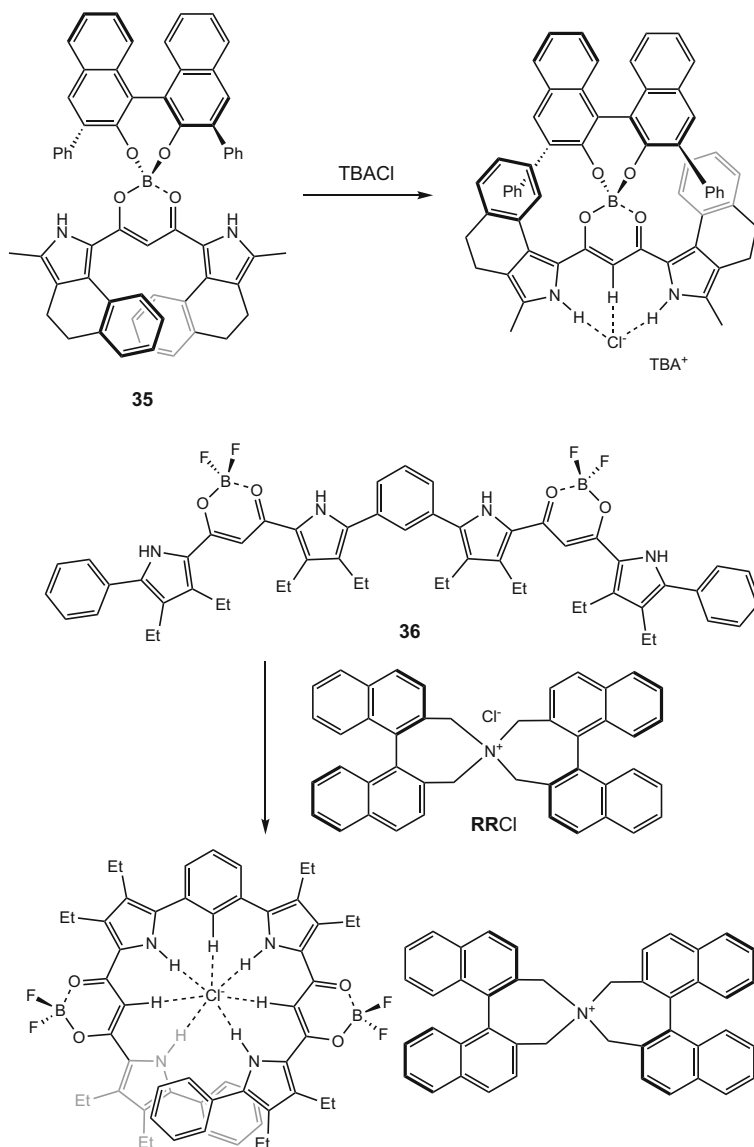


Fig. 9.18 Anion-responsive CPL of pyrrrole-based anion receptors

g_{lum} of 1.0×10^{-2} in the presence of Cl⁻, whereas almost no CPL was observed without Cl⁻. *meta*-Phenylene-bridged dimeric anion-receptor **35** also displayed anion-responsive CPL [53]. **36** formed a helical complex with Cl⁻. Unlike the chiral anion-receptor **35**, **36** is an achiral molecule, and thus, the helical complex of **36**-Cl⁻ is a racemic mixture that exhibits no CPL without any chiral source. However, once Cl⁻ was added as a salt of chiral binaphthylammonium (RR⁺), the helicity of the complex

was induced since the helical anion complex formed an ion pair with the chiral cation in the dichloromethane solution. The ion pair of $36 \cdot \text{Cl}^- \cdot \text{RR}^+$ exhibited CPL with a g_{lum} of 1.8×10^{-2} in dichloromethane/octane solution (1:1, $1 \times 10^{-3} \text{ mol L}^{-1}$) at -70°C .

9.6 Summary

An achiral π -conjugated luminophore can exhibit CPL by the chiral arrangement of the achiral luminophore. The helical supramolecular assembly of an achiral luminophore is excellent for realizing CPL of the achiral luminophore since the highly assembled structure in the helical assembly provides good CPL activity. Furthermore, the supramolecular assembly has an advantage in its stimuli-responsiveness. The development of CPL-active supramolecular assemblies and their applications are in progress all over the world.

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