Chapter 3
Circularly Polarized Luminescence from Planar Chiral Compounds Based on [2.2]Paracyclophane

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Abstract In this chapter, recent development on molecules emitting intense circularly polarized luminescence (CPL) based on planar chiral [2.2]paracyclophane is described. Optical resolution routes of the planar chiral [2.2]paracyclophane compounds, optically active π-stacked molecules, and the CPL profiles are discussed. It is suggested that the optically active higher-ordered structures, such as V-, X-, triangle-, propeller-shaped structures, and so on, in the excited state are important for intense CPL with large dissymmetry factors (g_{lum} values).

3.1 Introduction

Cyclophanes are cyclic compounds containing at least one aromatic ring (arylene) in the cyclic skeleton. They have been well studied, particularly in the field of organic chemistry [1, 2]. A typical example of a cyclophane is [2.2]paracyclophane, which was synthesized for the first time in 1949 by the pyrolysis of *para*-xylene [3]. Later, in 1951, it was synthesized directly by the Wurtz-type intramolecular cyclization of 1,4-bis-bromomethylbenzene [4]. [2.2]Paracyclophane has a unique structure consisting of two π-stacked benzene rings that are fixed in the para-position with two ethylene chains. There are many studies on its synthetic routes, reactivities, and physical properties, in the field of organic chemistry [1]. However, there are not many examples where [2.2]paracyclophane is effectively utilized in the fields of polymer chemistry and materials chemistry [5–16].

The two face-to-face benzene rings in close proximity (~3.0 Å apart) in [2.2]paracyclophane completely suppress their rotational movement. The resulting [2.2]paracyclophane becomes a planar chiral compound (Fig. 3.1) upon the introduction of substituent(s) at appropriate position(s) of the benzene ring(s) [17–22]. Planar chirality attained by [2.2]paracyclophane makes it structurally stable, because of which this compound has been utilized as a chiral auxiliary or chiral ligand in the

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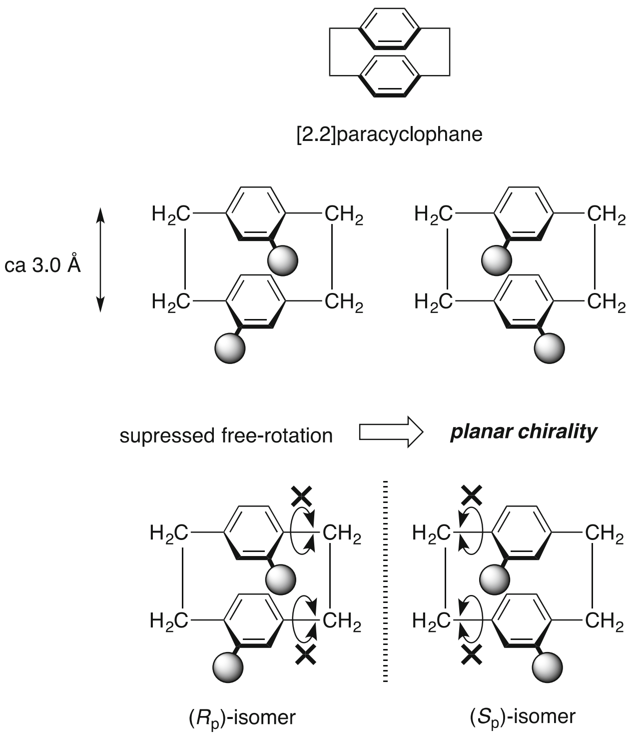


Fig. 3.1 Structure of [2.2]paracyclophane and its planar chirality

fields of synthetic organic chemistry and organometallic chemistry. Despite this, it has not been used in the fields of polymer chemistry and materials chemistry, as well.

In this chapter, the author has focused on the planar chirality of [2.2]paracyclophane. Optical resolution of disubstituted and tetrasubstituted [2.2]paracyclophane and their use as chiral building blocks for the syntheses of optically active π-stacked compounds are described. Application of molecules containing planar chiral [2.2]paracyclophane in materials emitting circularly polarized luminescence (CPL) is also shown.

3.2 Optical Resolution of [2.2]Paracyclophane Compounds

Optical resolutions of mono-substituted [2.2]paracyclophanes are well established, and various enantiopure *ortho*-, pseudo-*geminal*-, and *syn*-*latero*-disubstituted [2.2]paracyclophanes have been synthesized [17–22].

Several methods for the optical resolution of pseudo-*ortho*-disubstituted [2.2]paracyclophanes have been reported [23–32]. Optical resolution of *rac*-pseudo-*ortho*-bis(diarylphosphino)[2.2]paracyclophane (*rac*-[2.2]PHANEPHOS) by

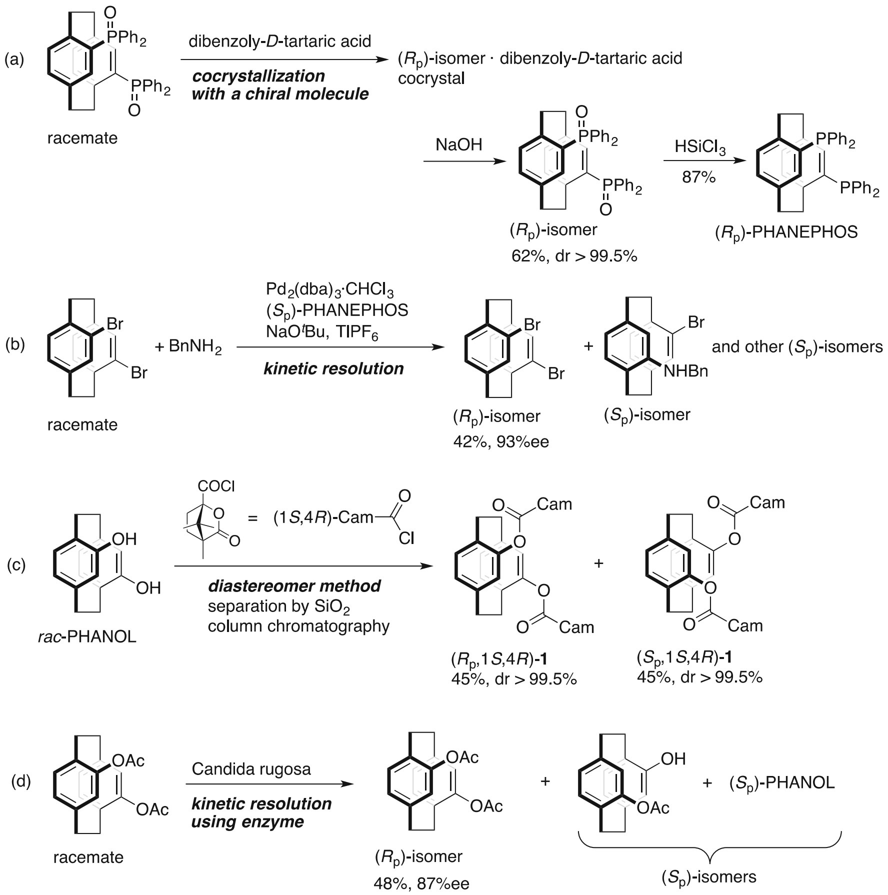


Fig. 3.2 Representative optical resolutions of pseudo-*ortho*-disubstituted [2.2]paracyclophanes

co-crystallization with a tartaric acid derivative is a successful examples (Fig. 3.2a) [23], and planar chiral (S_p)- and (R_p)-[2.2]PHANEPHOS are the commercially available chiral ligands for the transition metal-catalyzed asymmetric reactions. $Pd_2(dba)_3$/[2.2]PHANEPHOS-catalyzed amination of *rac*-pseudo-*ortho*-dibromo [2.2]paracyclophane enabled the kinetic resolution [24] for obtaining the enantioenriched pseudo-*ortho*-dibromo[2.2]paracyclophane (Fig. 3.2b). Optical resolutions of *rac*-4-bromo-12-hydroxy[2.2]paracyclophane [25], *rac*-pseudo-*ortho*-dihydroxy[2.2]paracyclophane (*rac*-PHANOL) [26], and *rac*-pseudo-*ortho*-dihydroxymethyl[2.2]paracyclophane [27] were achieved by a diastereomer method using chiral camphanic acid chloride as the chiral auxiliary; the optical resolution of PHANOL is shown in Fig. 3.2c as a representative example. The enzyme-catalyzed kinetic resolutions of *rac*-pseudo-*ortho*-disubstituted [2.2]paracyclophanes were also reported [28–30], and the representative example is shown in Fig. 3.2d. Optical resolution of *rac*-pseudo-*ortho*-dibromo[2.2]paracyclophane was carried out in

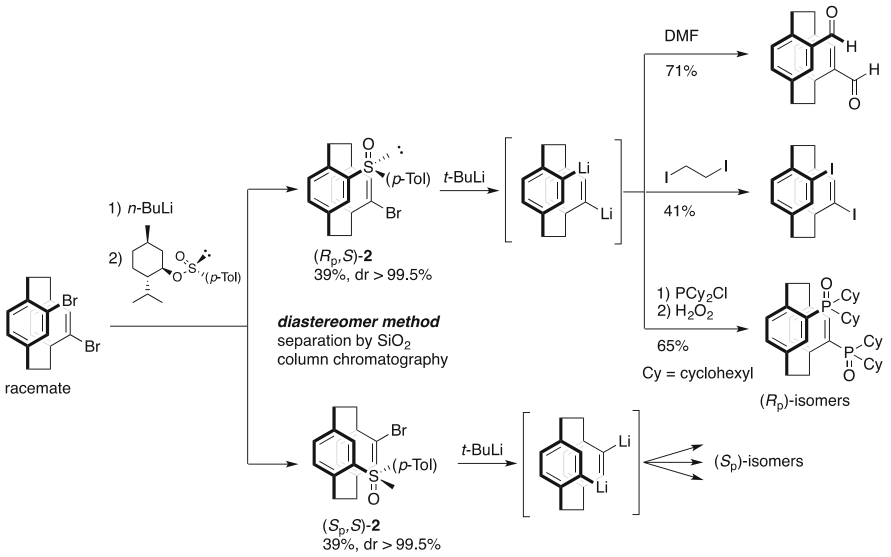


Fig. 3.3 Optical resolution of pseudo-*ortho*-disubstituted [2.2]paracyclophane using (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate as a chiral auxiliary

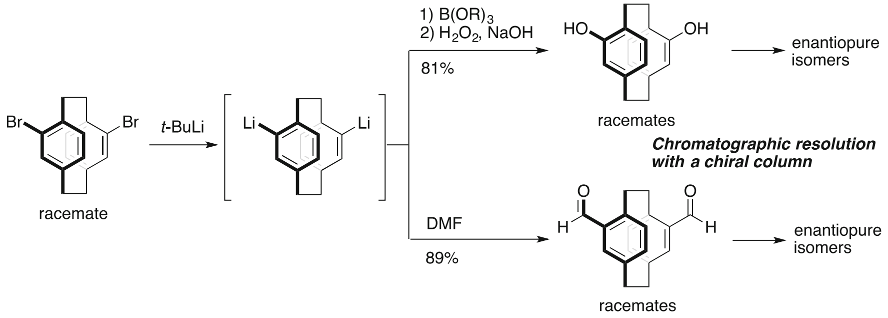


Fig. 3.4 Optical resolution of *rac*-pseudo-*meta*-disubstituted [2.2]paracyclophane

2012 using (1*R*,2*S*,5*R*)-(–)-menthyl (*S*)-*p*-toluenesulfinate as a chiral auxiliary [31], as shown in Fig. 3.3, and the obtained diastereomers could be used as the parent compounds to produce a wide variety of [2.2]paracyclophane-based chiral molecules. Optical resolution of *rac*-pseudo-*ortho*-disubstituted [2.2]paracyclophanes by chiral columns was reported [32]. The chromatographic optical resolution of *rac*-pseudo-*meta*-disubstituted [2.2]paracyclophanes was also reported by Lutzen, and several enantiopure pseudo-*meta*-disubstituted [2.2]paracyclophanes were produced [33]. Figure 3.4 shows the representative examples of the successful optical resolutions obtained using a chiral column.

In 2008, Hopf and coworkers reported the optical resolutions of bis-(*ortho*)-pseudo-*meta*-4,5,15,16-tetrasubstituted [2.2]paracyclophane and 4,5,15-

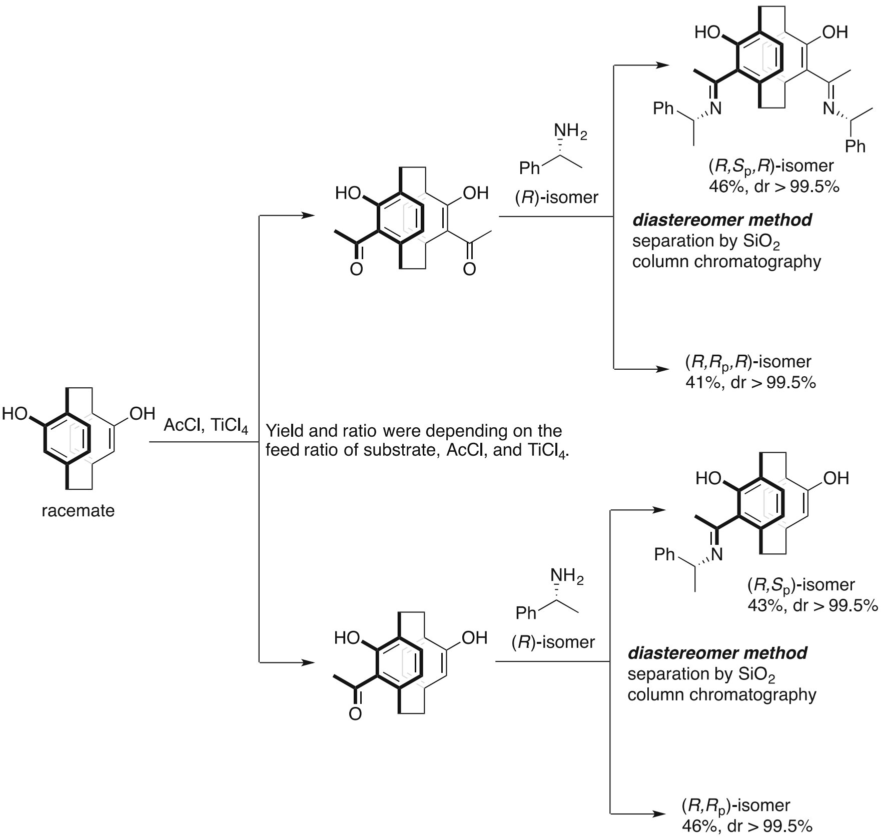


Fig. 3.5 Optical resolutions of bis-(*ortho*)-pseudo-*meta*-4,5,15,16-tetrasubstituted [2.2] paracyclophane and 4,5,15-trisubstituted [2.2]paracyclophane

trisubstituted [2.2]paracyclophane (Fig. 3.5) by diastereomer methods [34]. The optical resolution of 4,7,12,15-tetrasubstituted [2.2]paracyclophane was achieved in 2014 [35], as shown in Fig. 3.6. The racemate 4,7,12-tribromo-15-hydroxy[2.2] paracyclophane was synthesized from the corresponding tetrabromide, and the reaction with (1*S*,4*R*)-(-)-camphanic chloride afforded the diastereomers (R_p,1*S*,4*R*)- and (S_p,1*S*,4*R*)-isomers. The diastereomers could be separated in gram scale using the simple silica gel column chromatography, and the diastereomer ratios were over 99.5%. The hydroxy group was converted to the trifluoromethanesulfonyl group, which is an active site for the Pd-catalyzed cross-coupling, in addition to the bromo groups.

Optical resolution of *rac*-PHANOL [26] was applied to produce enantiopure bis-(*para*)-pseudo-*ortho*-4,7,12,15-tetrasubstituted [2.2]paracyclophanes [36], as shown in Fig. 3.7. The obtained diastereomers were reacted with bromine, in the presence of iron, to afford bis-(*para*)-pseudo-*ortho*-4,7,12,15-tetrasubstituted [2.2] paracyclophanes (R_p,1*S*,4*R*)- and (S_p,1*S*,4*R*)-isomers, wherein bromine was

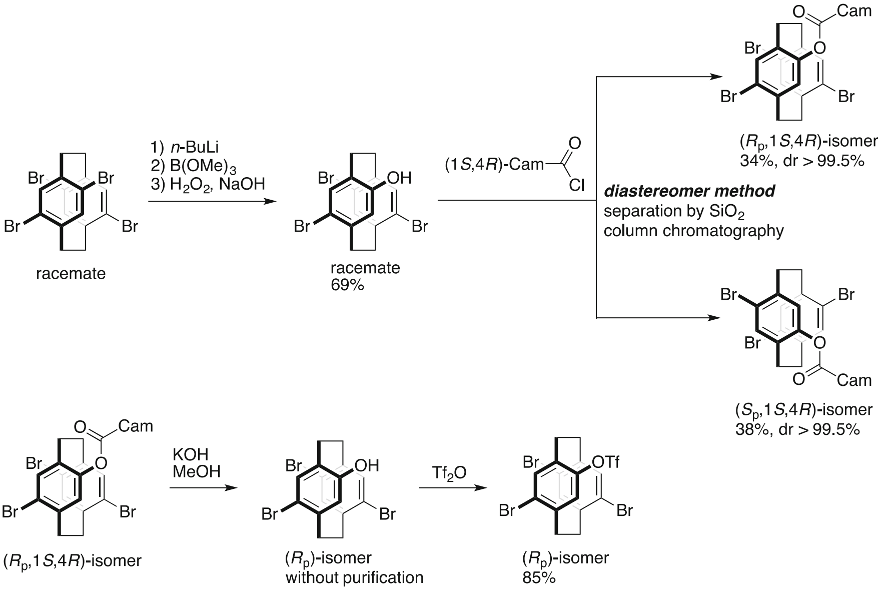


Fig. 3.6 Optical resolution of 4,7,12,15-tetrasubstituted [2.2]paracyclophane and the transformation

selectively substituted to the *para*-position with respect to their oxygen substituent. The chiral auxiliary groups were removed using KOH to obtain the enantiopure dibrominated PHANOL. The reaction with trifluoromethanesulfonic anhydride as well as MeI affords bis-(*para*)-pseudo-*ortho*-type tetrasubstituted [2.2]paracyclophanes. Optical resolution could also be carried out after the bromination of the mixture of diastereomers, as shown in Fig. 3.8. This modified route involved a single bromination step to produce both the diastereomers [37].

Enantiopure bis-(*para*)-pseudo-*meta*-tetrasubstituted [2.2]paracyclophane derivatives were successfully synthesized (Fig. 3.9) [38]. The starting material, racemic 4,7,12-tribromo-15-hydroxy[2.2]paracyclophane, was reacted with *n*-BuLi. First, the phenol in *rac*-**2** was reacted with *n*-BuLi to form lithium phenoxide. Then, *n*-BuLi attacked selectively at the corresponding pseudo-*meta*-position because of the electronic effect. The optical resolution was achieved by the diastereomer method using camphanoyl chloride as the chiral auxiliary. The camphanoyl groups could be removed by saponification, and the obtained 4,15-dibromo-7,12-dihydroxy[2.2]paracyclophane was converted to (R_p)- and (S_p)-4,15-dibromo-7,12-trifluoromethanesulfonyloxy[2.2]paracyclophanes, for using them as chiral building blocks.

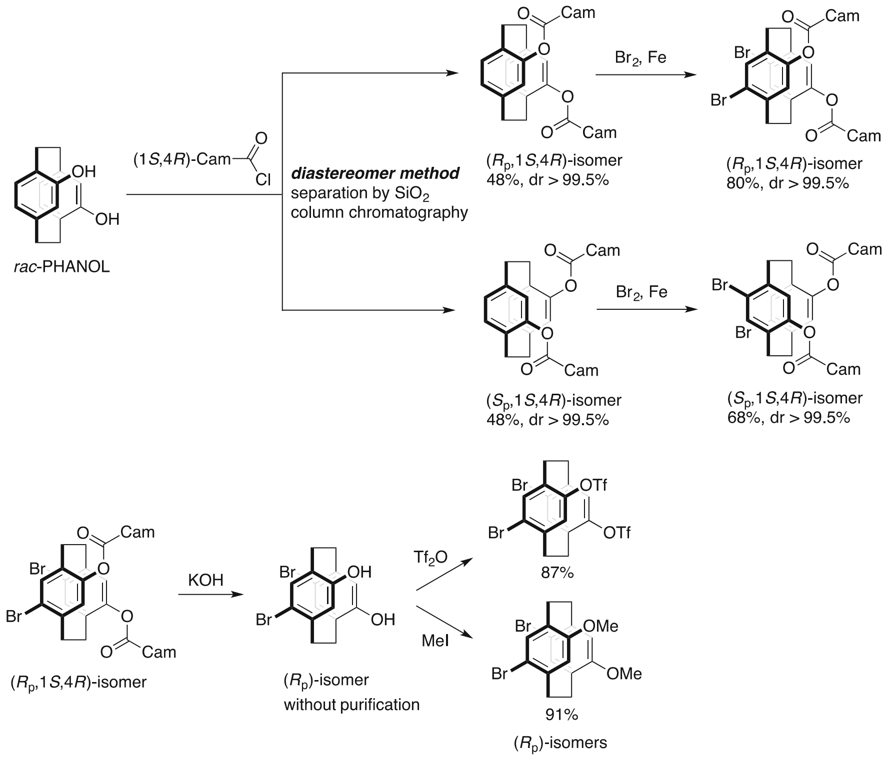


Fig. 3.7 Synthesis of enantiopure bis-(*para*)-pseudo-*ortho*-4,7,12,15-tetrasubstituted [2.2] paracyclophanes

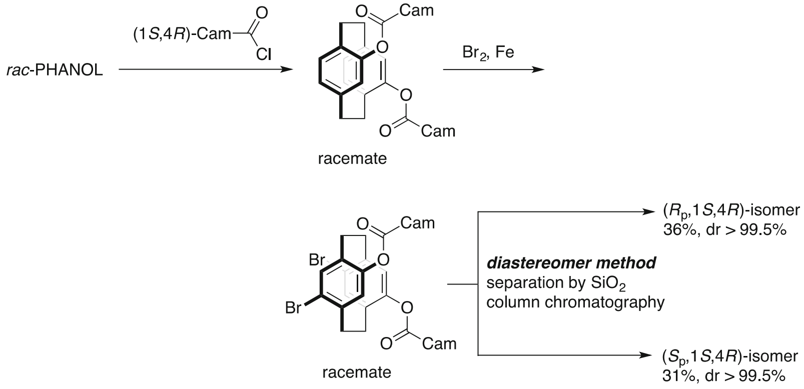


Fig. 3.8 Modified optical resolution of *rac*-PHANOL

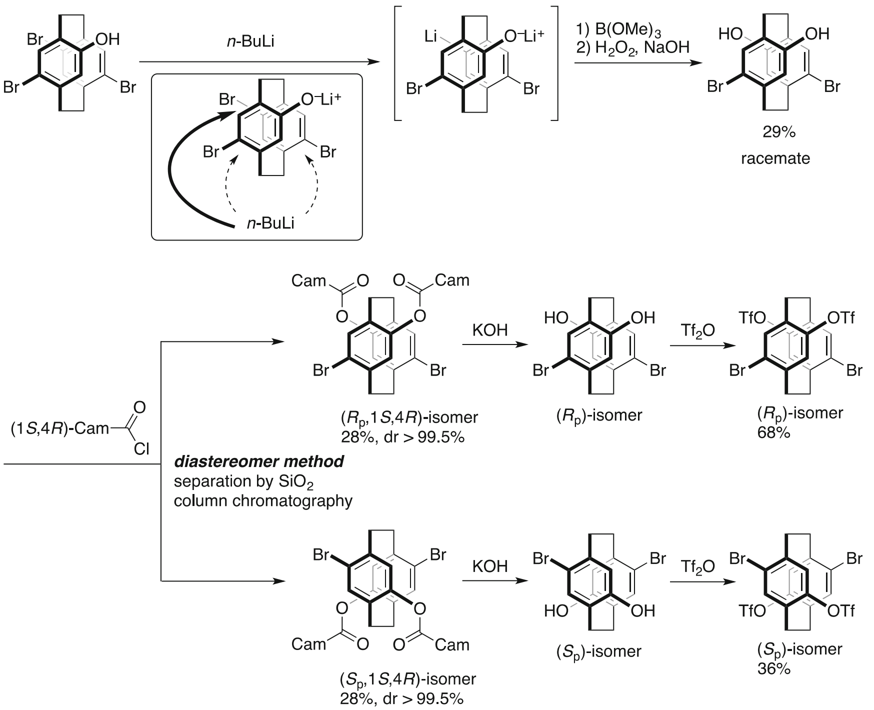


Fig. 3.9 Synthesis of enantiopure bis-(*para*)-pseudo-*meta*-4,7,12,15-tetrasubstituted [2.2] paracyclophanes

3.3 Optically Active Molecules Based on Planar Chiral [2.2] Paracyclophane and Their CPL Profiles

Various optically active molecules emitting CPL, synthesized from the chiral building blocks based on planar chiral [2.2]paracyclophane described above, will be introduced in this section.

Figure 3.10 shows the optically active V-, N-, and W-shaped π-stacked molecules ((R_p)-**1**-**3**), in which two, three, and four phenylene-ethynylene π-electron systems, respectively, are stacked at the terminal benzene ring(s) [39]. Figure 3.10 contains an optically active triangle-shaped π-stacked molecule (R_p)-**4** consisting of three phenylene-ethynylene π-electron systems [39]. They were prepared from enantiopure pseudo-*ortho*-disubstituted [2.2]paracyclophane. Their photoluminescence (PL) and CPL spectra in dilute $CHCl_3$ and the optical data are shown in Fig. 3.11a.

The PL spectra of (R_p)-**1**-**3** were gradually red-shifted, depending on the number of stacked π-electron systems. Vibronic structures were observed in the PL spectra, with good PL quantum efficiencies (Φ_{PL}) of approximately 0.8. The decay curves could be fitted with a single exponential function, indicating that the emission from

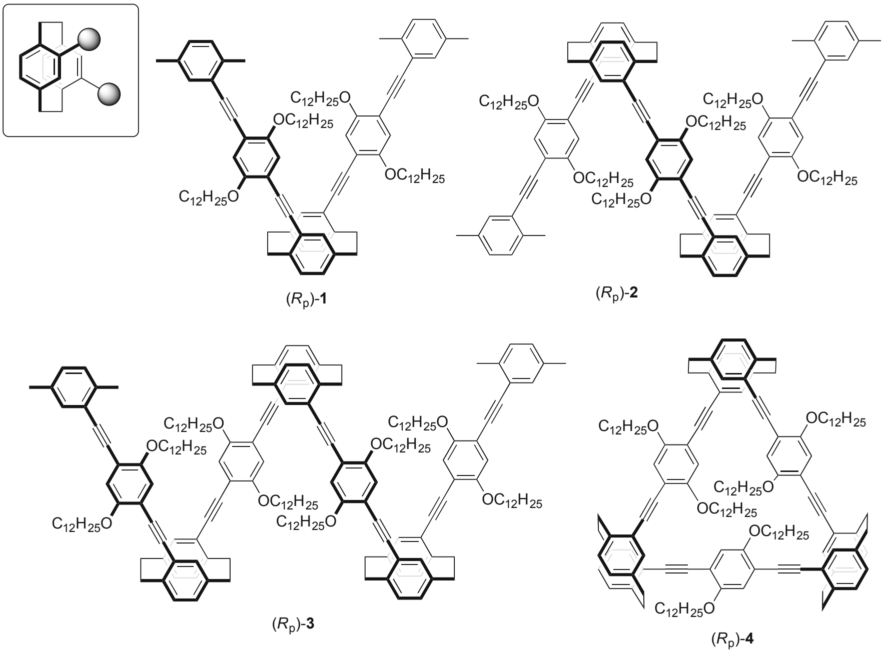


Fig. 3.10 Optically active V-, N-, and W-shaped π-stacked molecules

(R_p)-**1**-**3** occurred from the chromophore state rather than from the phane state [40–44]. CPL spectra for (R_p)-**1**-**3** and (S_p)-**1**-**3** in dilute $CHCl_3$ (1.0×10^{-5}M) were obtained. Intense CPL signals of $I_L - I_R$, where I_L and I_R are the intensities of left- and right-handed PL, respectively, were obtained. The CPL signals of the two compounds were the mirror images of each other. Interestingly, the CPL dissymmetry factors $g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$ increased gradually with increasing number of the stacked π-electron systems. This result suggests the emergence of additional chirality, besides the planar chirality of the [2.2]paracyclophane skeleton.

Figure 3.11b shows the PL and CPL spectra of the linear trimer **2** (N-shaped molecule) and cyclic trimer **4** (chiral triangle-shaped molecule). Molecules **2** and **4** exhibited identical PL and CPL profiles. The cyclic trimer has chiral triangle-shaped chirality, i.e., a chiral second-ordered structure, in addition to the planar chirality of the [2.2]paracyclophane skeleton. Considering the identical CPL profiles between the linear and cyclic trimers, linear trimer **2** should form the chiral second-ordered structure as the additional chirality in addition to the planar chirality. It is suggested that a one-handed helical structure (left-handed helix for (R_p)-isomer) is formed in the excited stated of linear trimer **2**, as shown in Fig. 3.12.

4,7,12,15-Tetraethynyl[2.2]paracyclophane was prepared from 4,7,12-Tribromo-15-trifluoremethanesulfonyl[2.2]paracyclophane (Fig. 3.13), followed by the synthesis of the optically active cyclic molecule **5** [35]. The optically active molecule **5** formed the chiral second-ordered structure such as one-handed propeller-shaped

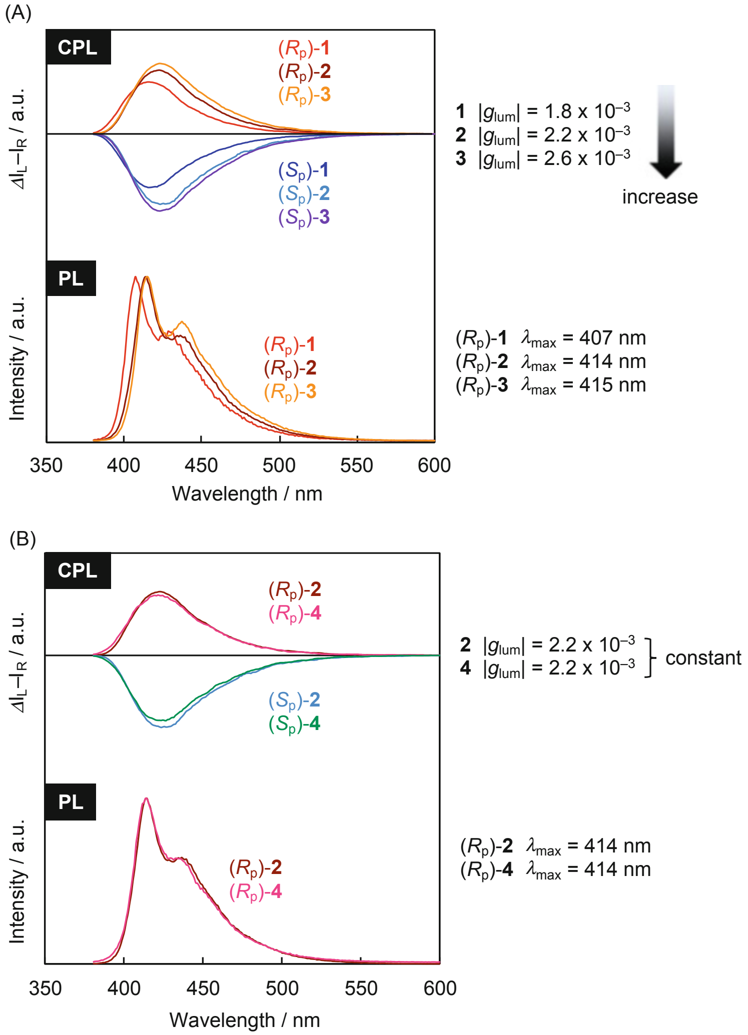


Fig. 3.11 (**a**) CPL and PL spectra of **1**–**3** in $CHCl_3$ (10×10^{-5}M), (**b**) CPL and PL spectra of **2** and **4** in $CHCl_3$ (10×10^{-5}M)

structure, which induced large chirality in both the ground state and the excited state. The specific rotation reached 1500 (c 0.5, $CHCl_3$), and the molar ellipticity was approximately 3,000,000 deg cm^2 $dmol^{-1}$. Molecule **5** emitted intense CPL, and the spectra of the enantiomers are shown in Fig. 3.14. The $|g_{lum}|$ value at $\lambda_{PL,max}$ was estimated to be in the order of 10^{-2}, with $|g_{lum}| = 1.3 \times 10^{-2}$. This g_{lum} value is large for a monodispersed organic molecule in solution. The optically active second-ordered structure, i.e., optically active propeller-shaped structure, contributes greatly to the induction of chirality in the excited state. Although the Φ_{PL} was 0.45, the

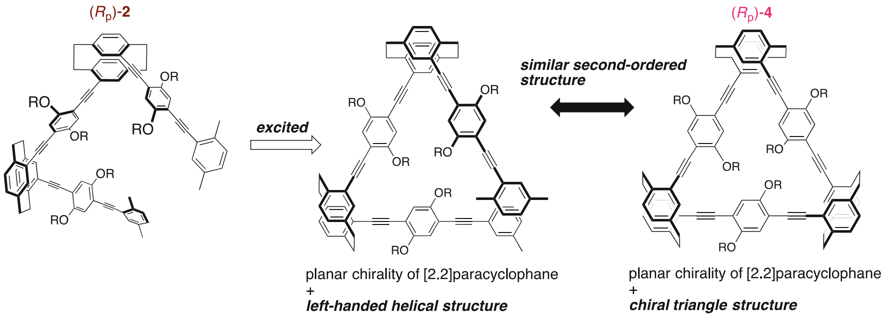


Fig. 3.12 Plausible conformations of linear trimer **2** and cyclic trimer **4**

molar absorption coefficient (ε) of 130,000M^{-1} cm^{-1} indicates that this molecule emits bright PL. In addition, optically active propeller-shaped molecules **6** [45] and **7** [46] were prepared (Fig. 3.13). Both the compounds exhibited high molar absorption coefficients, good Φ_{PL}, and large CPL g_{lum} values.

Simple X-shaped molecules have been synthesized from 4,7,12,15-tetraethynyl [2.2]paracyclophane [47], and the structures and other data are briefly shown in Fig. 3.15. The phenyl- and naphthyl-containing molecules, **8** and **9**, emitted intense CPL, while a weak CPL signal was observed from the anthracene-containing molecule **10**. In particular, the naphthyl-containing molecule **9** was an excellent CPL emitter, with a large g_{lum} in the order of 10^{-3}, large ε of 0.79×10^5 cm^{-1} M^{-1}, and good Φ_{lum} of 0.78.

Figure 3.15 shows an optically active X-shaped molecule (R_p)-**11** that emits intense CPL, with a Φ_{PL} of 0.87 in a dilute solution and the g_{lum} value of -1.2×10^{-3} [48]. The g_{lum} value of the spin-coated film was positive with $g_{\text{lum}} = +2.1 \times 10^{-2}$, which was larger by an order of magnitude. Furthermore, the g_{lum} value of the annealed thin film was negative and in the order of 10^{-1} (-0.25). The g_{lum} value of the thin film obtained by the casting method was negative and still larger by an order of magnitude (-3.0×10^{-2}). When it was annealed, the sign was reversed, and the same g_{lum} value (-0.25) was observed. An optically active higher-ordered structure was formed in the thin film because of the van der Waals force of the long alkyl chains and π-π interactions. Thus, a thermodynamically stable higher-ordered structure was formed by annealing.

Not only arylene-ethynylenes but also arylene-vinylenes were chosen as π-electron systems. Figure 3.16 shows the optically active X-shaped molecules consisting of arylene-vinylenes prepared from 4,7,12,15-tetraethynyl[2.2] paracyclophane [49]. Molecule **12** [40, 49] exhibited aggregation-caused quenching of PL ($\Phi_{\text{PL}} = 0.03$) because of the high planarity of the stacked π-electron system, while **13** exhibited moderate PL properties both in the dilute solution ($\Phi_{\text{PL}} = 0.58$) and in the aggregated state ($\Phi_{\text{PL}} = 0.24$). In the dilute solution, **12** showed good CPL properties ($\Phi_{\text{PL}} = 0.78$ and $|g_{\text{lum}}| = 3.7 \times 10^{-3}$), and in the aggregated state, **13** showed good CPL properties (Φ_{PL} of 0.24 and $|g_{\text{lum}}| = +0.90 \times 10^{-3}$) which were observed.

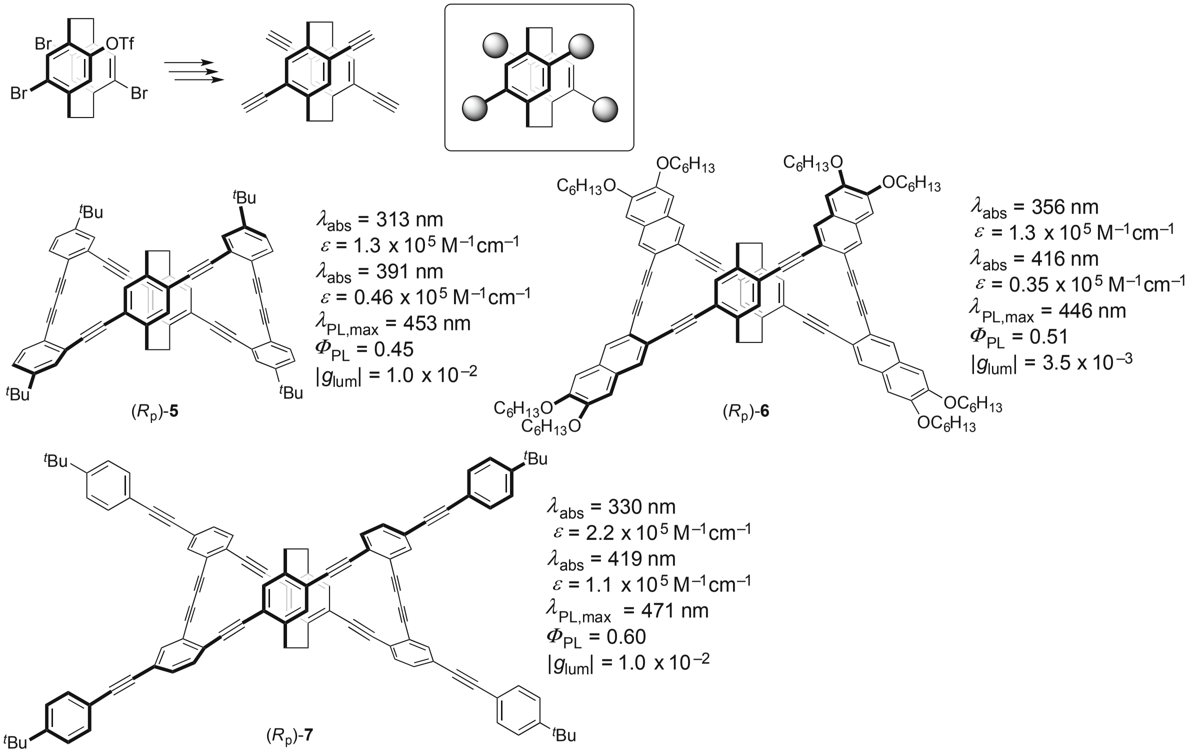


Fig. 3.13 Structures and optical data of propeller-shaped cyclic molecules **5**–**7**

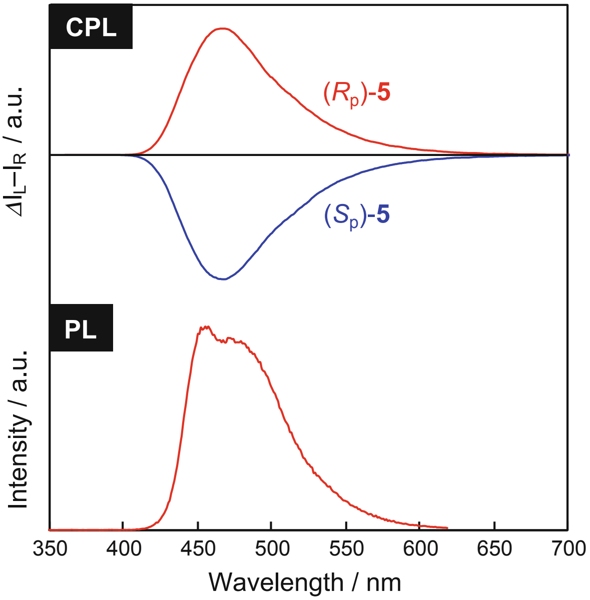


Fig. 3.14 CPL and PL spectra of (R_p)- and (S_p)-**5** in $CHCl_3$ (10×10^{-6}M)

Although the planar chiral molecules discussed above emit intense CPL in a dilute solution, their fluorescence quantum yield is basically lowered in the solid state due to the general aggregation-caused quenching. The problem of quenching can be overcome by introducing Fréchet-type dendrons [50, 51] into the X-shaped molecules [52]. Figure 3.17 shows the third-generation dendrimer **14**, and the CPL spectrum of the thin film. The Φ_{PL} of **14** was estimated to be 0.65, which is almost the same as the value of 0.66 observed in the dilute solution. This was because of the X-shaped core being isolated by the dendrons. The CPL $|g_{lum}|$ value of **14** was 1.8×10^{-3}. A thin film emitting CPL with high intensity, high efficiency, and high dissymmetry factor could be obtained because of the light-harvesting effect of the benzene rings of the dendrimer.

Recently, catalytic system that enables chemoselective Sonogashira-Hagihara coupling was developed [35]. The combination of $Pd_2(dba)_3/P^tBu_3$ reacted predominantly with Ar-Br instead of Ar-OTf; thus, 4,7,12-tribromo-15-trifluoromethanesulfonyl[2.2]paracyclophane (Fig. 3.6) was converted to the corresponding triyne (Fig. 3.18). This triyne could be used as a chiral building block to obtain the X-shaped molecules **15**, which consisted of heterogeneous π-electron systems could be obtained. The optical properties were almost identical to those of the X-shaped molecule **16**, and they were excellent CPL emitters [53]. It is possible to layer heterogeneous π-electron systems possessing various electron-accepting and electron-donating groups.

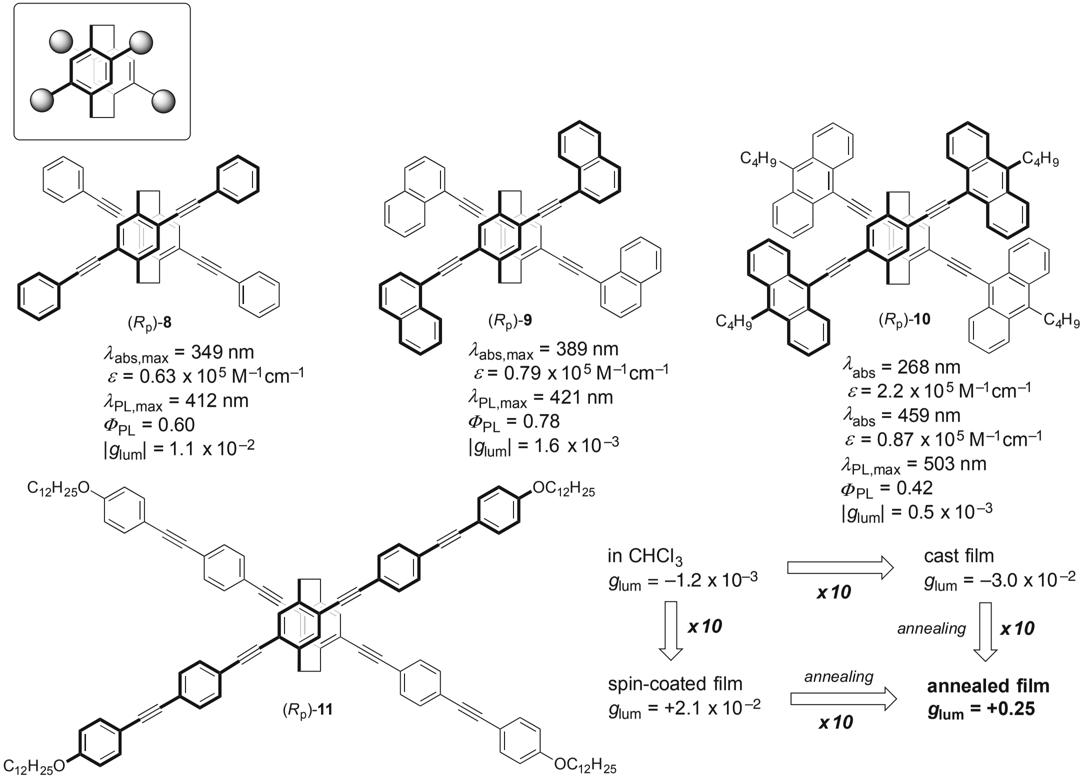


Fig. 3.15 Structures and optical data of X-shaped molecules **8–11**

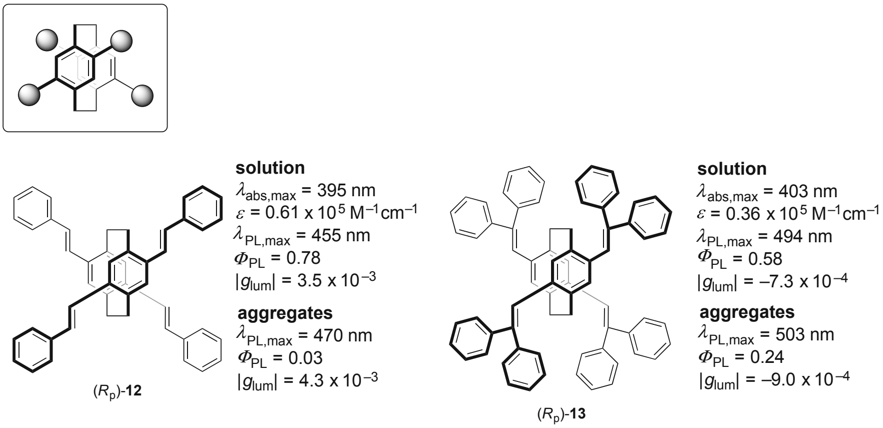
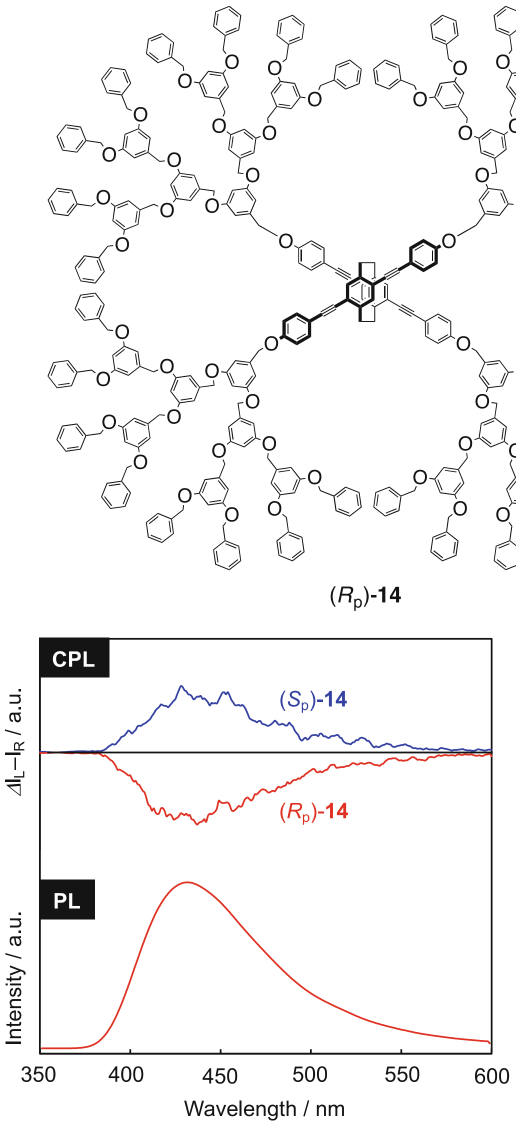


Fig. 3.16 Structures and optical data of X-shaped molecules **12** and **13**

Bis-(*para*)-pseudo-*ortho*-4,7,12,15-tetrasubstituted [2.2]paracyclophanes (Fig. 3.7) were applied in the chemoselective Sonogashira-Hagihara coupling to afford the corresponding diyne, which could be employed as a chiral building block [36]. Different π-conjugated substituents could be introduced at the 4,12- and 7,15-positions. As shown in Fig. 3.19, one-handed double helical structure was constructed; for example, boomerang-shaped π-electron systems were stacked at the second and fourth phenylene rings to form a left-handed helix from the (R_p)-isomer. The double helical compounds (R_p, R_p)- and (S_p, S_p)-**17** were highly emissive with excellent chiroptical properties in the ground state and, in particular, in the excited state ($|g_{lum}| = 1.6 \times 10^{-3}$); that is to say, they were also excellent organic CPL emitters [36].

Optically active V-shaped molecule **18** (Fig. 3.20) could be prepared from MeO-substituted bis-(*para*)-pseudo-*ortho*-4,7,12,15-tetrasubstituted [2.2] paracyclophane (Fig. 3.7) [37]. π-Electron systems were stacked at the terminal benzene rings. The properties were compared with the corresponding X-shaped molecule **16**, in which the π-electron systems were stacked at the central benzene rings. The CPL signs of the V- and X-shaped molecules were positive and negative, respectively. Positive and negative CPL signs appeared from V-shaped molecule (R_p)-**18** and X-shaped molecule (R_p)-**16**, respectively. The stacking positions of the two π-electron systems leads to the different CPL signs despite the same absolute configuration.

The electronic transition dipole moments and magnetic transition dipole moments from S1 to S0 of molecules **18** and **16** were simulated (Fig. 3.21); the simulation was carried out for (S_p)-isomers. The g_{lum} value is defined by $4|\boldsymbol{\mu}||\boldsymbol{m}|\cos\theta/(|\boldsymbol{\mu}|^2+|\boldsymbol{m}|^2)$, where $\boldsymbol{\mu}$ and $\boldsymbol{m}$ represent electric and magnetic transition dipole moments, respectively, and the θ represents the angle between the $\boldsymbol{\mu}$ and $\boldsymbol{m}$ [54–56]. The sign of a g_{lum} value is decided by this angle. The angle θ between $\boldsymbol{\mu}$ and $\boldsymbol{m}$ of (S_p)-**18** was estimated to be 144°, while that of (S_p)-**16** was estimated to be 87°. Theoretical results



solution

λ_{abs} = 279 nm

$\varepsilon = 1.00 \times 10^5$ M^{-1}cm^{-1}

λ_{abs} = 365 nm

$\varepsilon = 0.68 \times 10^5$ M^{-1}cm^{-1}

$\lambda_{PL,max}$ = 417 nm

Φ_{PL} = 0.66

$|g_{lum}| = 1.4 \times 10^{-3}$

thin film

$\lambda_{PL,max}$ = 421 nm

Φ_{PL} = 0.65

$|g_{lum}| = 1.8 \times 10^{-3}$

Fig. 3.17 Structure of third-generation dendrimer **14**. The CPL and PL spectra of the dendrimer film excited at 279 nm are shown

predicted opposite CPL signs for **18** and **16**, and this was also supported by the experimental results.

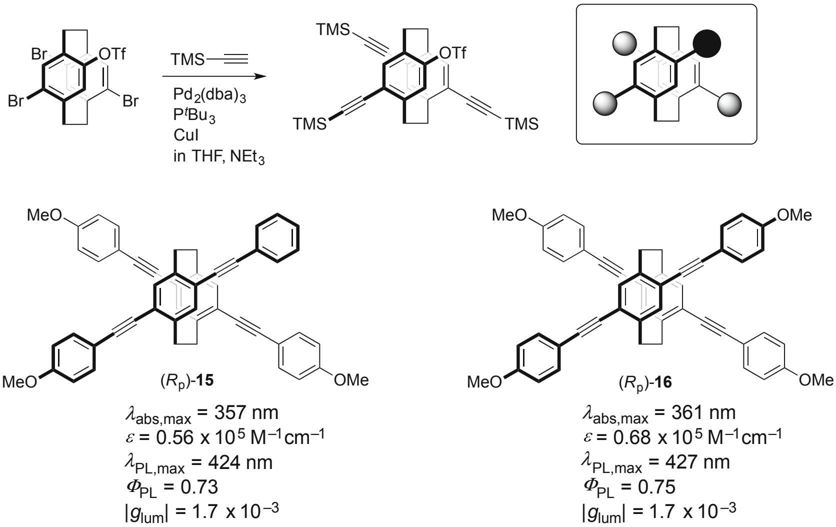


Fig. 3.18 Structures and optical data of X-shaped molecules **15** and **16** in which different π-electron systems are stacked

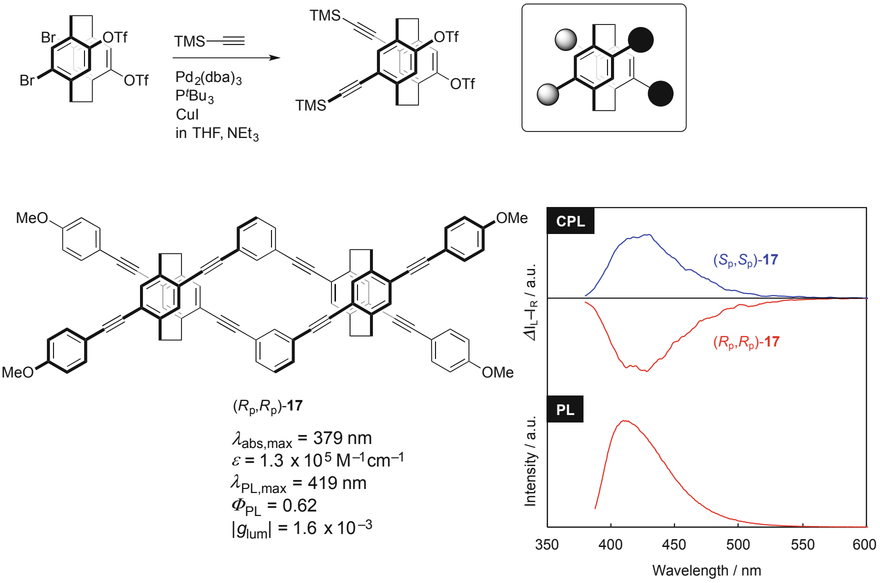


Fig. 3.19 One-handed double helical molecule **17** and the CPL and PL spectra in $CHCl_3$ (10 × 10^{-5}M)

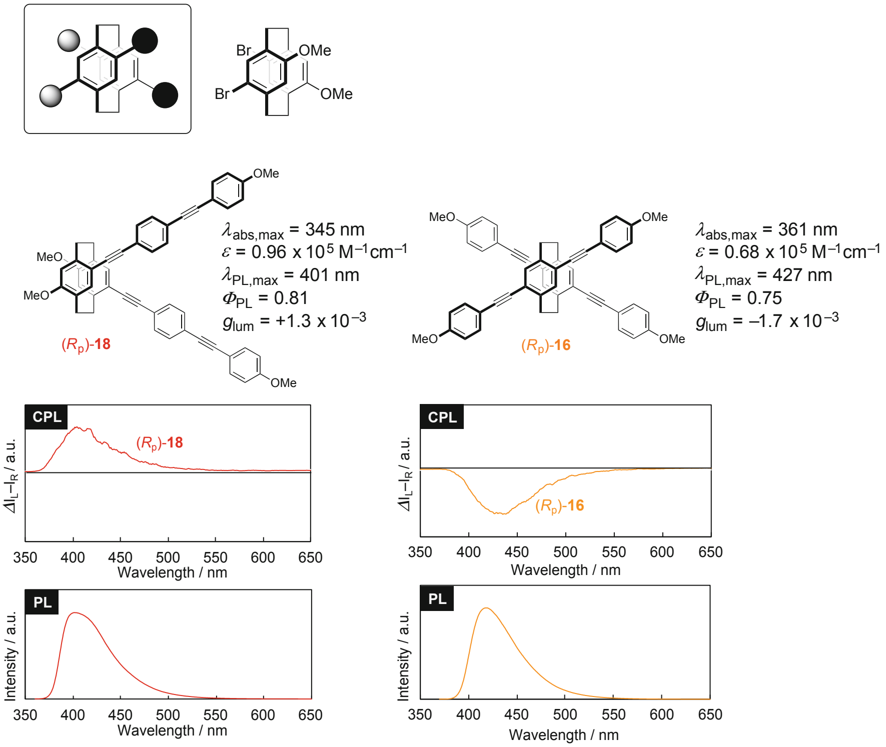


Fig. 3.20 CPL and PL spectra of (R_p)-**18** and **16** in $CHCl_3$ (10×10^{-5}M)

3.4 Conclusion

In summary, the author described the recent synthetic routes for the optical resolution of di- and tetrasubstituted [2.2]paracyclophane for the development of molecules based on the planar chiral [2.2]paracyclophane molecule that could emit CPL. Various optically active π-stacked small molecules, oligomers, macrocycles, and polymers were prepared using the optically active [2.2]paracyclophane as a chiral building block. It has been suggested that the optically active higher-ordered structures, such as V-, X-, triangle-, and propeller-shaped structures, in the excited state are important for strong CPL with large g_{lum} values. The results introduced in this chapter are the first example of application of the optically active [2.2] paracyclophane molecule in the fields of polymer and materials chemistry. The π-conjugated molecules based on [2.2]paracyclophane emit luminescence basically with high Φ_{PL}. Their ε values are large due to the extended π-electron systems, which lead to the excellent CPL emission. It is difficult to obtain materials that emit

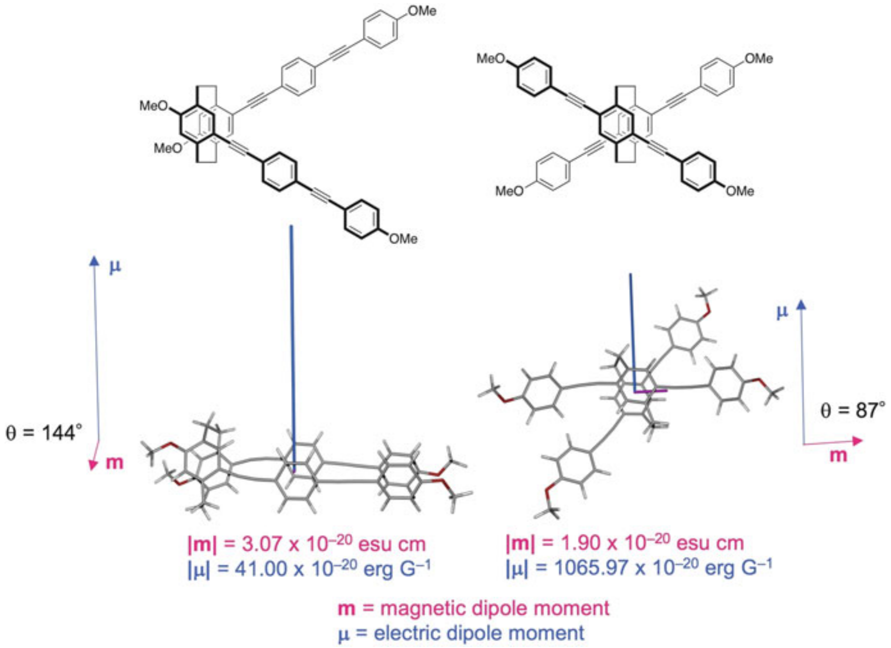


Fig. 3.21 Simulations of the transition dipole moments of (S_p)-**18** and (S_p)-**16** in the excited states by using the TD-DFT calculations at the ωB97XD/6-31G(d,p) level of theory with following options: TD = (N_{States} = 10, Root = 1), SCRF = (SOLVENT = Chloroform). Lengths of the dipole moments on the structures are based on the atomic units

high intensity CPL, with high quantum efficiency, and have high anisotropy as well in other chiral scaffolds. The author believes that the planar chiral [2.2]paracyclophane skeleton is an ideal scaffold for developing materials exhibiting strong CPL.

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