

# Chapter 10

## Circularly Polarized Luminescence (CPL) Based on Planar Chiral [2.2]Paracyclophane



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**Abstract** In this chapter, chiroptical properties, especially circularly polarized luminescence (CPL) properties of optically active molecules based on planar chiral [2.2]paracyclophane are mainly introduced. In addition, practical optical resolution methods of disubstituted and tetrasubstituted [2.2]paracyclophane molecules are also focused on. The enantiopure [2.2]paracyclophane compounds have been used as chiral building blocks to synthesize the optically active molecules by means of optical resolution. The [2.2]paracyclophane-based molecules are  $\pi$ -stacked molecules, which construct optically active second-ordered structures, such as V-, X-, triangle-shaped, and one-handed double helical structures, due to the orientation of stacked  $\pi$ -electron systems. Photoexcitation allows them to emit bright CPL with good photoluminescence (PL) quantum efficiencies and large dissymmetry factors ( $g_{\text{lum}}$  values). Thus, planar chiral [2.2]paracyclophane is the ideal scaffold to achieve excellent CPL properties.

**Keywords** Circularly polarized luminescence · [2.2]Paracyclophane · Planar chirality

### 10.1 Introduction: Circularly Polarized Luminescence (CPL)

Circularly polarized luminescence (CPL) is a chiroptical (chiral + optical) property that is responsible for the difference in luminescence intensity between left-handed and right-handed emissions. Circular dichroism (CD) is another chiroptical property that is responsible for the difference in molar extinction coefficients between left- and right-polarized light. CPL and CD spectroscopy provide important information about the orientation of luminophores and chromophores, respectively (Berova et al. 2000). Many optically active molecules exhibit CPL and CD in the excited and

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ground states, respectively, but these phenomena cannot be always observed even if the molecules possess a chiral source.

CPL is evaluated by the anisotropic factor (dissymmetric factor), referred to as  $g_{\text{lum}}$  value (by Berova et al. 2000; Riehl and Richardson 1986; Riehl and Muller 2012), which can be calculated as the following Eq. (10.1):

$$g_{\text{lum}} = \Delta I / I \quad (10.1)$$

$\Delta I$  = (emission intensity of left-handed CPL) – (emission intensity of right-handed CPL) and  $I$  = emission intensity

The  $g_{\text{lum}}$  value can also be expressed as

$$g_{\text{lum}} = 4|\boldsymbol{\mu}||\mathbf{m}| \cos \theta / (|\boldsymbol{\mu}|^2|\mathbf{m}|^2) \quad (10.2)$$

Here,  $\boldsymbol{\mu}$  and  $\mathbf{m}$  represent electric and magnetic transition dipole moments, respectively, and the  $\theta$  represents the angle between them (Berova et al. 2000; Riehl and Richardson 1986; Riehl and Muller 2012). Thus, the maximum absolute  $g_{\text{lum}}$  value is calculated to be  $|g_{\text{lum}}| = +2$ .

Ideally, forbidden electric transitions and allowed magnetic transitions are preferred. Generally, the  $g_{\text{lum}}$  values of chiral lanthanide complexes are much larger than those of chiral organic molecules. The emission of lanthanides is derived from the Laporte forbidden f-f transition (Muller 2014); therefore, the  $\boldsymbol{\mu}$  is small and  $\mathbf{m}$  is large. It is reported that the chiral Eu(III) complex, tetrakis(3-heptafluoro-butylryl-(+)-camphorato) Eu(III), has a  $g_{\text{lum}}$  value of +1.38 (Lunkley et al. 2008).

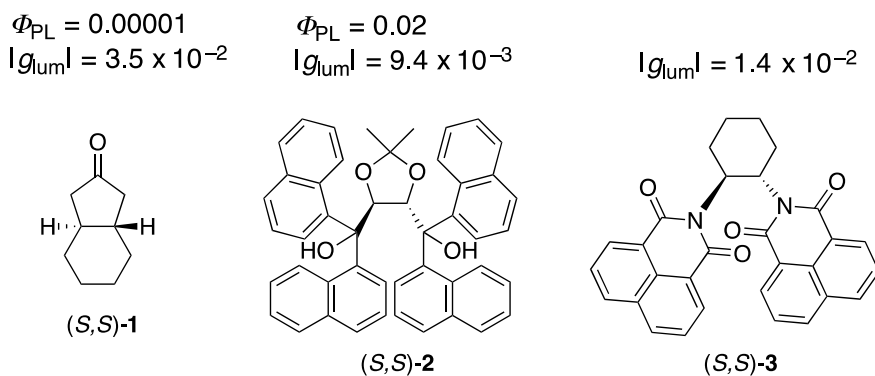
Many of  $g_{\text{lum}}$  values of organic molecules reported are within the range  $10^{-3}$ – $10^{-5}$  order due to the much smaller  $\mathbf{m}$ . Therefore, Eq. (10.2) can be simply converted to the approximated Eq. (10.3).

$$g_{\text{lum}} = 4|\mathbf{m}| \cos \theta / |\boldsymbol{\mu}| \quad (10.3)$$

Considering the photoluminescence quantum efficiency ( $\Phi_{\text{PL}}$ ) and emission intensity, an allowed electronic transition is preferable. It is a challenging task to achieve a large  $\mathbf{m}$  and small  $\boldsymbol{\mu}$ , and their linear orientation (their angle  $\theta = 0^\circ$  or  $180^\circ$ ) in the organic molecules. Organic CPL dyes are attractive luminescent materials due to their light-weight, as well as the ease of fabrication, functional group modification, and emission color control. These dyes are expected to be promising candidates for next-generation emissive materials such as light-emitting diodes for three-dimensional displays, security inks, light for plant growth, bioimaging materials, etc.

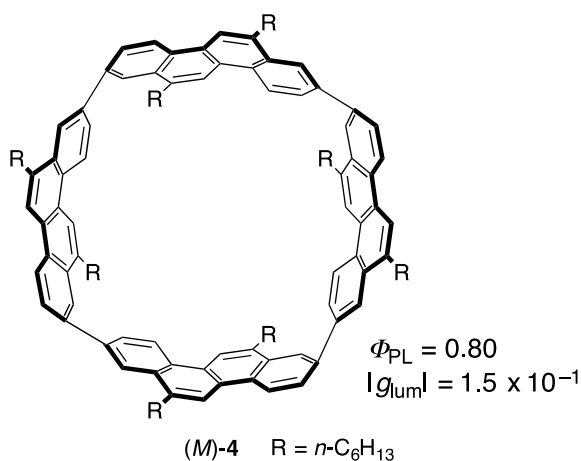
A wide variety of organic CPL emitters have been reported thus far, and the last five years have seen a marked increase in the number of related manuscripts because of the widespread use of CPL spectrometers (Maeda and Bando 2013; Sánchez-Carnerero et al. 2015; Tanaka et al. 2018; Chem and Yan 2018). The CPL-emitting small organic molecules in the dispersed state are briefly introduced below. In 1967, CPL from organic molecules was reported for cyclic ketones with a central chirality (Emeris

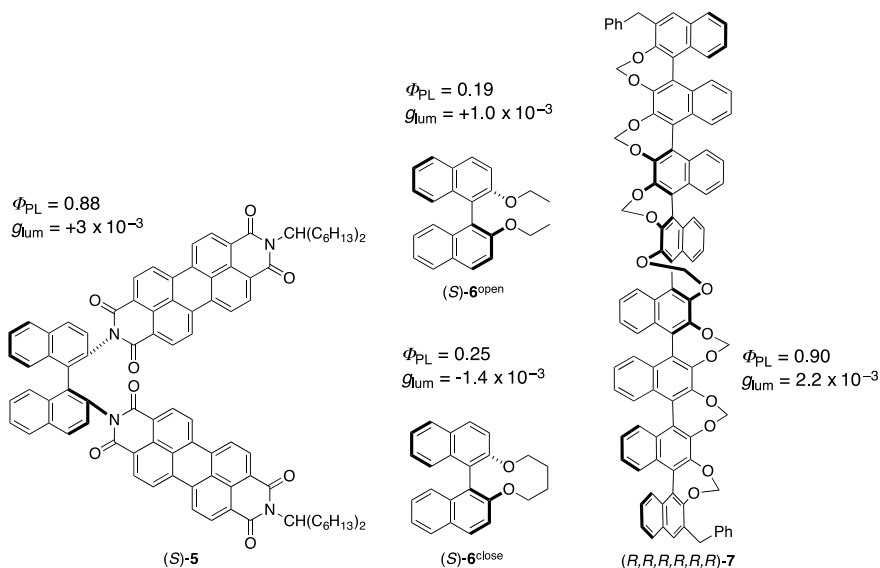
and Oosterhoff 1967); a representative example is shown in Fig. 10.1. Because of the forbidden  $n-\pi^*$  transition, the molecule emitted CPL with a very large  $g_{\text{lum}}$  value of  $+3.5 \times 10^{-2}$ . This value was long considered the champion value for a long time in the small organic molecules in a diluted solution, although the  $\Phi_{\text{PL}}$  was quite low ( $\Phi_{\text{PL}} = 1 \times 10^{-5}$ ). Various CPL emitters with the central chirality have been reported to show large  $g_{\text{lum}}$  values. As the representative examples, naphthyl (Amako et al. 2014) and naphthalimide (Sheng et al. 2016) emissive units were connected on chiral cyclic scaffolds, which showed CPL emission from the intramolecular aggregate (excimer) of the aromatic units with  $|g_{\text{lum}}|$  values of  $9.4 \times 10^{-3}$  ( $\Phi_{\text{PL}} = 0.02$ ) and  $1.4 \times 10^{-2}$ , respectively. In 2017, the champion  $g_{\text{lum}}$  value was updated for the cylindrical molecule **4** with cylinder helicity (Fig. 10.2), and it was on the order of  $10^{-1}$  ( $|g_{\text{lum}}| = 1.5 \times 10^{-1}$  and  $\Phi_{\text{PL}} = 0.80$ ) (Sato et al. 2017). Theoretical studies revealed a large  $\mathbf{m}$ , as well as linearly oriented  $\mathbf{m}$  and  $\boldsymbol{\mu}$  ( $\theta = 180^\circ$ ).



**Fig. 10.1** Representative examples of CPL emitters with central chirality

**Fig. 10.2** Cylindrical molecules with an excellent CPL profile

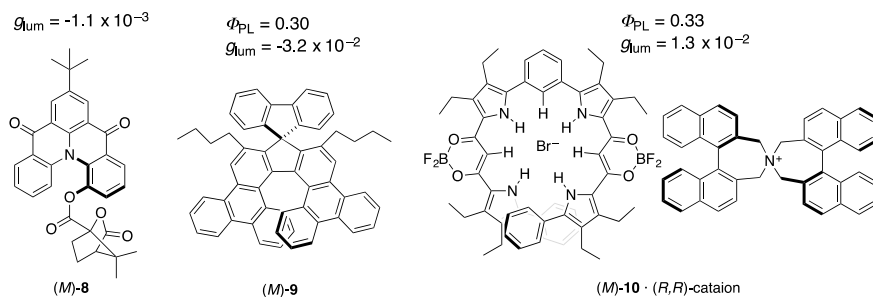




**Fig. 10.3** Representative examples of oligoaryl-based CPL emitters with axial chirality

Biaryl-based axial chirality is an easily accessible chiral scaffold for CPL emission. Figure 10.3 shows the binaphthyl-based molecules. In 2007, perylenebis(carboxydiimide)-containing binaphthylene (S)-5 was prepared (Kawai et al. 2007). This compound showed intense emission with  $\Phi_{\text{PL}}$  of 0.88, and the  $g_{\text{lum}}$  was estimated to be approximately  $3 \times 10^{-3}$ . Simple biaryl-based molecules (open- and closed-type molecules (S)-6<sup>open</sup> and (S)-6<sup>close</sup>, respectively) were synthesized (Kimoto et al. 2012). Despite their similar photoluminescence behavior and identical absolute configuration, these molecules showed different CPL signals. The values for (S)-6<sup>open</sup> and (S)-6<sup>close</sup> were calculated to be  $+1.0 \times 10^{-3}$  ( $\Phi_{\text{PL}} = 0.19$ ) and  $-1.4 \times 10^{-3}$  ( $\Phi_{\text{PL}} = 0.25$ ), respectively. Optically active naphthalene oligomers were synthesized; the representative molecule (R,R,R,R,R,R)-7 consisting of eight naphthyl moieties is also shown in Fig. 10.3 (Takaishi et al. 2017). This molecule showed bright CPL emission with  $g_{\text{lum}} = +2.2 \times 10^{-3}$  and  $\Phi_{\text{PL}} = 0.90$ . Compound (S)-5 emitted from the perylene-diimide moieties, whereas (S)-6 and 7 showed emission from the oligoaryl scaffolds.

Helical chirality is also employed for CPL emission. Generally,  $\Phi_{\text{PL}}$  of a helical molecule is not very high; however, its  $g_{\text{lum}}$  value is very large, often on the order of  $10^{-2}$ . Figure 10.4 shows the helicene derivatives (M)-8 (Field et al. 2003) and (M)-9 (Sawada et al. 2012) as representative examples. Molecule 8 is the first helicene emitting CPL in dilute solution. This molecule was obtained as a diastereomer due to the attachment of a camphanate unit as the chiral auxiliary. The  $|g_{\text{lum}}|$  value was calculated to be  $1.1 \times 10^{-3}$ . A very large  $|g_{\text{lum}}|$  value of  $3.2 \times 10^{-2}$  ( $\Phi_{\text{PL}} = 0.30$ ) was obtained from molecule 9, which was prepared by the Rh-catalyzed enantioselective [2 + 2 + 2] cycloaddition. Molecule 10 is a stimuli-responsive compound used for



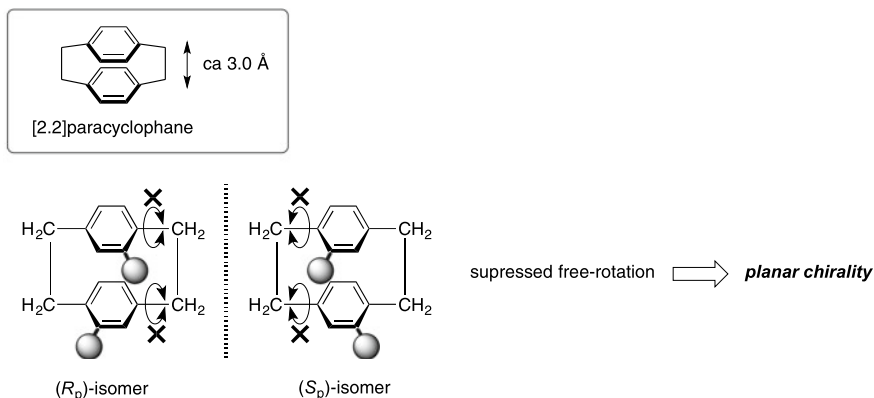
**Fig. 10.4** Representative examples of helical CPL emitters

capturing halogen anions to form a helix (Haketa et al. 2012). The chiral counter cation is allowed for the introduction of one-handed helicity in dilute solution. The resulting ion pair was emissive, and the  $|g_{lum}|$  value was calculated to be  $1.3 \times 10^{-2}$  with  $\Phi_{PL}$  of 0.33.

Recently, planar chirality has also been applied to CPL emission. However, there are fewer CPL emitters based on planar chirality as compared to those based on axial and helical chiralities. Unique optically active molecules have been prepared by taking advantage of the planar chirality of a [2.2]paracyclophane scaffold, and large  $g_{lum}$  values, as well as high  $\Phi_{PL}$  were achieved (Morisaki and Chujo 2019). Various interesting second-ordered structures were also constructed. This chapter focuses on planar chirality and CPL emission in the mono-dispersed state from the optically active small organic molecules based on the planar chiral [2.2]paracyclophanes.

## 10.2 Introduction: [2.2]Paracyclophane and Its Planar Chirality

Cyclophane is a cyclic compound containing at least one aromatic ring in the main chain skeleton. It is a well-known cyclic compound and have been used particularly in the field of synthetic organic chemistry and organometallic chemistry (Vögtle 1993; Gleiter and Hopf 2004). The typical cyclophane is [2.2]paracyclophane (Fig. 10.5), in which two phenylenes are stacked in proximity (the distance between two benzene rings is approximately 3.0 Å). [2.2]Paracyclophane was first synthesized in 1949, by pyrolysis of *para*-xylene (Brown and Farthing 1949); subsequently, a direct synthesis from 1,4-bis-bromomethylbenzene by Wurtz-type intramolecular cyclization was reported in 1951 (Cram and Steinberg 1951). Since then, various synthetic routes have been developed to prepare a wide variety of [2.2]paracyclophane molecules. [2.2]Paracyclophane has a unique  $\pi$ -stacked structure, and there have been many studies on its physical properties within the field of organic chemistry (Gleiter and Hopf 2004; Brown and Farthing 1949).



**Fig. 10.5** Structure of [2.2]paracyclophane and the corresponding planar chirality

Although [2.2]paracyclophane is a molecule that has generally been used in the field of organic chemistry and organometallic chemistry, its utilization is not widespread in the fields of polymer chemistry and materials chemistry (Hopf 2008; Morisaki and Chujo 2006, 2008, 2009, 2011, 2012; Mizogami and Yoshimura 1985; Guyard and Audebert 2001; Guyard et al. 2002; Salhi et al. 2002; Salhi and Collard 2003; Jagtap and Collard 2010; Weiland et al. 2019). In terms of the through-space conjugated system, [2.2]paracyclophane-based  $\pi$ -stacked molecules have been systematically prepared, and their electronic communication between the stacked  $\pi$ -electron systems have been known since 1998 (Oldham et al. 1998; Bazan et al. 1998; Bartholomew and Bazan 2001; Bazan 2007). In 2001, thiophene-substituted [2.2]paracyclophanes were polymerized electrochemically; however, the polymer was deposited on the electrode and was insoluble in solvents (Guyard and Audebert 2001). In 2002, soluble  $\pi$ -stacked polymers consisting of [2.2]paracyclophane as a repeating unit in the main chain were synthesized (Morisaki and Chujo 2002). Since then, various  $\pi$ -stacked polymers have been prepared (Morisaki and Chujo 2006, 2008, 2009, 2011, 2012). The structures have been well-characterized, and the properties, such as optical properties, have been shown due to their solubility in organic solvents. Since their optical properties changed continuously depending on the number of the stacked  $\pi$ -electron systems, they were called “through-space conjugated polymers”. Highly efficient unidirectional fluorescence resonance energy transfer (FRET) (Morisaki et al. 2013, 2014a, 2014b, 2017), as well as through-space electron transfer (Molina-Ontoria et al. 2011; Wielopolski et al. 2013) was achieved by precisely designing the stacked  $\pi$ -electron systems. [2.2]Paracyclophane-based through-space conjugated polymers and oligomers can act as single molecular wires.

As described above, [2.2]paracyclophane consists of two phenylene units fixed in proximity; therefore, the rotational movement of the benzene rings is suppressed. By introducing a substituent at appropriate positions on the benzene ring(s), the corresponding [2.2]paracyclophane becomes a planar chiral molecule (Fig. 10.5) (Cram and Allinger 1955; Rozenberg et al. 2004; Rowlands 2008; Gibson and Knight 2003;

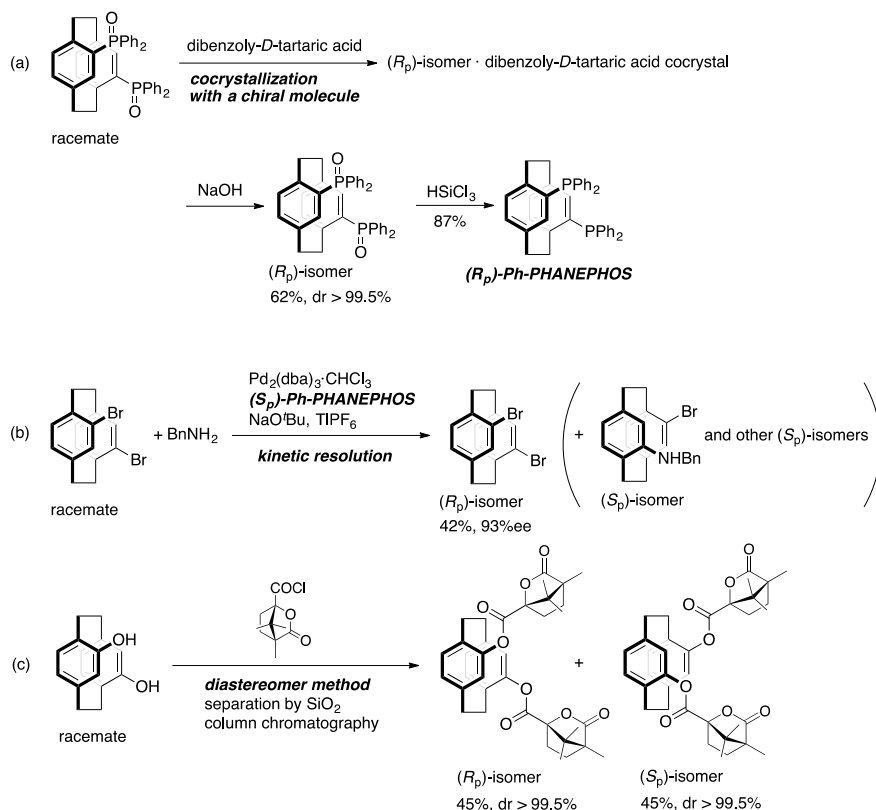
Aly and Brown 2009; Paradies 2011). The planar chirality of [2.2]paracyclophane is well-known in the fields of organic chemistry and organometallic chemistry, and planar chiral [2.2]paracyclophanes have been utilized as chiral auxiliaries and chiral ligands. However, until recently, the planar chirality of [2.2]paracyclophane has been ignored in the fields of polymer chemistry and materials chemistry until recently. In 2012, a new optical resolution method was developed for pseudo-*ortho*-disubstituted [2.2]paracyclophane, and the transformation and polymerization of the enantiopure [2.2]paracyclophanes were reported (Morisaki et al. 2012a, b). The resulting optically active polymer emitted CPL (Morisaki et al. 2012).

This chapter highlights and introduces the recent results on the synthesis of enantiopure disubstituted and tetrasubstituted [2.2]paracyclophanes. The preparation of optically active molecules based on the [2.2]paracyclophanes for their application in the fields of polymer and materials chemistry as the CPL emitters is also described.

### 10.3 Synthesis of Enantiopure Disubstituted [2.2]Paracyclophane and Optically Active $\pi$ -Stacked Molecules

Optical resolution routes of mono-substituted [2.2]paracyclophanes were developed, and various enantiopure *ortho*-, pseudo-*geminal*-, and *syn-latero*-disubstituted [2.2]paracyclophanes were prepared (Cram and Allinger 1955; Rozenberg et al. 2004; Rowlands 2008; Gibson and Knight 2003; Aly and Brown 2009; Paradies 2011). In addition, several synthetic routes to the syntheses of enantiopure disubstituted [2.2]paracyclophanes, e.g., pseudo-*ortho*-disubstituted [2.2]paracyclophanes, have been reported (Pye et al. 1997; Rossen et al. 1997; Zhuravsky et al. 2008; Jiang and Zhao 2004; Jones et al. 2003; Pamperin et al. 1997; Pamperin et al. 1998; Braddock et al. 2002), as shown in Fig. 10.6. A representative example is the synthesis of enantiopure pseudo-*ortho*-bis(diarylphosphino)[2.2]paracyclophane (Ph-PHANEPHOS) (Fig. 10.6a) (Pye et al. 1997). The resulting (*S<sub>p</sub>*)- and (*R<sub>p</sub>*)-Ph-PHANEPHOS are the commercially available chiral ligands for the transition metal-catalyzed asymmetric reactions. This PHANEPHOS makes it possible to produce enantioenriched pseudo-*ortho*-dibromo[2.2]paracyclophane (Fig. 10.6b) by kinetic resolution (Rossen et al. 1997). Synthesis of optically active 4-bromo-12-hydroxy[2.2]paracyclophane (Zhuravsky et al. 2008), pseudo-*ortho*-dihydroxy[2.2]paracyclophane (PHANOL) (Jiang and Zhao 2004), and pseudo-*ortho*-dihydroxymethyl[2.2]paracyclophane (Jones et al. 2003) were successfully synthesized by using chiral camphanic acid chloride as the chiral auxiliary; for example, Fig. 10.6c shows the optical resolution of PHANOL racemate. The enzyme-promoted kinetic resolutions of pseudo-*ortho*-disubstituted [2.2]paracyclophanes have also been developed (Pamperin et al. 1997, 1998; Braddock et al. 2002).

A practical route to the optical resolution of pseudo-*ortho*-dibromo[2.2]paracyclophane was reported in 2012, in which (1*R*,2*S*,5*R*)-(-)-menthyl

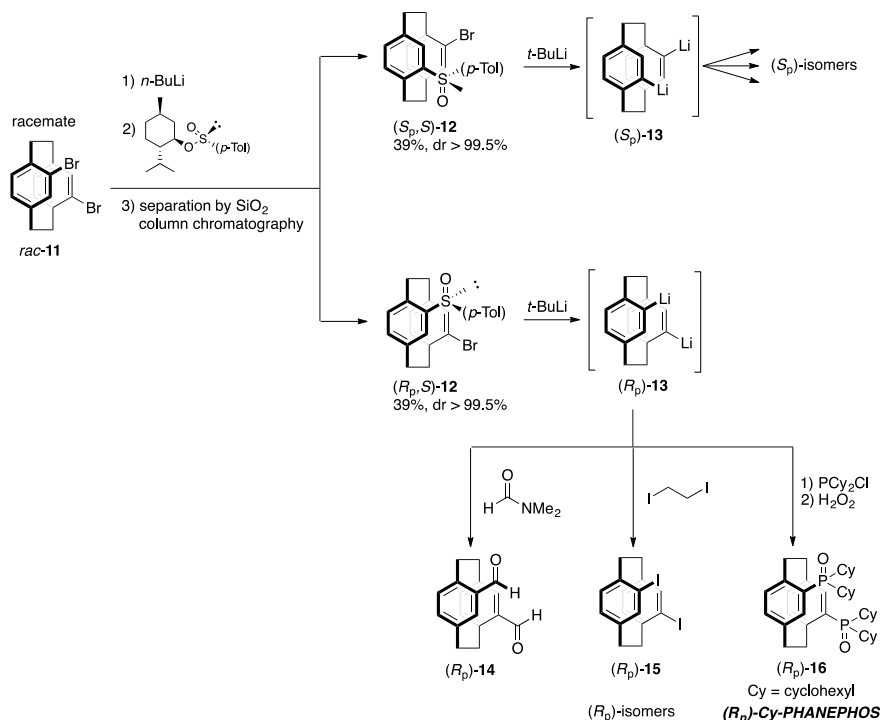


**Fig. 10.6** Examples of optical resolution of pseudo-*ortho*-disubstituted [2.2]paracyclophanes

(*S*)-*p*-toluenesulfinate was used as the chiral auxiliary (Fig. 10.7) (Morisaki et al. 2012). Racemic pseudo-*ortho*-dibromo[2.2]paracyclophane *rac*-**11** was reacted with *n*-butyllithium (*n*-BuLi). Then, the reaction with (1*R*,2*S*,5*R*)-(-)-menthyl-*p*-toluenesulfinate afforded the diastereomers (*R*<sub>p</sub>,*S*)- and (*S*<sub>p</sub>,*S*)-**12**, which could be separated by using SiO<sub>2</sub> column chromatography. The isolated diastereomers were reacted with *t*-BuLi to form dilithiated intermediate **13**; not only the lithium-halogen exchange reaction, but also the lithium-sulfur exchange reaction occurred (Rowlands 2008; Clayden 2002; Hitchcock et al. 2005; Parmar et al. 2010). The subsequent reaction with various electrophiles produced enantiopure pseudo-*ortho*-disubstituted [2.2]paracyclophanes (Fig. 10.7). (*R*<sub>p</sub>)- and (*S*<sub>p</sub>)-Diformyl[2.2]paracyclophanes **14** could be separated by chiral column chromatography; thus, their chromatographic optical resolution was also possible (Morisaki et al. 2012). This synthetic route can be used to produce new PHANEPHOS; for example, cyclohexyl groups could be introduced on phosphorus atoms to produce Cy-PHANEPHOS **16** (Fig. 10.7).

Pseudo-*ortho*-diformyl[2.2]paracyclophane **14** could be converted to the corresponding diethynyl[2.2]paracyclophane **17** using the Ohira-Bestmann reagent



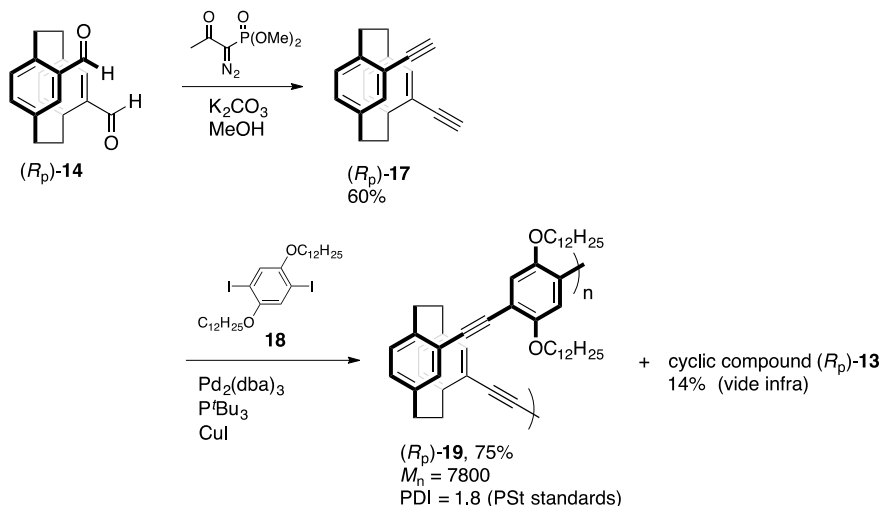


**Fig. 10.7** Optical resolution of pseudo-*ortho*-disubstituted [2.2]paracyclophane and transformations

(Fig. 10.8) (Ohira 1989; Müller et al. 1996), which was used as a monomer to synthesize poly(*p*-arylene-ethynylene)s (poly-PAEs) via Sonogashira-Hagihara coupling (Tohda et al. 1975; Sonogashira 2002) polymerization. The treatment of **17** with 1,4-diiodobenzene derivative **18** affords the optically active through-space conjugated polymers (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**19** (Morisaki et al. 2012). Chiroptical properties (chiral optical properties) of **9** showed the intense CPL in the emission region (Fig. 10.9). In addition, its absolute photoluminescence (PL) quantum efficiency ( $\Phi_{\text{PL}}$ ) was approximately 80% and the  $\lg_{\text{lum}}$  value was  $2.2 \times 10^{-3}$  in dilute CHCl<sub>3</sub> solution. These results indicated that the optically active polymer **19** is a good CPL emitter.

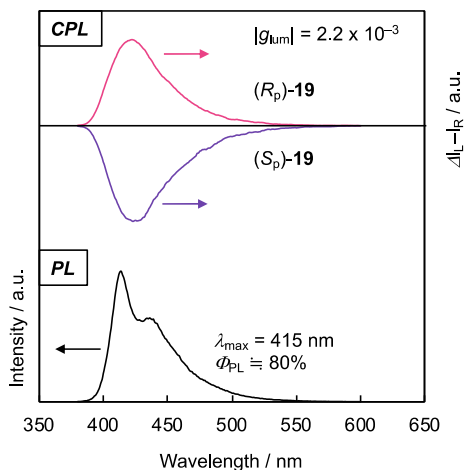
The chiroptical properties of PAE oligomers were investigated (Morisaki et al. 2014). As shown in Fig. 10.10, the optically active PAE-type  $\pi$ -stacked dimer (*R<sub>p</sub>*)-**20**, trimer (*R<sub>p</sub>*)-**21**, tetramer (*R<sub>p</sub>*)-**22**, and cyclic trimer (*R<sub>p</sub>*)-**23** were prepared from (*R<sub>p</sub>*)-**15** (shown in Fig. 10.7) and (*R<sub>p</sub>*)-**17** as the key chiral building blocks.

Figure 10.10 includes the optical and chiroptical data. The absolute anisotropic factors of absorbance ( $g_{\text{abs}}$  values = [(molar absorption coefficient of left-handed circular polarized light) – (molar absorption coefficient of right-handed circular polarized light)]/(molar absorption coefficient) at  $\lambda_{\text{abs,max}}$ ) were calculated from the

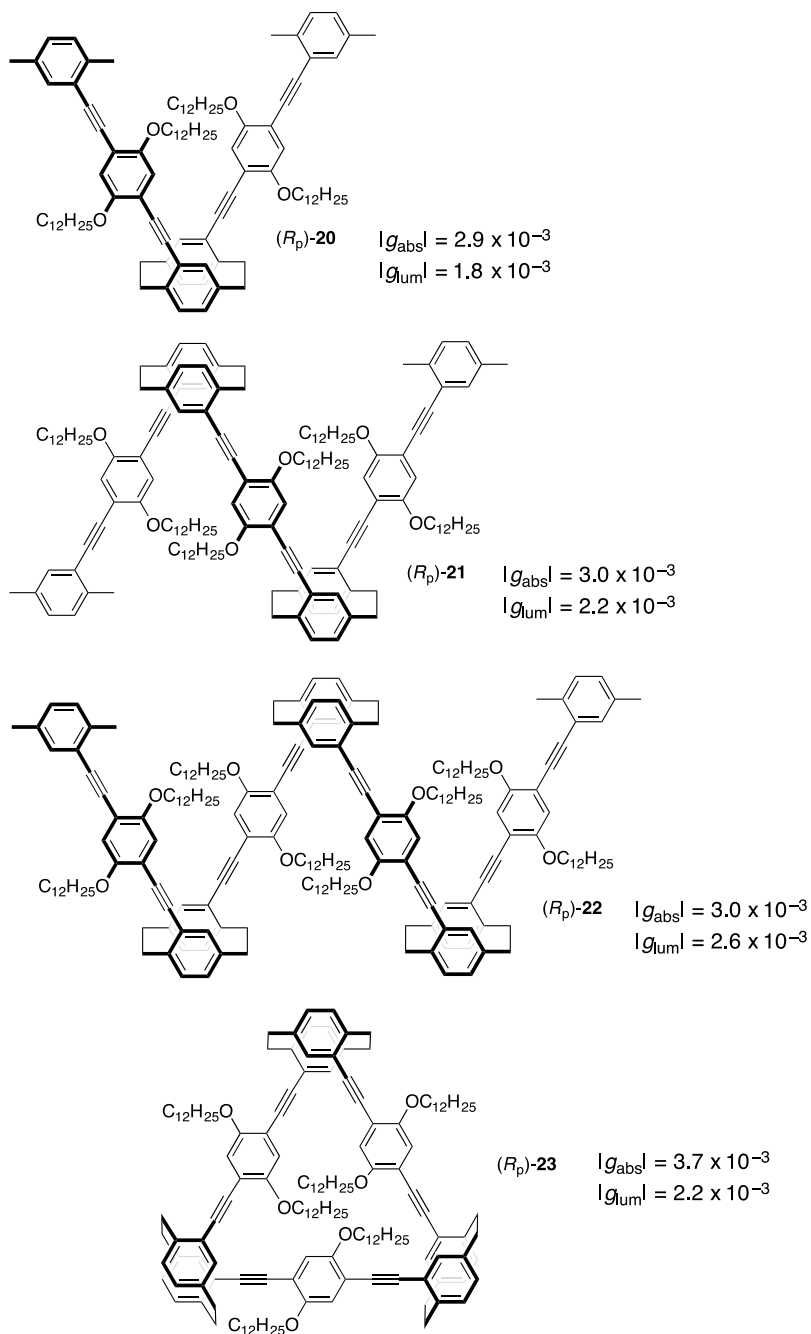


**Fig. 10.8** Synthesis of optically active polymer

**Fig. 10.9** CPL and PL spectra of  $(R_p)$ - and  $(S_p)$ -**19** in  $\text{CHCl}_3$  ( $10 \times 10^{-5}$  M) excited at 290 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL



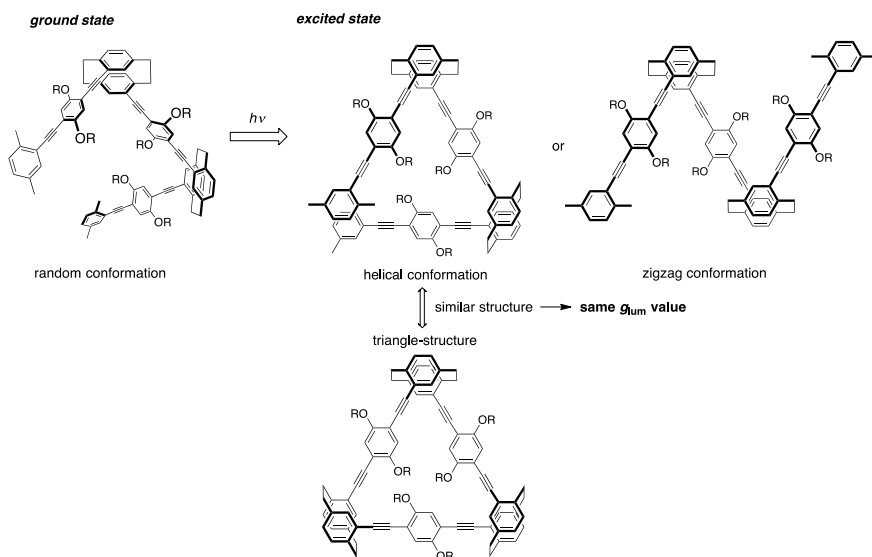
CD spectra of the optically active oligomers, and the  $|g_{lum}|$  values at  $\lambda_{\text{PL,max}}$  calculated from CPL spectra. The  $|g_{\text{abs}}|$  values of **20–22** were substantially constant at  $3.0 \times 10^{-3}$ , regardless of the number of stacked  $\pi$ -electron systems. Linearly  $\pi$ -stacked structures of **20–22** in the ground state can adopt various conformations in dilute solution, leading to the constant  $g_{\text{abs}}$  values. In other words, the constant  $g_{\text{abs}}$  values reflect only the chirality of optically active V-shaped skeleton of the cyclophane moiety. A  $g_{\text{abs}}$  value is a normalized value; therefore, the  $g_{\text{abs}}$  values of **20–22** were constant independent of the number of stacked  $\pi$ -electron systems.



**Fig. 10.10** Optically active PAE-type  $\pi$ -stacked oligomers ( $R_p$ )-20–22 and cyclic trimer ( $R_p$ )-23

In contrast, the  $g_{\text{lum}}$  values of **20–22** increased depending on the number of stacked  $\pi$ -electron systems. It is speculated that some sort of chirality is induced in addition to the optically active V-shaped structure of the cyclophane moiety in the excited state. The comparison of linear trimer **21** with cyclic trimer **23** gave the answer to this question. The  $g_{\text{abs}}$  values of **21** and **23** were different, and their  $g_{\text{lum}}$  values were identical. The cyclic structure is a fixed chiral triangle structure (fixed optically active second-order structure), whereas the linear  $\pi$ -stacked structure adopts various conformations in the ground state. Thus, chiralities of both the second-order structure (chiral triangle structure) and the V-shaped structure affect the larger  $g_{\text{abs}}$  value of **23** ( $3.7 \times 10^{-3}$ ) more than that of **21** ( $3.0 \times 10^{-3}$ ). On the other hand, the  $g_{\text{lum}}$  values of **21** and **23** were identical, indicating that **21** and **23** adopt a similar structure in the excited state. PAEs, poly(*p*-arylenevinylene)s (PAVs), and poly(*p*-arylene)s (PAs) are known to form planar structures in the excited states, because of the contribution of the quinoid moiety in the excited state. Considering the conformation of **21** in the excited state, each of the three  $\pi$ -electron systems of **21** assumes a planar structure, producing either a zigzag structure or a helical structure (foldamer) in the excited state. The  $g_{\text{lum}}$  values of **21** and **23** were identical; therefore, **21** forms a structure similar to a cyclic one, i.e., a one-handed helical structure (optically active second-order structure), as shown in Fig. 10.11.

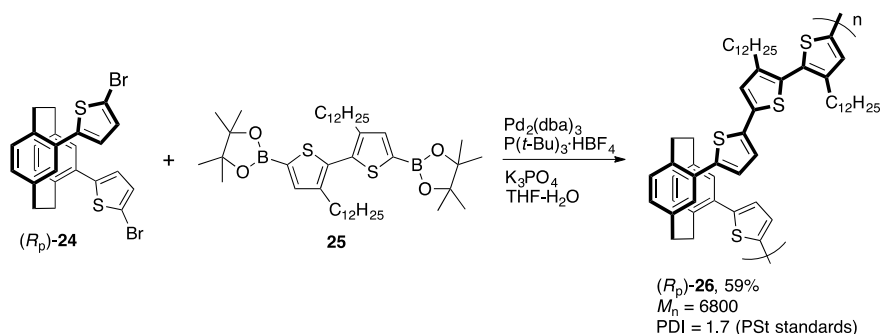
Optically active through-space conjugated polymer **26** consisting of enantiopure planar chiral 4,12-disubstituted [2.2]paracyclophane and quaterthiophene was synthesized by Suzuki-Miyaura coupling (Miyaura et al. 1979) between **24** and



**Fig. 10.11** Plausible conformations of the monomeric unit and linear trimer in the ground and excited states

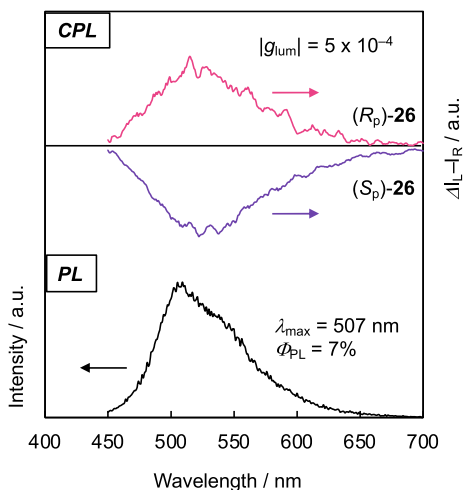
**25** (Fig. 10.12) (Morisaki et al. 2015). Moderate CPL was observed (Fig. 10.13), and the  $\Phi_{\text{PL}}$  and  $|g_{\text{lum}}|$  values were estimated to be 0.07 and  $5 \times 10^{-4}$ , respectively.

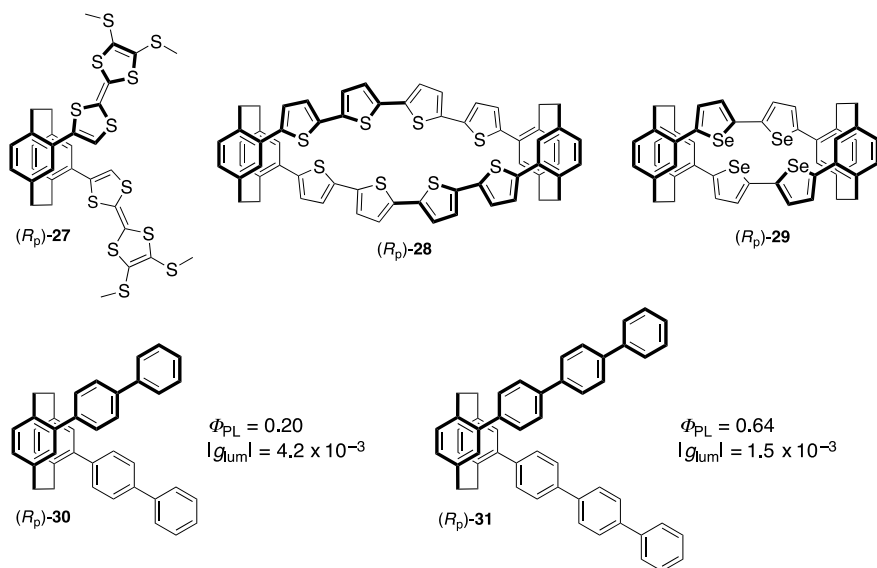
Chromatographic optical resolutions of pseudo-*ortho*-disubstituted [2.2]paracyclophanes were reported by Lützen (Meyer-Eppler et al. 2013) and Hasegawa (Kobayakawa et al. 2014; Hasegawa et al. 2017, 2019; Ishioka et al. 2019), and several enantiopure  $\pi$ -stacked molecules have been produced. Figure 10.14 shows the (*R<sub>p</sub>*)-isomers prepared by Hasegawa and coworkers (Kobayakawa et al. 2014; Hasegawa et al. 2017; Hasegawa et al. 2019; Ishioka et al. 2019). Although the CPL properties of these compounds were not reported, their interesting chiroptical and electrochemical properties were shown. Compound **27** was used as a chiral dopant for nematic liquid crystals with a helical twisting power of around  $10 \text{ m}^{-1}$  (Kobayakawa et al. 2014), and **28** (Hasegawa et al. 2017) and **29** (Hasegawa et al. 2019) exhibited



**Fig. 10.12** Synthesis of optically active polymer consisting of [2.2]paracyclophane and quaterthiophene

**Fig. 10.13** CPL and PL spectra of (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**26** in  $\text{CHCl}_3$  ( $10 \times 10^{-5} \text{ M}$ ) excited at 380 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL



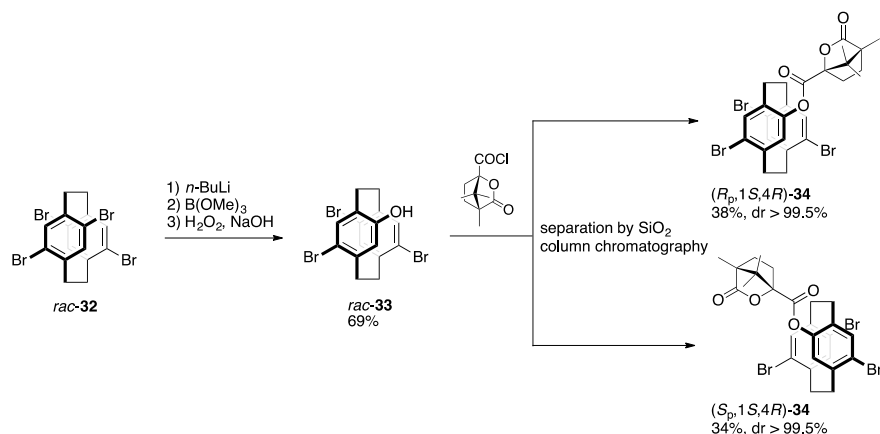


**Fig. 10.14** Pseudo-*ortho*-disubstituted [2.2]paracyclophane-based chiral molecules

unique redox behaviors owing to the closely stacked quaterthiophenes and biselenophenes, respectively. Recently, PA-type  $\pi$ -stacked molecules **30** and **31** have been reported, in which terphenylenes and quaterphenylenes were stacked at the terminal benzene rings (Ishioka et al. 2019), respectively, as shown in Fig. 10.14. Intense CPL was observed from **30** with  $\Phi_{\text{PL}}$  of 0.20 and  $|g_{\text{lum}}|$  of  $4.2 \times 10^{-3}$  as well as **31** with  $\Phi_{\text{PL}}$  of 0.64 and  $|g_{\text{lum}}|$  of  $1.5 \times 10^{-3}$ .

## 10.4 Synthesis of Enantiopure 4,7,12,15-Tetrasubstituted [2.2]Paracyclophane and Optically Active $\pi$ -Stacked Molecules

In 2014, an optical resolution method of 4,7,12,15-tetrasubstituted [2.2]paracyclophane was reported (Fig. 10.15) (Morisaki et al. 2014). The racemate 4,7,12,15-tetrabromo[2.2]paracyclophane *rac*-**32** was synthesized by Chow and coworkers (Chow et al. 2005). One of the bromo groups of *rac*-**32** was converted to a hydroxy group to obtain *rac*-**33**, and the reaction with (1*S*,4*R*)-(-)-camphanic chloride as a chiral auxiliary resulted in the diastereomers (*R*<sub>p</sub>,1*S*,4*R*)-**34** and (*S*<sub>p</sub>,1*S*,4*R*)-**34**. The absolute configuration could be determined by X-ray crystallography. Separation of diastereomers was readily carried out in gram-scale by simple SiO<sub>2</sub> column chromatography.

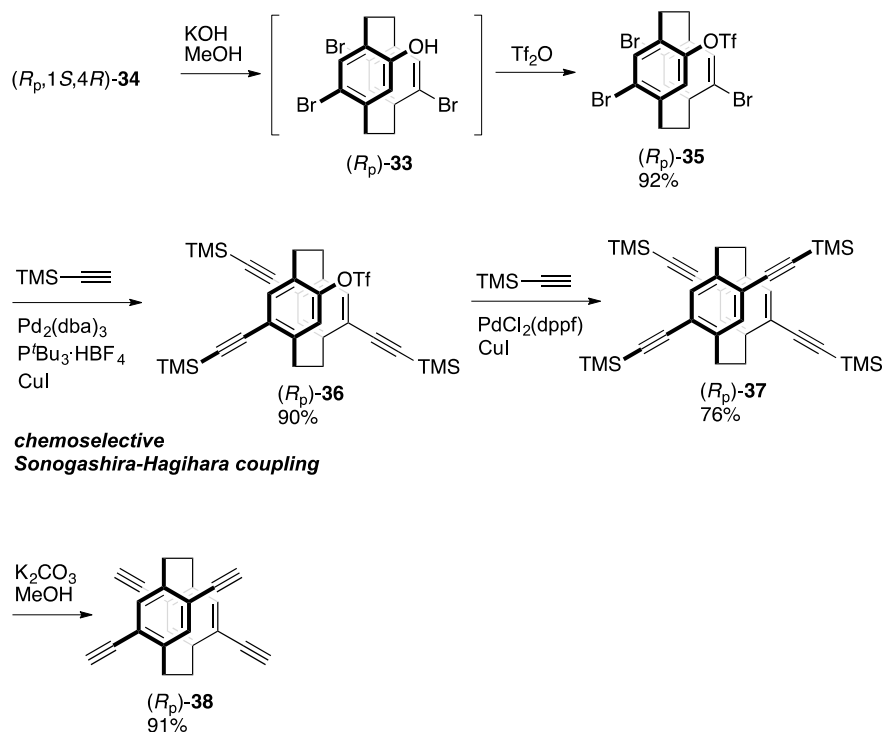


**Fig. 10.15** Optical resolution of 4,7,12,15-tetrabromo [2.2]paracyclophane

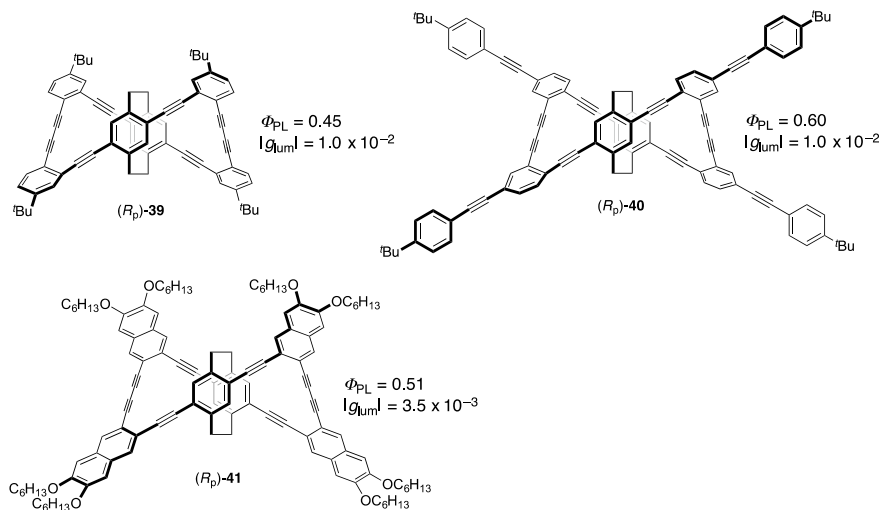
The chiral unit was easily removed by hydrolysis to afford the optically active phenol **33** (Fig. 10.16). The treatment of **33** with trifluoromethanesulfonic anhydride afforded the optically active 4,7,12,15-tetrabromo [2.2]paracyclophane **35**. Subsequent Sonogashira-Hagihara coupling between the optically active cyclophane **35** with trimethylsilyl (TMS) acetylene proceeded smoothly to afford triyne **36** with good yield. Interestingly, Pd<sub>2</sub>(dba)<sub>3</sub>/P'<sup>t</sup>Bu<sub>3</sub>/CuI catalyst system (dba = dibenzylideneacetone and P'<sup>t</sup>Bu<sub>3</sub> = tri(*t*-butyl)phosphine) led to chemoselective coupling with bromo groups. Then, the remaining trifluoromethylsulfonyl group could be reacted with TMS acetylene using a PdCl<sub>2</sub>(dppf) catalyst (dppf = 1,1'-bis(diphenylphosphino)ferrocene) to give the optically active tetrayne **37**. The TMS groups were removed to give the optically active 4,7,12,15-tetraethynyl[2.2]paracyclophane **38**.

Optically active cyclic molecules **39–41** were synthesized with **38** serving as a chiral building block (Fig. 10.17), and their chiroptical properties were revealed. The large chirality was induced in both the ground state and the excited state. For example, the specific rotation of **39** was approximately 1,500, and the molar ellipticity reached 3,000,000 deg cm<sup>2</sup> dmol<sup>-1</sup>. Cyclic molecule **39** exhibited excellent CPL profiles (Fig. 10.18), and the  $|g_{\text{lum}}|$  value at  $\lambda_{\text{PL,max}}$  was on the order of 10<sup>-2</sup> with  $\Phi_{\text{PL}}$  of 0.45. In addition to the planar chirality of the [2.2]paracyclophane skeleton, the chiral second-order structure, namely, the chiral two blades propeller-shaped structure contributed to the chiral induction in the excited state. The propeller-shaped molecules **40** (Gon et al. 2015) and **41** (Gon et al. 2016) showed a large molar absorption coefficient, good  $\Phi_{\text{PL}}$ , and large CPL  $g_{\text{lum}}$  value. Especially, propeller-shaped molecule **40** was also an excellent CPL emitter with a large  $g_{\text{lum}}$  value and good  $\Phi_{\text{PL}}$  of 0.60.

Optically active X-shaped molecules **42–44** were synthesized from 4,7,12,15-tetrabromo [2.2]paracyclophane **38** (Fig. 10.19) (Gon et al. 2015). Various aromatic units such as benzene, naphthalene, and anthracene could be introduced to

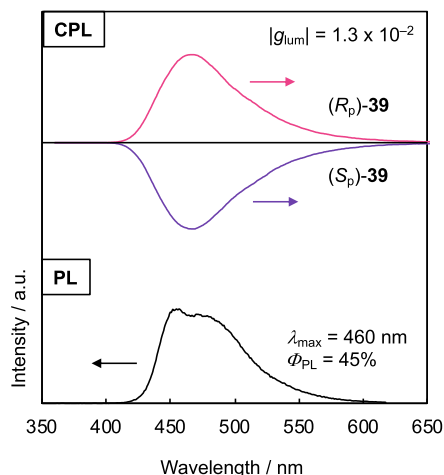


**Fig. 10.16** Synthesis of optically active 4,7,12,15-tetrasubstituted [2.2]paracyclophane building blocks

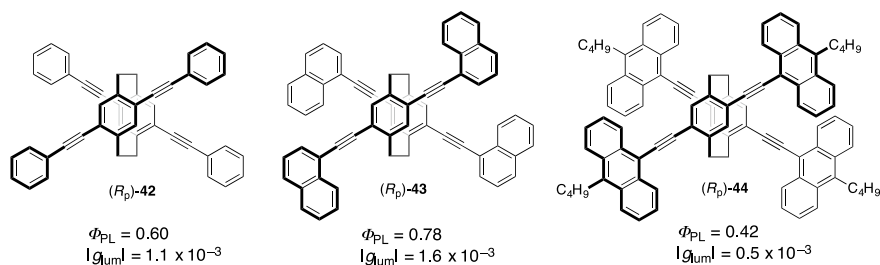


**Fig. 10.17** Chiral propeller-shaped molecules based on optically active 4,7,12,15-tetrasubstituted [2.2]paracyclophane





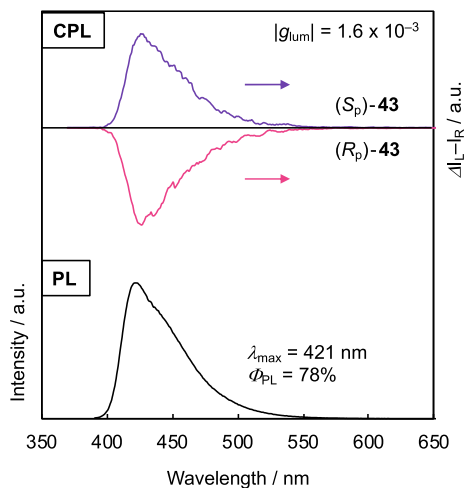
**Fig. 10.18** CPL and PL spectra of (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**39** in  $\text{CHCl}_3$  ( $10 \times 10^{-6}$  M) excited at 314 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL



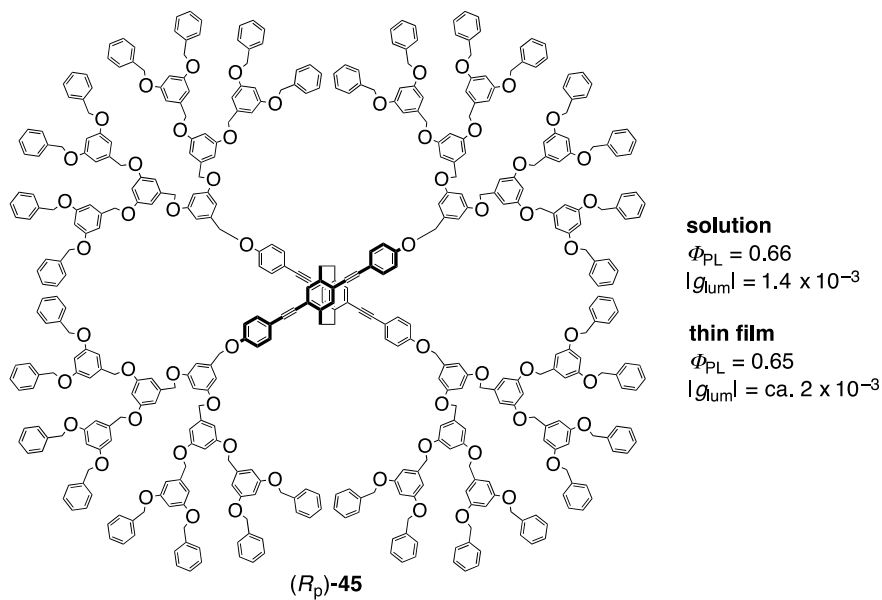
**Fig. 10.19** Structures of chiral X-shaped molecules

the 4,7,12,15-tetrasubstituted [2.2]paracyclophane skeleton. All compounds emitted CPL with good  $\Phi_{\text{PL}}$ , and large CPL  $g_{\text{lum}}$  value; as a representative example, PL and CPL spectra of **43** are shown in Fig. 10.20.

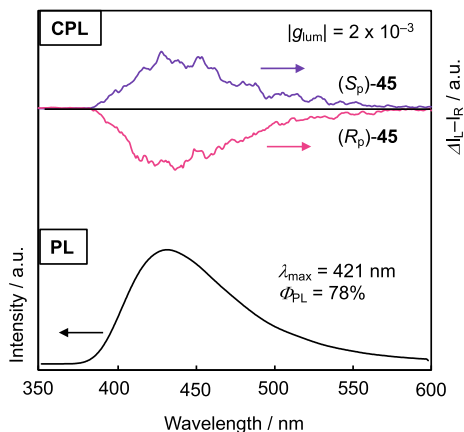
Figure 10.21 shows the 3rd generation chiral dendrimer (Gon et al. 2016) consisting of a chiral X-shaped core and Fréchet-type dendrons that were prepared by the convergent method (Hawker and Fréchet 1990; Fréchet 1994). The 2nd to 4th generation dendrimers exhibited good film-forming ability, and the thin films could be obtained by the spin-coating approach. The thin film emitted bright CPL from the chiral core unit upon excitation of the benzene rings of dendrons. Energy transfer occurred from the dendrons to the chiral core, and intense PL was emitted. Due to the dendrons, aggregation-caused quenching was completely suppressed, and thus, the bright CPL was observed; CPL and PL spectra are shown in Fig. 10.22. The  $\Phi_{\text{PL}}$  of the thin films were estimated to be 65%, and the  $g_{\text{lum}}$  value at  $\lambda_{\text{PL,max}}$  was approximately  $2 \times 10^{-3}$ .



**Fig. 10.20** CPL and PL spectra of (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**43** in  $\text{CHCl}_3$  ( $10 \times 10^{-5}$  M) excited at 300 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL

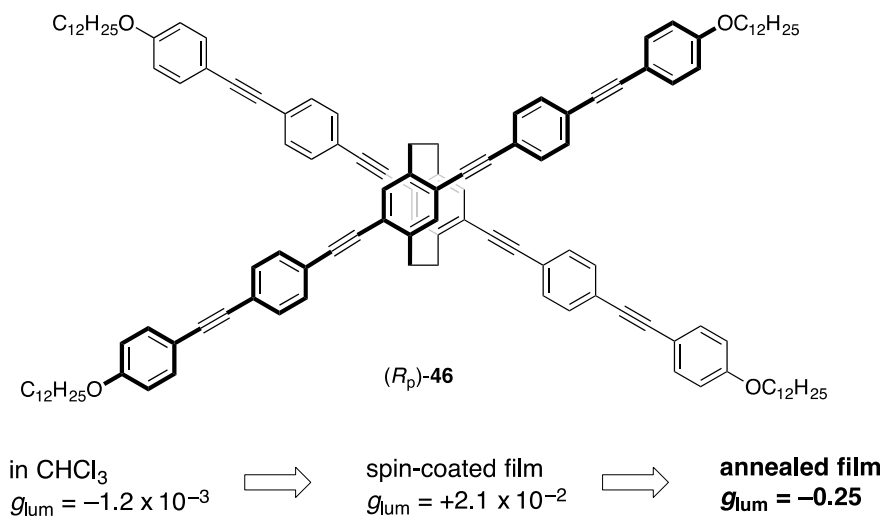


**Fig. 10.21** Structure of chiral dendrimer with a chiral X-shaped [2.2]paracyclophane core

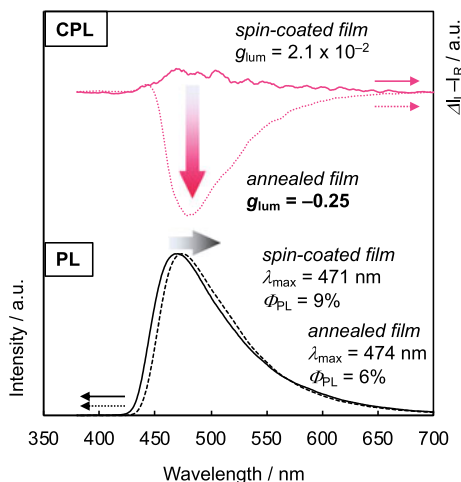


**Fig. 10.22** CPL and PL spectra of the thin film of (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**45** excited at 279 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL

An optically active X-shaped molecule **46** consisting of a more extended  $\pi$ -conjugation system was prepared from **38** as a chiral building block (Fig. 10.23) (Gon et al. 2017). The X-shaped molecule **46** emitted CPL with  $\Phi_{\text{PL}}$  of 87% in the dilute solution with a good  $|g_{\text{lum}}|$  value of  $1.2 \times 10^{-3}$ . In addition, this molecule showed good film formability. The  $g_{\text{lum}}$  value of the thin film formed by the spin-coating method exhibited the positive CPL signal with the  $g_{\text{lum}}$  value of  $+2.1 \times 10^{-2}$  (Fig. 10.24), which was larger by one order of magnitude compared with that the dilute solution. The annealed spin-coated film exhibited a negative  $g_{\text{lum}}$  value of



**Fig. 10.23** Structure of chiral X-shaped molecule (*R<sub>p</sub>*)-**46** and the CPL profiles

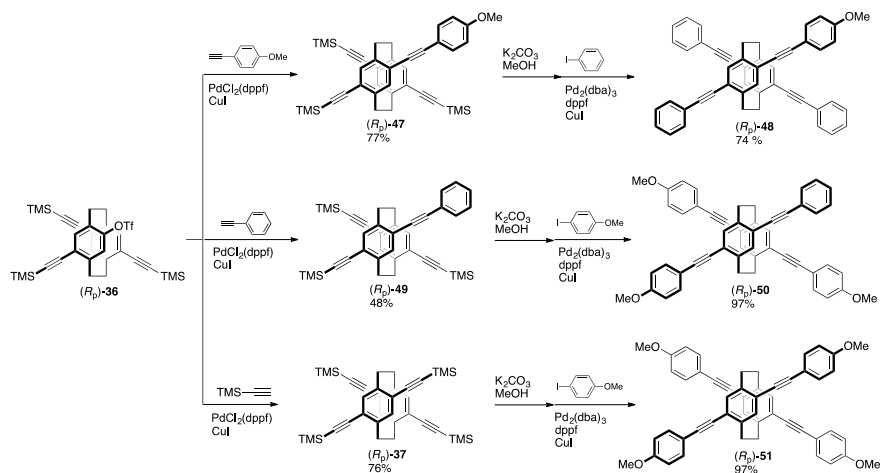


**Fig. 10.24** CPL and PL spectra of the spin-coated and the annealed film of (*R<sub>p</sub>*)-**46**

−0.25 (Fig. 10.24), which was a very large value on the order of  $10^{-1}$ . The optically active higher-ordered structure was constructed in the thin film by  $\pi$ - $\pi$  interactions among the extended  $\pi$ -conjugation systems, as well as the van der Waals force of the  $C_{12}H_{25}$  chains. It seems that the thermodynamically stable higher-ordered structure was formed by the heating protocol.

Chemoselective Sonogashira-Hagihara coupling using  $Pd_2(dba)_3/P^tBu_3$  catalyst system was utilized to stack different  $\pi$ -electron systems (Sasai et al. 2018). The triyne **36** mentioned above was used as the substrate to produce chiral X-shaped  $\pi$ -stacked dimers **48** and **50** consisting of different  $\pi$ -electron systems as shown in Fig. 10.25. Normal X-shaped molecule **51** was also prepared from **36** via **37** (Gon et al. 2017; Kikuchi et al. 2019). The optical, as well as chiroptical properties of **48** and **50**, were almost the same as those of the corresponding X-shaped molecule **51** (Table 10.1). The number of methoxy groups increased, spectra were redshifted and  $\Phi_{PL}$  and  $g_{lum}$  values were increased. Thus, they were excellent CPL emitters.

Optically active *p*-arylene-vinylenes (PAVs)-stacked X-shaped molecules **52** and **53** were also prepared (Gon et al. 2017), and the structures are shown in Fig. 10.26. Racemic molecule **52** was prepared and their properties were investigated in detail (Bazan et al. 1998; Bartholomew and Bazan 2001; Bazan 2007; Morisaki and Chujo 2002). Molecule **52** exhibited CPL with a good  $\Phi_{PL}$  of 0.78 and  $|g_{lum}|$  value of  $3.7 \times 10^{-3}$ , while the PL of the aggregates quenched to exhibit  $\Phi_{PL}$  of 0.03 with good  $|g_{lum}| = 4.3 \times 10^{-3}$ . Molecule **53** showed moderate PL profiles both in solution ( $\Phi_{PL} = 0.58$ ) and in the aggregated state ( $\Phi_{PL} = 0.24$ ), and moderate CPL properties with  $|g_{lum}|$  in the order of  $10^{-4}$  in solution, as well as in the aggregation state were observed. The optical and chiroptical properties varied drastically by attaching phenyl groups to the ethene moieties.

Fig. 10.25 Synthesis of X-shaped  $\pi$ -stacked dimersTable 10.1 Optical and chiroptical data of **48**, **50**, and **51** in the diluted solutions

Compound	UV $\lambda_{\max}/\text{nm}$ ( $\epsilon/10^5 \text{ cm}^{-1} \text{ M}^{-1}$ )	PL $\lambda_{\max}/\text{nm}$	$\Phi_{\text{PL}}$	CPL $ g_{\text{lum}} $
<b>48</b>	352 (0.60)	420	0.71	$1.5 \times 10^{-3}$
<b>50</b>	357 (0.56)	424	0.73	$1.7 \times 10^{-3}$
<b>51</b>	361 (0.68)	427	0.75	$1.7 \times 10^{-3}$

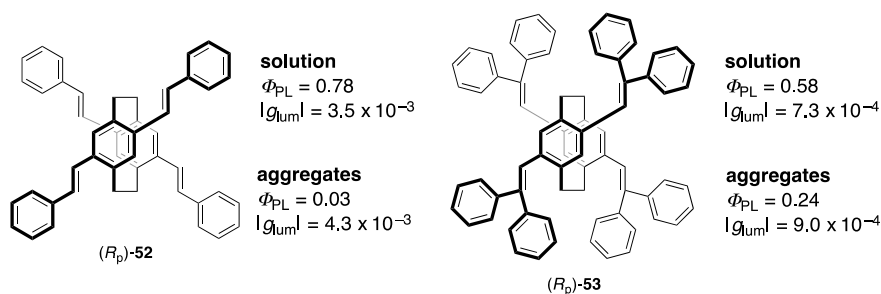
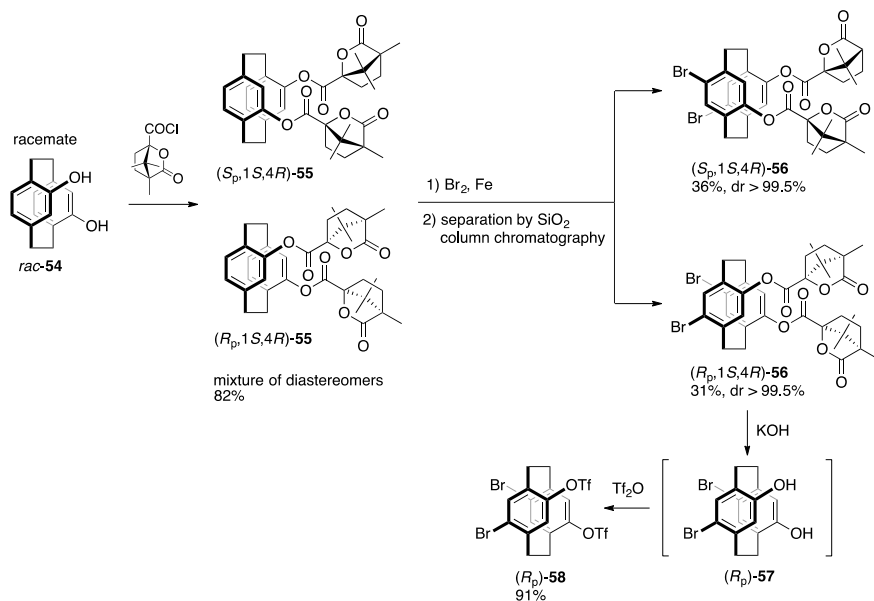


Fig. 10.26 Structures of chiral X-shaped molecules consisting of PAVs

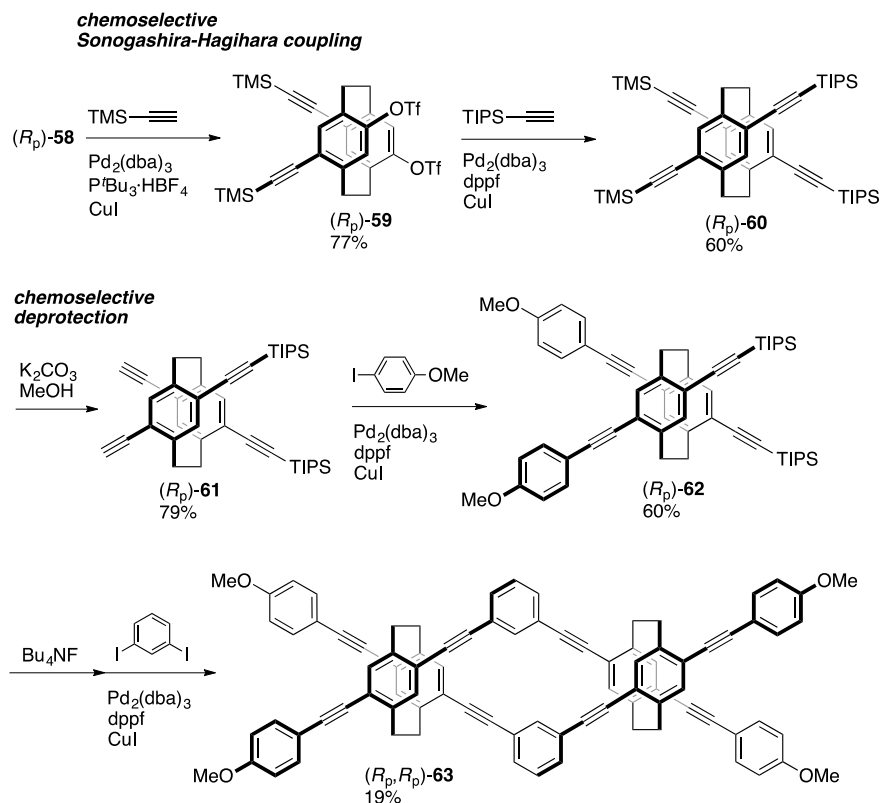
## 10.5 Synthesis of Enantiopure Bis-(*Para*)-Pseudo-*Ortho*-Tetrasubstituted [2.2]Paracyclophane and Syntheses of Optically Active $\pi$ -Stacked Molecules

In 2016, a new type of enantiopure 4,7,12,15-tetrasubstituted [2.2]paracyclophane was produced. Racemic bisphenol *rac*-**54** was used as a starting material and reacted with (1*S*,4*R*)-(-)-camphanic chloride as a chiral auxiliary to obtain the diastereomers (*R<sub>p</sub>*,1*S*,4*R*)-**55** and (*S<sub>p</sub>*,1*S*,4*R*)-**55** (Figs. 10.6c, 10.27) (Jiang and Zhao 2004). The diastereomers were reacted with bromine using iron without separation (Fig. 10.27). Regioselective bromination proceeded with iron to obtain 4,7,12,15-tetrasubstituted [2.2]paracyclophanes (*R<sub>p</sub>*,1*S*,4*R*)-**56** and (*S<sub>p</sub>*,1*S*,4*R*)-**56** (Kikuchi et al. 2019; Morisaki et al. 2016); this tetrasubstituted isomer is called bis-(*para*)-pseudo-*ortho*-tetrasubstituted [2.2]paracyclophane (Vorontsova et al. 2008). The diastereomers were separated by simple column chromatography using SiO<sub>2</sub>. Removal of the chiral auxiliary groups with KOH formed chiral bisphenol **57**, and the successive reaction with trifluoromethanesulfonic anhydride resulted in enantiopure bis-(*para*)-pseudo-*ortho*-type tetrasubstituted [2.2]paracyclophane building blocks **58** (Morisaki et al. 2016).

Chemoselective Sonogashira-Hagihara coupling was available for **58**. The treatment of **58** with TMS acetylene in the presence of a catalytic amount of



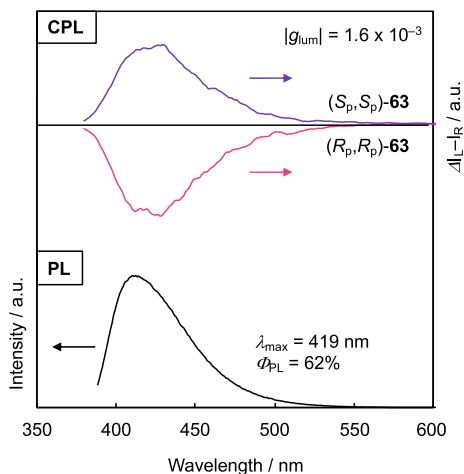
**Fig. 10.27** Optical resolution of 4,7,12,15-bis-(*para*)-pseudo-*ortho*-type tetrasubstituted [2.2]paracyclophane and the transformations



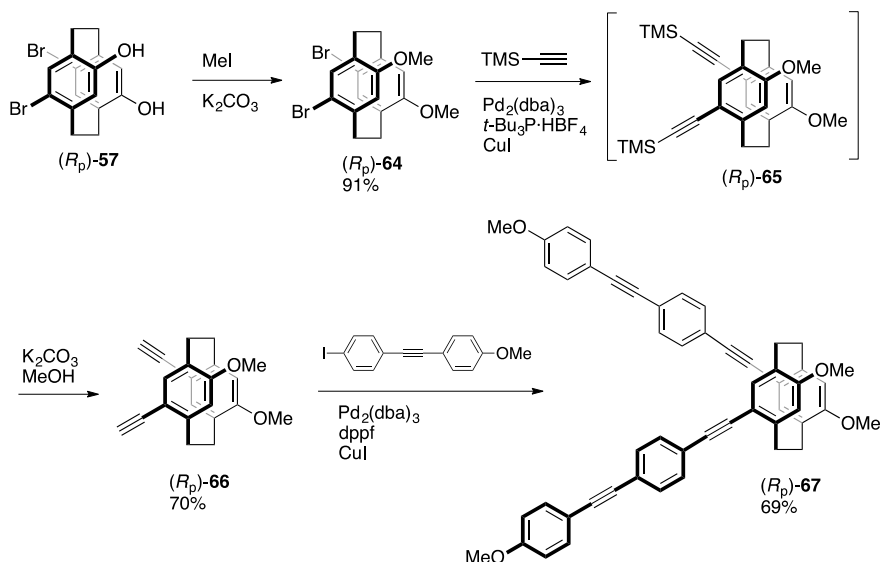
**Fig. 10.28** Synthesis of one-handed double helical molecule

$\text{Pd}_2(\text{dba})_3/\text{P}'\text{Bu}_3/\text{CuI}$  afforded the diyne **59** selectively, as shown in Fig. 10.28. The coupling reaction between **59** with triisopropylsilyl (TIPS) acetylene using a  $\text{Pd}_2(\text{dba})_3/\text{dppf}$  catalyst system enabled us to obtain the corresponding tetrayne **60**.  $\text{K}_2\text{CO}_3/\text{MeOH}$  allowed the chemoselective removal of the TMS group from **60** to obtain diyne **61**. Then, Sonogashira-Hagihara coupling of **60** with *p*-iodoanisole produced **62**. The TIPS group was easily removed by  $\text{Bu}_4\text{NF}$ , and the reaction with *m*-diiodobenzene provided enantiopure cyclic molecule **63** consisting of two optically active cyclophanes, in which boomerang-shaped arylene-ethynylene containing five benzene rings are stacked at the second and fourth phenylene moieties. This cyclic molecule forms a one-handed double helical structure; for example, the (*R<sub>p</sub>*, *R<sub>p</sub>*)-isomer construct left-handed double helices. This double helical molecule also emitted intense CPL with  $\Phi_{\text{PL}}$  of 0.62 and  $|g_{\text{lum}}| = 1.6 \times 10^{-3}$ ; the PL and CPL spectra are shown in Fig. 10.29.

Enantiopure bisphenol **57** was reacted with  $\text{K}_2\text{CO}_3$  and MeI to obtain a new chiral building block (*R<sub>p</sub>*)-**64** in high yield (Fig. 10.30) (Kikuchi et al. 2019). The reaction of (*R<sub>p</sub>*)-**64** with TMS acetylene in the presence of  $\text{Pd}_2(\text{dba})_3/\text{P}'\text{Bu}_3/\text{CuI}$



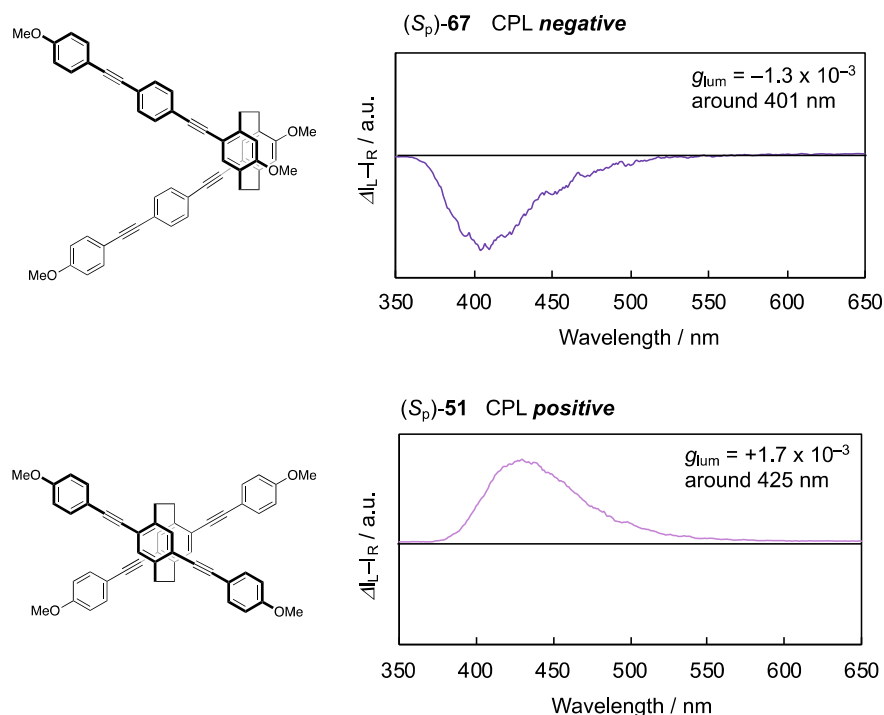
**Fig. 10.29** CPL and PL spectra of (*R<sub>p</sub>*)- and (*S<sub>p</sub>*)-**63** in  $\text{CHCl}_3$  ( $10 \times 10^{-5}$  M) excited at 300 nm for CPL and  $\lambda_{\text{abs,max}}$  for PL



**Fig. 10.30** Synthesis of chiral V-shaped molecule

catalyst system proceeded smoothly to obtain the cross-coupling product (*R<sub>p</sub>*)-**65**. The TMS groups of (*R<sub>p</sub>*)-**65** were easily removed by  $\text{K}_2\text{CO}_3/\text{MeOH}$  to obtain diene (*R<sub>p</sub>*)-**66**. The Sonogashira-Hagihara reaction of (*R<sub>p</sub>*)-**66** with iodotoluene derivative resulted in the corresponding V-shaped molecule (*R<sub>p</sub>*)-**67** (Fig. 10.30). In molecule **67**,  $\pi$ -electron systems are stacked at the terminal benzene rings, whereas the same

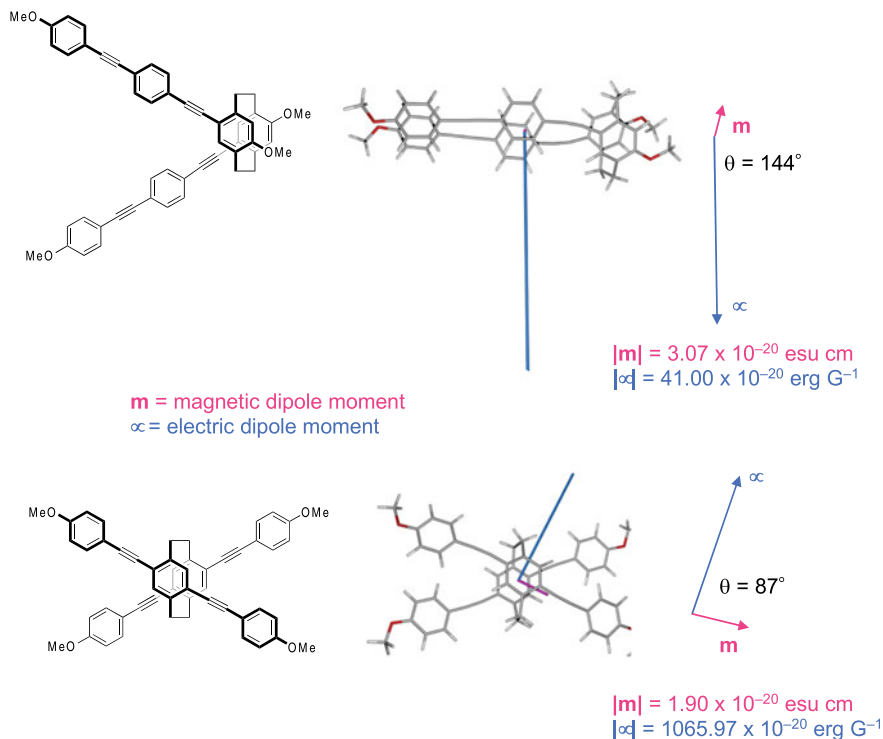




**Fig. 10.31** CPL spectra of (*S<sub>p</sub>*)-**67** and **51** in  $\text{CHCl}_3$  ( $10 \times 10^{-5}$  M)

$\pi$ -electron systems are stacked at the central benzene rings in the X-shaped molecule **51** (Fig. 10.25). Their CPL spectra are shown in Fig. 10.31, indicating the opposite CPL signs in spite of having the same absolute configuration. Incidentally, Fig. 10.31 shows the spectra of (*S<sub>p</sub>*)-isomers, because the simulation was carried out for them (vide infra).

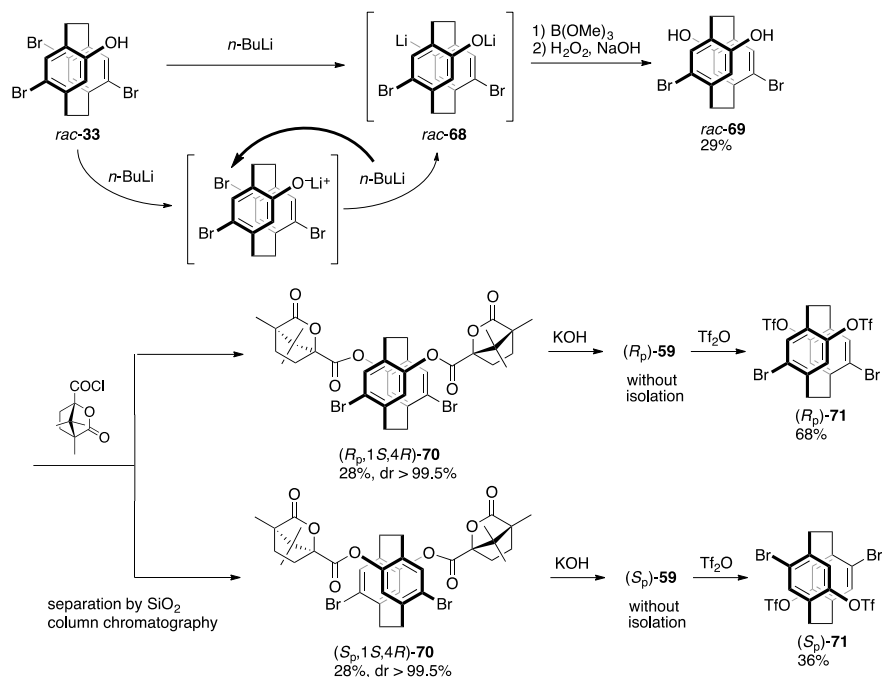
The electronic transition dipole moments and magnetic transition dipole moments were simulated for V-shaped **67** and X-shaped **51** (Fig. 10.32) (Kikuchi et al. 2019); the simulations were carried out for (*S<sub>p</sub>*)-isomers. Theoretically, a  $g_{lum}$  value is expressed in the following equation:  $4|\boldsymbol{\mu}||\mathbf{m}|\cos\theta/(|\boldsymbol{\mu}|^2 + |\mathbf{m}|^2)$  as mentioned. The  $\boldsymbol{\mu}$  and  $\mathbf{m}$  represent electric and magnetic transition dipole moments, respectively, and the  $\theta$  represents the angle between the  $\boldsymbol{\mu}$  and  $\mathbf{m}$ . The angle  $\theta$  between  $\boldsymbol{\mu}$  and  $\mathbf{m}$  of (*S<sub>p</sub>*)-**67** was estimated to be  $144^\circ$ , and that of (*S<sub>p</sub>*)-**51** was estimated to be  $87^\circ$ . Simulation results predicted opposite CPL signs for **67** (negative due to  $\theta = 144^\circ$ ) and **51** (positive due to  $\theta = 87^\circ$ ), which was supported by the experimental results (Fig. 10.31). Thus, the appropriate construction of the intermolecular orientations of  $\pi$ -electron systems is important not only for CPL intensity, but also for CPL signs. In other words, negative and positive signs of CPL can be controlled by the orientation of the  $\pi$ -electron systems.



**Fig. 10.32** Simulation results: the transition dipole moments of (*S<sub>p</sub>*)-**67** and (*S<sub>p</sub>*)-**51** in the excited states by using the TD-DFT calculations at the  $\omega$ B97XD/6-31G(d,p) level of theory with following options; TD = (NStates = 10, Root = 1), SCRF = (SOLVENT = Chloroform). Lengths of the dipole moments on the structures are based on the atomic units

## 10.6 Synthesis of Enantiopure Bis-(*Para*)-Pseudo-*Meta*-Tetrasubstituted [2.2]Paracyclophane

In 2018, enantiopure bis-(*para*)-pseudo-*meta*-tetrasubstituted [2.2]paracyclophane derivatives were prepared as new chiral building blocks by means of diastereomeric optical resolution (Sawada et al. 2018). On the other hand, Lützen and coworkers had already reported the chromatographic optical resolution of disubstituted analogs in 2014 (Meyer-Eppler et al. 2014). Racemic 4,7,12,15-tetrasubstituted [2.2]paracyclophane *rac*-**33** was used as the starting material, which was reacted with BuLi to form the dilithiated intermediate *rac*-**68** (Fig. 10.33). After the formation of lithium phenoxide, the next lithium-halogen exchange occurred at pseudo-*meta*-position due to the electronic effect, leading to bis-(*para*)-pseudo-*meta*-type dilithiated [2.2]paracyclophane. Addition of B(OMe)<sub>3</sub> to the intermediate and the treatment with H<sub>2</sub>O<sub>2</sub>/NaOH resulted in dibromodihydroxy[2.2]paracyclophane *rac*-**69**.



**Fig. 10.33** Optical resolution of 4,7,12,15-bis-(*para*)-pseudo-*meta*-type tetrasubstituted [2.2]paracyclophane and the transformations

Diastereomer approach using (1*S*,4*R*)-(-)-camphanic chloride enabled the optical resolution of the bis-(*para*)-pseudo-*meta*-type tetrasubstituted [2.2]paracyclophane (Fig. 10.33). The resulting diastereomers (*R*<sub>p</sub>,1*S*,4*R*)-**70** and (*S*<sub>p</sub>,1*S*,4*R*)-**70** were separated by simple column chromatography using SiO<sub>2</sub>. The reaction of **70** with KOH afforded the bisphenol and the next reaction with trifluoromethanesulfonic anhydride produced enantiopure bis-(*para*)-pseudo-*meta*-type tetrasubstituted [2.2]paracyclophanes **71**. These enantiomers are also used as the chiral building blocks for various CPL emitters.

## 10.7 Conclusion

In summary, the authors have focused on the planar chirality of [2.2]paracyclophane and the intense CPL emission from the enantiopure [2.2]paracyclophane-based molecules in this chapter. Their optical resolution methods basically consisted of diastereomer resolution methods using the common chiral auxiliaries such as (1*R*,2*S*,5*R*)-(-)-menthyl-*p*-toluenesulfinate and (1*S*,4*R*)-(-)-camphanic chloride

instead of chromatographic resolution by chiral columns. A wide variety of optically active  $\pi$ -stacked molecules, cyclic molecules, oligomers, and polymers were prepared using the obtained enantiopure disubstituted and tetrasubstituted [2.2]paracyclophanes as chiral building blocks. They were used to construct the chiral higher-ordered structures such as V-shaped, X-shaped, propeller-shaped, triangle-shaped, and double helical structures both in the ground and excited states due to the structurally stable planar chiral cyclophanes. This is important to show excellent CPL performance. [2.2]Paracyclophane-based molecules exhibit good PL property with high  $\Phi_{\text{PL}}$ . Their  $\epsilon$  values are large because of the extended  $\pi$ -electron systems. Generally, it is difficult to produce the materials emitting intense CPL with high  $\Phi_{\text{PL}}$  and large  $g_{\text{lum}}$ . The planar chiral [2.2]paracyclophane skeleton seems to be an ideal scaffold for developing materials exhibiting strong CPL.

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