Chapter 1
Element-Block Materials: New Concept for the Development of Advanced Hybrids and Inorganic Polymers

Masayuki Gon, Kazuo Tanaka, and Yoshiki Chujo

Abstract By incorporating highly functional inorganic units in organic materials, the creation of advanced materials possessing both advantages of organic components such as designability and good processability and inorganic elements can be expected. However, there are several difficulties in combination with organic and inorganic components due to intrinsic low compatibility between organic and inorganic components. Although organic-inorganic hybrids have been developed, further strategies for material design such as for precise controls of nanostructures in the hybrids are strongly required. To meet these demands, we propose the new concept for material design based on an "element-block" which is defined as a minimum functional unit composed of heteroatoms. In this chapter, the basic idea of an "element-block" and the recent progresses in the development of "element-block materials" are mainly from our recent works. As a representative example, we illustrate the element-blocks involving specific steric structures such as polyhedral oligomeric silsesquioxane (POSS), modified boron dipyrromethenes (BODIPYs) having the cardo boron and [2.2]paracyclophanes as a chiral source and explain material properties originated from these element-blocks. The roles of these element-blocks in the materials are explained.

Keywords Hybrid · POSS · Boron · BODIPY · [2.2]Paracyclophane

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1.1   Introduction

1.1.1   New Concept for Material Design Based on "Element-Blocks"

Inorganic materials show high performances especially in photonics, electronics, and magnetics, and many researchers have continuously devoted huge efforts for exploring new substances. By incorporating these functional inorganic units in organic materials, it can be expected that advanced materials possessing both advantages of organic components such as designability and good processability as well as inorganic elements. However, there are several difficulties in combination with organic and inorganic components. Basically, due to distinct different compatibility between both elements, further technological advancements are commonly needed in all size scales. In the molecular scale, only small electronic interaction between both components was often obtained. Moreover, the introduction of heteroatoms often caused distortion of molecular skeletons, followed by loss of electronic conjugation. From the nano-sizes to bulk sizes, phase separation often occurred, resulting in losses of physical properties as a material. To overcome this problem, the idea of organic-inorganic hybrids was proposed, and indeed when homogeneous mixing states were able to be realized, synergetic effects were obtained [1]. However, in the conventional preparation methods for hybrid formation known as a sol-gel method, chemical modification to each component and/or severe condition controls are necessary to achieve homogeneous mixtures which are essential to express superior functions. Moreover, it is still challenging to form nanostructures according to the design. In view of this situation, we proposed the new concept "element-block materials" [2]. An element-block is defined as a minimum functional unit composed of heteroatoms, and it was expected that element-block materials can be fabricated by combination, assembly, and organization with these element-blocks (Fig. 1.1). Through discovery of new element-blocks and development of element-block materials, we desired not only to accumulate significant information on interaction and interfaces among element-blocks and matrices but also to establish robust and effective hybridization protocols between organic and inorganic components for producing advanced functional materials based on the preprogrammed design.

1.1.2   Overview

We describe here several examples from our recent works based on the idea of "element-block materials." As a representative research, we selected the element-blocks involving specific steric structures such as polyhedral oligomeric silsesquioxane (POSS), modified boron dipyrromethenes (BODIPYs) having the cardo boron and [2.2]paracyclophanes as a chiral source and explain material
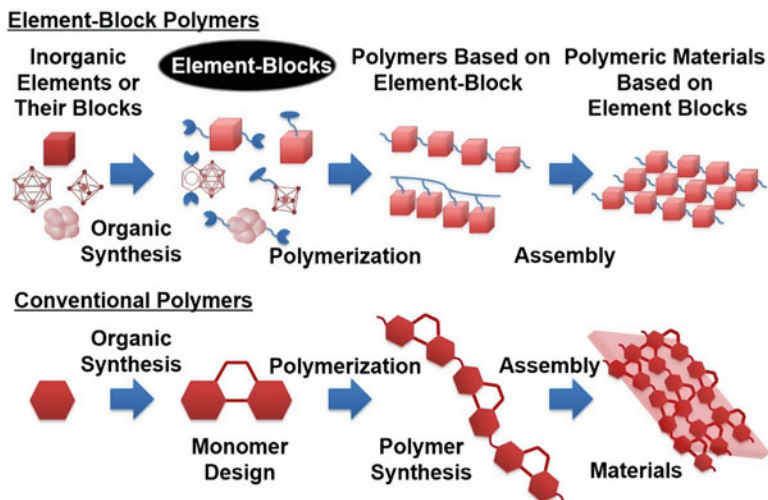
Fig. 1.1 Schematic models of the development of element-block materials
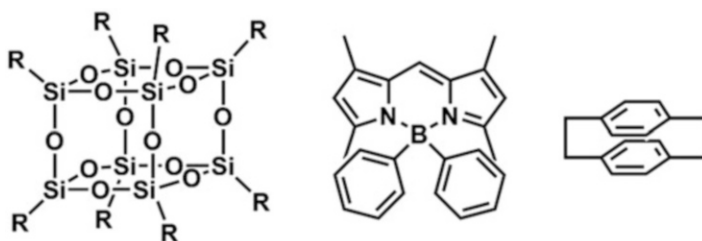

Fig. 1.2 Element-blocks introduced in this section

properties originated from these element-blocks (Fig. 1.2). Initially, the recent progresses in organic-inorganic hybrids based on POSS element-blocks with high thermal stability and extra functions are demonstrated. By employing POSS, various optical materials can be transformed to the hybrid materials. As a result, thermally stable optical materials were obtained. Furthermore, multiple functions including the trade-off relationships were observed. The mechanisms are explained here. Next topics are on the construction of conjugated polymers involving the cardo boron. The series of phenyl-bearing modified BODIPYs with the cardo structure were built, and their luminescent properties were evaluated. Characteristic behaviors in solid-state emission and energy transferring through the cardo boron are shown here. The roles of [2.2]paracyclophane element-blocks in the optically active materials are also described as the last topic. By incorporating the [2.2]paracyclophane unit into electronic conjugation, significant optical behaviors can be induced. Unique functions originated from structural features of these element-blocks are presented here.

1.2   Unique Thermal Properties of "Designable Hybrids" Based on POSS Element-Blocks

1.2.1   Fundamental Properties of POSS Element-Blocks

Initially, several POSS-based element-block materials and their multiple functions including unique thermal properties are demonstrated. Generally, by linking or interacting to the cubic core of POSS, [3–5] thermal stability of the connected molecules can be improved [6–11]. Suppression of molecular motions would efficiently occur because of the rigid cubic silica, followed by prohibition of degradation processes. This effect is versatile for enhancing thermal stability with various matrices which have been never used in a hybrid material. Therefore, it can be said that simply by employing POSS element-blocks, hybrid materials possessing thermal stability would be obtained. Additionally, the highly symmetric structure can play a significant role in elevating transition temperatures in the thermal processes by decreasing transition entropy changes [12–15]. This character has potential to be applicable for maintaining the compensate relationship to thermal property. Thus, unique behaviors were often observed from the POSS-based element-block materials. As a representative example, extension of the temperature range of the liquid crystal phase is explained according to the researches with the POSS-tethering ionic salts.

1.2.2   POSS Ionic Liquid Crystal

Ionic liquid crystals have attracted much attention as a platform for preparing multiple functional materials having optical property and anisotropic ion-carrier ability. Therefore, enhancement to thermal stability of liquid crystal phases as well as durability of ionic components is strongly required. One of the strategies to meet these demands is to introduce POSS [12–15]. According to POSS-containing ionic liquids, by connecting the ion pairs to POSS, molecular tumbling would be highly restricted. As a result, pyrolysis was able to be suppressed. Moreover, the POSS core played a critical role in isolation of ion pairs, followed by lowering melting temperatures of the ion pairs. Finally, it was shown that ionic liquid phases can be greatly stabilized by the POSS element-block. From these data, we presumed that similar effects on thermal properties were able to be expected with ionic liquid crystals. To examine the validity of this idea, the ion pairs composed of carboxylate and imidazolium with variable alkyl chains were prepared, and their properties were examined (Fig. 1.3) [16]. Initially, it was found from the X-ray analyses and polarized optical microscopic observation that the ion salts with the octadecyl alkyl chains at the imidazolium moiety formed the liquid crystal phases. Interestingly, the liquid crystal phases were maintained until the thermal decomposition occurred, while the pristine salt without POSS showed typical phase transition to the isotropic phase by heating. Furthermore, comparing to the pristine ionic salt, the
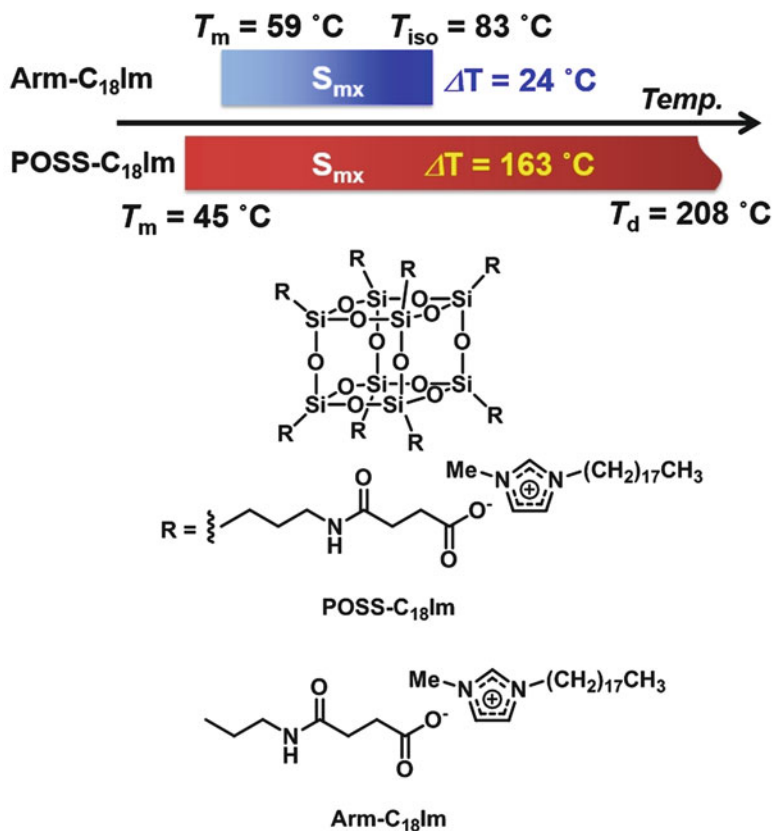
$T_m = 59 \, ^\circ C$ $T_{iso} = 83 \, ^\circ C$

Arm-C$_{18}$lm   S$_{mx}$ $\Delta T = 24 \, ^\circ C$ *Temp.*

POSS-C$_{18}$lm   S$_{mx}$ $\Delta T = 163 \, ^\circ C$

$T_m = 45 \, ^\circ C$ $T_d = 208 \, ^\circ C$

POSS-C$_{18}$lm

Arm-C$_{18}$lm

Fig. 1.3 Chemical structures and thermal properties of ionic liquid crystals

POSS-tethered ion pairs showed lower melting temperature. These data indicated that the temperature range of the liquid crystal phase was extended by the POSS core. The highly symmetric structure of POSS should contribute not only to the suppression of the molecular motions of the ion salts but also to the formation of the regular structures. This is one of the typical examples to offer the significant stabilization for nanostructures by the structural feature of the POSS element-block.

1.2.3   Thermally Stable Luminescent Materials

Next, it was demonstrated that the inorganic cubic core is an advantageous scaffold for realizing solid-state emissive materials with high thermal stability. Recently, higher affinity of POSS with conjugated polymers was demonstrated [17]. This fact implied that modified POSS with conjugated molecules can be thermally stable luminescent materials. The series of the modified POSS with π-conjugated
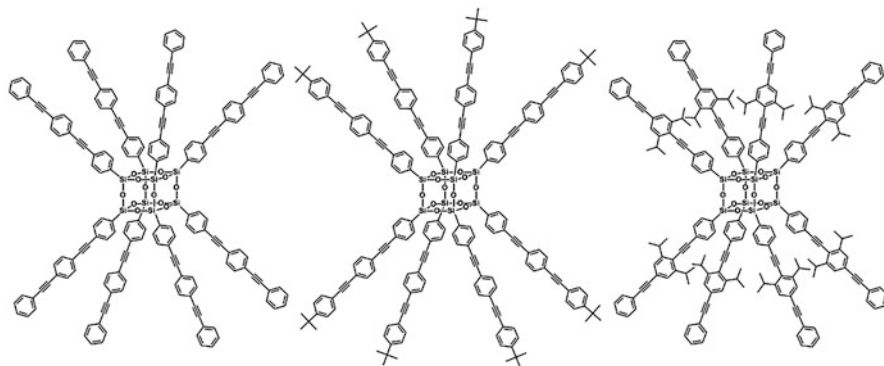
Fig. 1.4 Chemical structures of thermally stable luminescent molecules based on POSS

luminophores connected to eight vertices of the cubic were synthesized (Fig. 1.4) [18]. From the optical measurements in a dilute solution, the excimer formation was obtained. It was proposed that the π-conjugated luminophores around the POSS scaffold interacted with the neighboring π-conjugated luminophores. Indeed, the intrinsic luminescent property of the luminophore moieties was readily recovered by modification with bulky alkyl chains. In the solid state, intriguing behaviors were observed. The π-conjugated luminophores linked to the POSS scaffold presented similar optical properties to the intrinsic emission even in the absence of the bulky substituents. This result represents that POSS played a critical role in inhibition of intermolecular interaction, which often brings unfavorable alteration in optical properties such as aggregation-caused quenching (ACQ) and peak broadening in the condensed state. Furthermore, improvement of thermal stabilities of the π-conjugated luminophores by POSS was exhibited. Finally, it was demonstrated that the POSS materials presented bright blue emission even beyond 200 °C in the open air; meanwhile the π-conjugated luminophore no longer showed emission. Owing to the cubic structure of the POSS element-block, thermally durable optical materials were able to be produced.

1.2.4 Thermally Durable Mechanochromic Luminescent Material

Solid-state emissive molecules occasionally showed luminescent chromism by physical stresses such as pressing, crashing, and grinding [19–22]. These mechanochromic luminescent behaviors are especially beneficial for constructing pressure sensors as well as for fabricating optical recording/memory devices. Therefore, many researchers still have devoted their much efforts not only for exploring new materials but also for regulating chromic properties. The solid-state emissive boron complexes [23–33] were designed and connected to each vertex of POSS
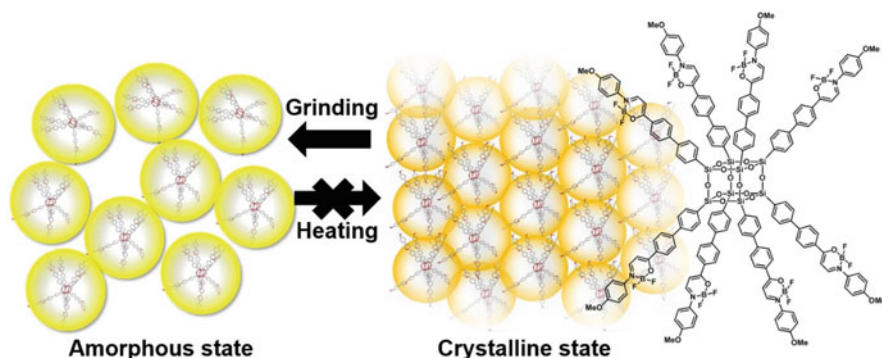
Fig. 1.5 Chemical structure of the dye-modified POSS with thermally durable mechanochromic luminescent property

(Fig. 1.5) [34]. The crystalline sample of the modified POSS presented the bathochromic emission band than that from the single molecule. By adding mechanical stresses to the crystalline sample, regular structures disappeared, followed by luminescent chromism from orange to yellow. This result indicated that each boron complex should be isolated from electronic interaction with other molecules even in the amorphous state after the grinding treatment. Interestingly, the emission color can be maintained by heating until melting. Commodity mechanochromic luminescent dyes often showed reversible changes by heating; meanwhile the POSS-tethered boron complex showed thermally durable luminescent chromism. Similar to the above results, the amorphous state can be stabilized by POSS. As a result, phase transition should be highly restricted. This thermally durable mechanochromic luminescent material is strongly required in the industrial applications as a pressure-sensing paint in the wind tunnel test. It is likely that luminescent chromism of commodity dyes induced by the air pressure could be spoiled by recovering with fraction heat which is inevitably generated by the air flow. On the other hand, the POSS-based "hybrid" dye would maintain the significant changes in luminescence color. Thus, precise detection system could be obtained.

1.2.5 Summary

Intrinsic lower stabilities of organic molecules than those of inorganics are still limitation to practical applications such as for organic optoelectronic devices. Although hybrid formation is one of the valid strategies for improving the durability of organic materials, distinctive inventions for obtaining homogeneous dispersion state at the nano-level such as chemical modification to organic units by polar groups are commonly necessary to receive reinforcement originated from the inorganic component. In contrast, simply by employing POSS, these demands can be readily satisfied without losses of optical and electrical properties of organic components in

the hybrid material. In particular, based on a preprogrammed design, intended functions are conquerable. Thus, it can be said that POSS should be the element-block for realizing "designable hybrids."

1.3 Construction of Conjugated System Involving Cardo Boron Element-Blocks

1.3.1 Optical and Electronic Properties of Cardo Structures

Next, optical properties of the conjugated polymers containing cardo boron element-blocks are illustrated. From the series of researches on the electronic properties of conjugated polymers involving the cardo fluorene, it was demonstrated that the cardo structure should be a versatile scaffold for obtaining multiple functional optical materials by assembling dye molecules [35–39]. For example, significant emission from the main-chain conjugation was observed in the film state by suppressing the ACQ owing to the substituents connected via the cardo carbon. Moreover, it was shown that the main-chain conjugation can be efficiently preserved even in the presence of the electron-donating and/or electron-withdrawing units at the end of the side groups via the cardo carbons [35, 36]. Furthermore, the energy transfer between the fluorescent dyes at the side chains and the main-chain conjugation was controllable in the dye-modified cardo fluorene polymers where several kinds of dyes were placed with orthogonal directions of each transition moment [37–39]. Finally, by choosing the type of the fluorescent dyes at the side chains and the copolymers in the main chain, not only the light-harvesting materials but also the multi-emissive polymer films were accomplished [37–39]. From these data, we constructed the cardo structure in the boron atom of BODIPY, which is known as a versatile luminescent dye because of various advantages, [40–46] and built up conjugated polymers containing the cardo boron structure.

1.3.2 Solid-State Luminescent Properties of Cardo BODIPYs

The BODIPY derivatives having single or dual phenyl groups into the boron center were prepared (Fig. 1.6) [47]. From optical measurements, it was observed that the pristine BODIPY showed the sharp intense emission band in the diluted solution, meanwhile critical ACQ and unexpected bathochromic peak shift occurred in the solid state. In contrast, it was revealed that the phenyl substituents played a significant role in suppression of critical losses of emission efficiencies in the solid state. Additionally, it should be noted that the single- and dual-phenyl substituted BODIPYs showed sharp emission bands both in the solution and solid states. It
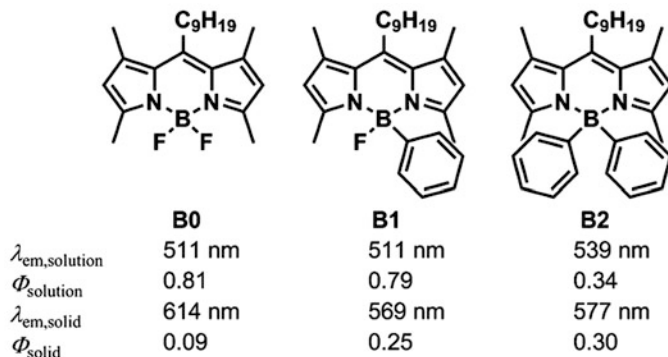
	B0	B1	B2
$\lambda_{em,solution}$	511 nm	511 nm	539 nm
$\Phi_{solution}$	0.81	0.79	0.34
$\lambda_{em,solid}$	614 nm	569 nm	577 nm
Φ_{solid}	0.09	0.25	0.30

Fig. 1.6 Chemical structures and optical properties of the pristine and cardo BODIPYs

was suggested that the steric hindrance by the phenyl groups can inhibit ACQ in the condensed state.

1.3.3 Conjugated Polymers Involving Cardo BODIPYs

Next, the conjugated polymers containing the cardo boron in BODIPY were synthesized, and influence of the substituent on electronic properties of the boron center was examined (Fig. 1.7) [48]. The electron-donating and/or electron-withdrawing groups were introduced into the phenyl substituents connected to the boron center. Similarly to the dye-modified cardo fluorene polymers, it was indicated that electronic structures of the main-chain conjugation can be preserved from the introduction of substituent groups. Both in the UV-vis absorption and photoluminescence spectra of the polymers, similar shapes were obtained. These data represent isolation of the main-chain conjugation in the conjugated polymers from the electronic interaction with the side chains by the cardo boron. Thus, it can be expected that the cardo boron element-block could be a potential platform for constructing multifunctional optoelectronic polymers by assembling the functional units according to the preprogrammed designs without losses of properties of each component.

1.4 [2.2]Paracyclophane as a Chiral Element-Block

1.4.1 General Evaluation of Chiroptical Properties

Final topics are concerned to the chiral element-blocks and their unique optical properties. When two mirror-image molecules are non-superimposable like a right
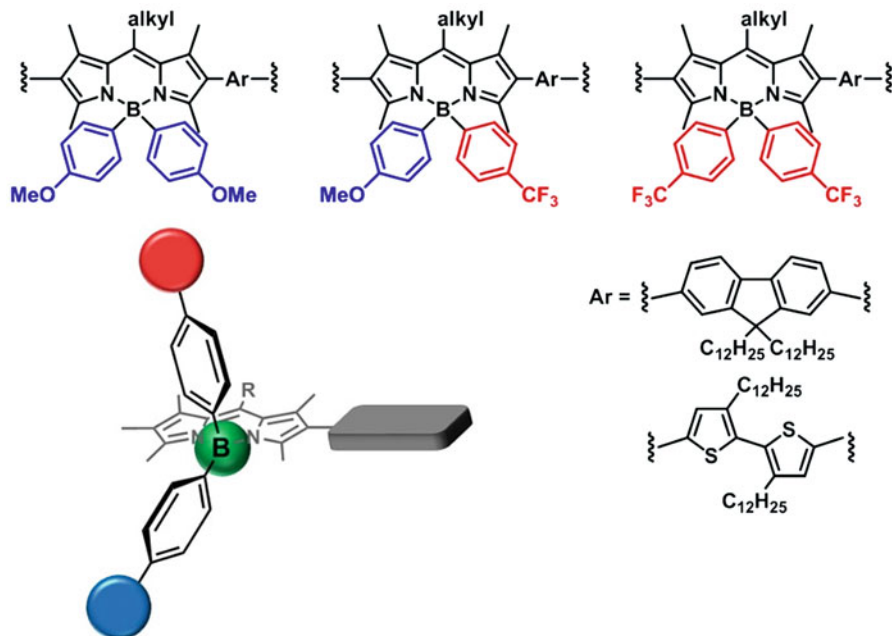
Fig. 1.7 Chemical structures of the conjugated polymers containing cardo BODIPYs

hand and a left hand, we call that the molecule is chiral. Chirality exists in various molecules including amino acids and sugars which make up natural world, and it is an essential for understanding the intrinsic properties of substances. Control of chirality is widely studied such as selective asymmetric synthesis with a chiral catalyst in the field of organic synthetic chemistry and biochemistry. Recognition of chirality is effective tool for discriminating the optically active compounds. Those methods definitely have developed the recent chiral chemistry. In addition, absorption and luminescent properties based on chirality are widely known as circularly dichroism (CD) and circularly polarized luminescence (CPL), respectively. The chiroptical data obtained from CD and CPL spectra measurements are useful for understanding the structural information in the ground state and in the excited state, respectively. Especially, CPL has received much attention as significant tools for potential application to cryptography, memory, or light source of a display. Therefore, chirality is important in the field of chemistry, and it is effective in creating functional materials. From those backgrounds, in this section, we suggest that functional units based on chiral molecules are called "chiral element-blocks," and combination of the element-blocks should create versatile functional materials. As examples of the chiral element-blocks, planar chiral [2.2]paracyclophanes were selected. Planar chiral [2.2]paracyclophanes [49, 50] are designed for constructing

chiral π-conjugated systems. As opposed to conformationally flexible chiral molecules, which have an axis of rotation as well as a rotatable bond around a stereogenic center, substituted [2.2]paracyclophanes are conformationally stable and show planar chirality because of the suppressed rotation of the aromatic rings [51–53]. In addition, the planarity of the [2.2]paracyclophanes takes great advantage for expanding π-conjugated systems via through-space conjugation and through-bond conjugation [41]. That is effective in obtaining good chiroptical performance such as CD and CPL [54–66]. To evaluate the chirality on CD and CPL spectra, dissymmetry factors, g_{abs} and g_{lum} were used. They were defined as $g_{abs} = \Delta\varepsilon/\varepsilon$ ($\Delta\varepsilon = \varepsilon_{left} - \varepsilon_{right}$), where ε_{left} and ε_{right} indicate absorbances of left- and right-handed circularly polarized light, respectively, and $g_{lum} = \Delta I/I$ ($\Delta I = I_{left} - I_{right}$), where I_{left} and I_{right} indicate luminescence intensities of left- and right-handed CPL, respectively. In this section, our recent researches based on the concept of chiral element-blocks are introduced briefly.

### 1.4.2 [2.2]Paracyclophane as a Chiral Element-Block

[2.2]Paracyclophane consists of face-to-face-oriented two benzene rings combined by two ethylene chains at *para* positions [49, 50]. It was known that several groups of substituted [2.2]paracyclophanes at the aromatic rings show planar chirality because of the restricted rotation of the aromatic rings. Therefore, the planar chirality can be handled as rigid and stable chirality [51–53]. In addition, the rigidity and planarity should be a great advantage for the expansion of π-conjugated systems, and that can be a different character from the other representative chiral sources such as chiral center, axial chirality, and helicity. However, planar chiral [2.2] paracyclophanes have not been studied in the field of material chemistry such as polymer, chemistry, or optoelectronics but in the field of organic and organometallic chemistry. From the above reasons, we consider that the planar chiral [2.2] paracyclophane can be effective chiral building blocks to construct π-conjugated system for the material chemistry, and the functional units can be treated as chiral element-blocks. Concretely, we focused on pseudo-*ortho*-disubstituted [2.2] paracyclophane and 4,7,12,15-terasubstituted [2.2]paracyclophane as planar chiral element-blocks and synthesized construct optically active second-ordered structures, such as V-, N-, M- [57], triangle- [56, 57], propeller- [59, 60, 63], and X-shaped [61, 62, 65, 66], one-handed double-helical [64] and self-assembled structures [65]. All compounds exhibited intense CPL [67, 68] with large molar extinction coefficients (ε), good photoluminescence (PL) quantum efficiencies (Φ_{PL}), and excellent CPL dissymmetry factors (g_{lum}). In this term, recently our works are demonstrated briefly.

1.4.3 Planar Chiral Pseudo-ortho-disubstituted [2.2] Paracyclophanes

At first, we started the development of the practical optical resolution method of planar chiral pseudo-*ortho*-disubstituted [2.2]paracyclophanes [55]. There are several reports about optical resolution method of them; however, the diversity for the functionality after the optical resolution was limited. We selected a diastereomer method as a practical optical resolution way because it is possible to separate enantiomers in large scale with SiO_2 column chromatography and the enantiomers were obtained with the same amount, respectively. The detail synthetic method is shown in Scheme 1.1. Treatment of commercially available *rac*-pseudo-*ortho*-dibromo[2.2]paracyclophane *rac*-1 with 1.1 equivalent of *n*-BuLi and (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate converted one of the bromines into a sulfinyl group. The resulting mixture of the diastereomers was readily separated by conventional SiO_2 column chromatography to obtain (R_p,*S*)-2 and (S_p,*S*)-2 (each in 39% isolated yield). The reaction of (R_p,*S*)-2 with 4 equiv. *t*-BuLi afforded the (R_p)-pseudo-*ortho*-dilithio[2.2]paracyclophane (R_p)-3, which was able to react with
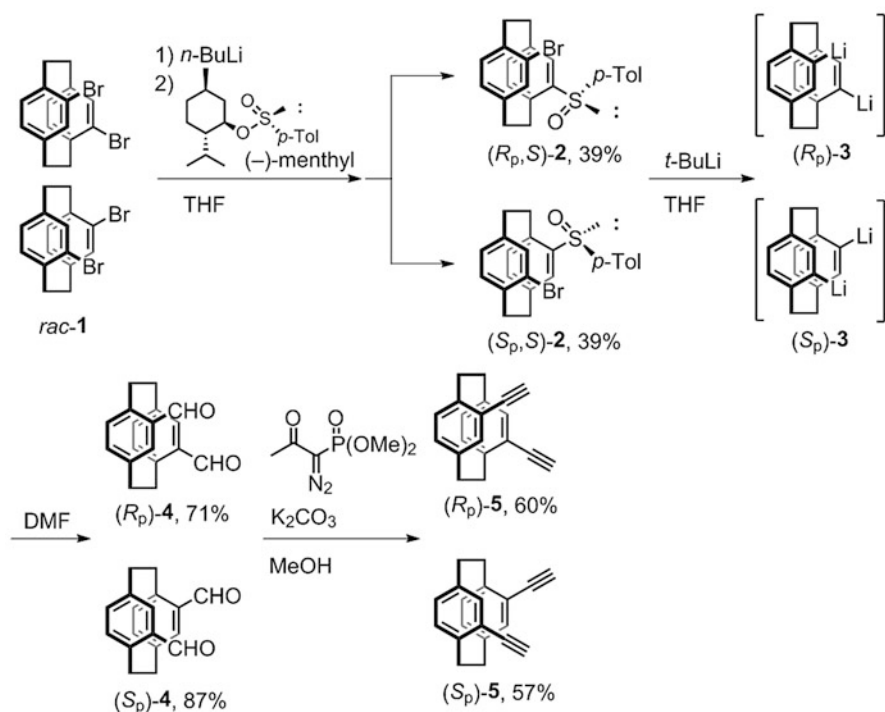

Scheme 1.1 Optical resolution of *rac*-1 and synthesis of (R_p) and (S_p)-5
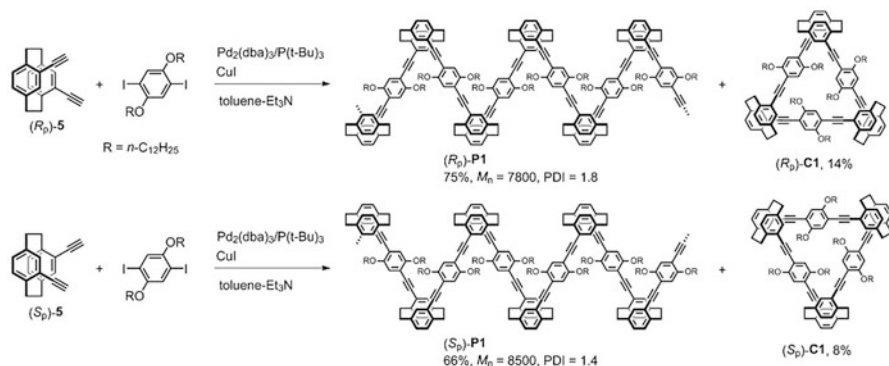
Scheme 1.2 Synthesis of polymers (R_p)- and (S_p)-**P1** and cyclic compounds (R_p)- and (S_p)-**C1**

various electrophiles [55–58]. For example, the (R_p)-**3** was allowed to react with DMF to afford (R_p)-pseudo-*ortho*-diformyl[2.2]paracyclophane (R_p)-**4**. Formyl groups of (R_p)-**4** (or (S_p)-**4**) were converted into ethynyl groups to afford (R_p)-pseudo-*ortho*-diethynyl[2.2]paracyclophane (R_p)-**5**, which is readily used for the chiral element-blocks to construct π-conjugated polymer. Through-space-conjugated polymers (R_p)-**P1** and (S_p)-**P1** were synthesized from (R_p)-**5** and (S_p)-**5**, respectively, by the Sonogashira-Hagihara coupling polymerization (Scheme 1.2). The π-electron systems of (R_p)-**P1** and (S_p)-**P1** partially overlapped to form chiral V-shaped zigzag structures, and the resulting polymers were mirror images of each other. At the same time, optically active cyclic trimers (R_p)-**C1** and (S_p)-**C1** were isolated in this reaction and separated by size exclusion column chromatography. The CD and CPL spectra of (R_p)-**P1** and (S_p)-**P1** in dilute CHCl$_3$ solution (1.0×10^{-5} M, excitation wavelength: 320 nm) exhibited mirror-image signals in the observed PL range (Fig. 1.8), and the g_{lum} of (R_p)-**P1** and (S_p)-**P1** at 415 nm were estimated to be $+2.3 \times 10^{-3}$ and -2.0×10^{-3}, respectively. (R_p)-**P1** and (S_p)-**P1** showed intense CPL with a large g_{lum} in dilute solutions (1.0×10^{-5} M) because of the rigid structure with planar chirality and the stacked π-electron systems. To elucidate the feature of the cyclic trimer (R_p)-**C1** and (S_p)-**C1**, V-shaped zigzag dimer, trimer, and tetramer were prepared from the oligomeric approach [57]. As a result, in the ground state, observed similarities in the CD profiles of the oligomers were attributed to the equivalent orientations of two adjacent chromophores. On the other hand, in the excited state, the oligomers were folded into a form analogous to a one-handed helix by photoexcitation. We successfully predicted the structure both in the ground state and in the excited state in comparing the cyclic trimer and the corresponding oligomers (Fig. 1.9). All the compounds in dispersed solution exhibited intense circularly polarized luminescence with relatively large dissymmetry factors on the order of 10^{-3}.
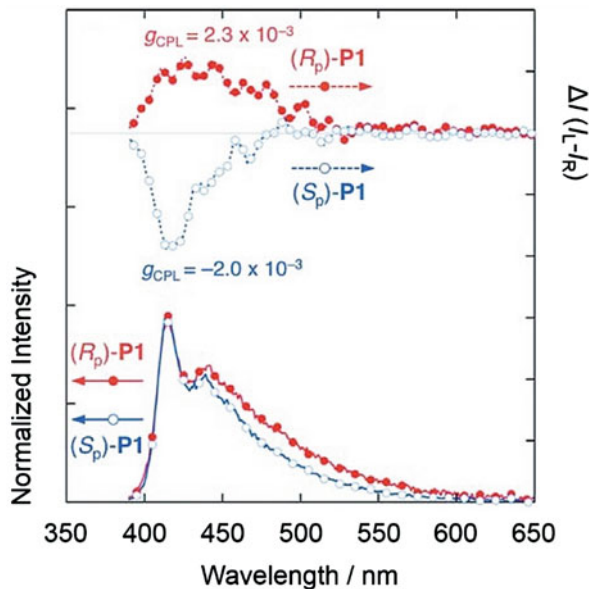
1.4.4 Planar Chiral Tetrasubstituted [2.2]Paracyclophanes

Next, as the other chiral element-blocks based on a planar chirality, we focused on
4,7,12,15-tetrasubstituted [2.2]paracyclophane scaffold. 4,7,12,15-Tetrasubstituted
[2.2]paracyclophane has highly symmetrical structure, and the π-conjugated system
was expanded whole of the molecule via through-space conjugation because the
through-space conjugation occurs at the center of the structure [54]. However, there
are no reports about the optical resolution method of planar chiral 4,7,12,15-
tetrasubstituted [2.2]paracyclophanes. Therefore, we developed the optical resolu-
tion method and induction way to the ethynyl moiety, planar chiral 4,7,12,15-
tetraethynyl [2.2]paracyclophane, which is key component for constructing
π-conjugated systems. Optical resolution of tetrasubstituted [2.2]paracyclophane
was carried out by a diastereomer method with (−)-(1*S*,4*R*)-camphanoyl chloride
(Scheme 1.3). One of bromines of 4,7,12,15-tetrabromo[2.2]paracyclophanes [69]
rac-**6**, was converted to a hydroxyl group to obtain *rac*-**7** in 69% isolated yield,
which was reacted with (−)-(1*S*,4*R*)-camphanoyl chloride to obtain a mixture of
diastereomers. These were readily separated by SiO_2 column chromatography and
purified by recrystallization to obtain (S_p,1*S*,4*R*)-**8** and (R_p,1*S*,4*R*)-**8** in 38% and 34%
isolated yield, respectively. Subsequent transformation of (S_p,1*S*,4*R*)-**8** into ethynyl
moiety is shown in Scheme 1.3. The reactions were proceeded in high yields, and
finally, we succeeded in synthesizing enantiopure 4,7,12,15-tetra-ethynyl[2.2]
paracyclophane (S_p)-**12**. The enantiomer (R_p)-**12** was synthesized as the same
method from (R_p,1*S*,4*R*)-**8**. They can be employed as conformationally stable chiral
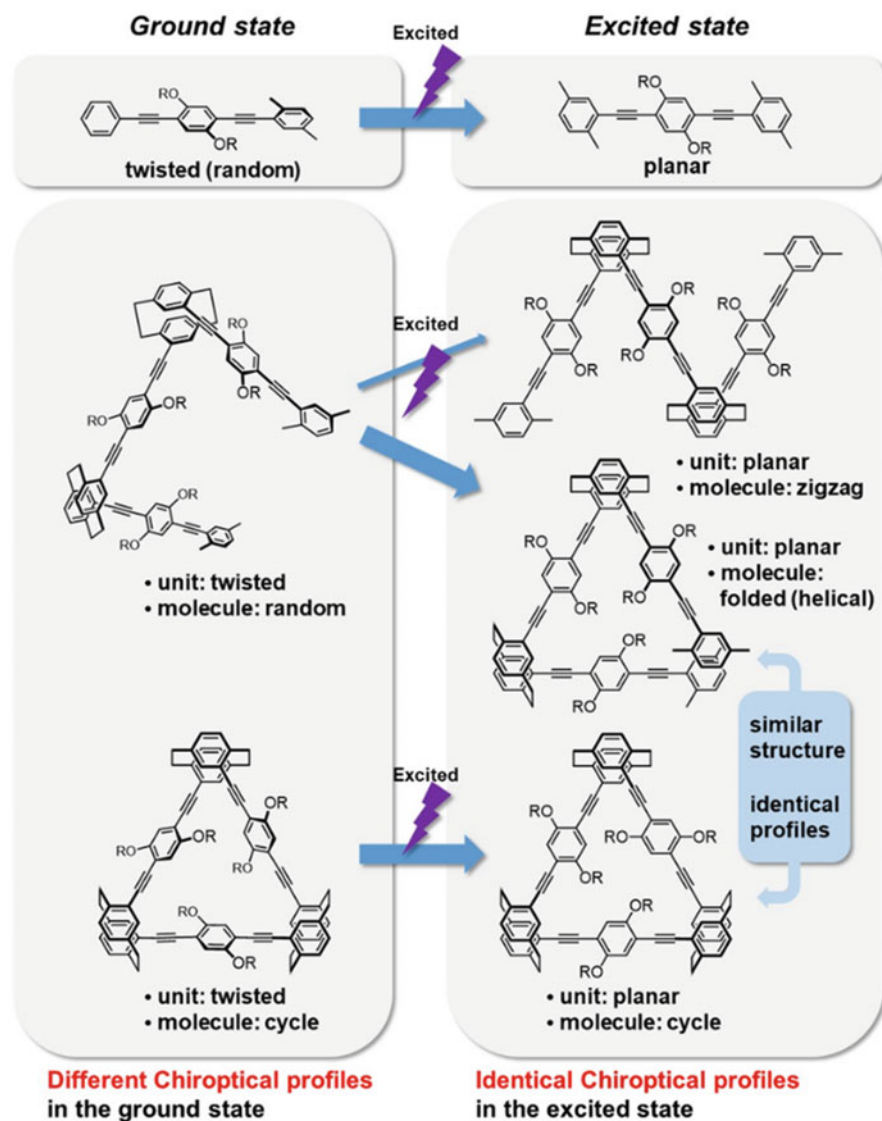building blocks for various optically active π-conjugated compounds. To investigate

Fig. 1.9 Plausible structures of the oligomers: the linear trimer versus the cyclic trimer in the ground and excited states

the chiroptical properties of planar chirality based on the tetrasubstituted [2.2] paracyclophane, optically active propeller-shaped macrocycles were synthesized. This structure has previously been synthesized by Hopf, Haley, and co-workers as a racemic compound [70], although the positions of the *t*-butyl groups were different. Surprisingly, the propeller-shaped macrocycle showed excellent CD and CPL performance ($g_{abs} = 0.88 \times 10^{-2}$, $\varepsilon_{abs} = 129,000 \ M^{-1} \ cm^{-1}$, $g_{lum} = 1.3 \times 10^{-2}$, and
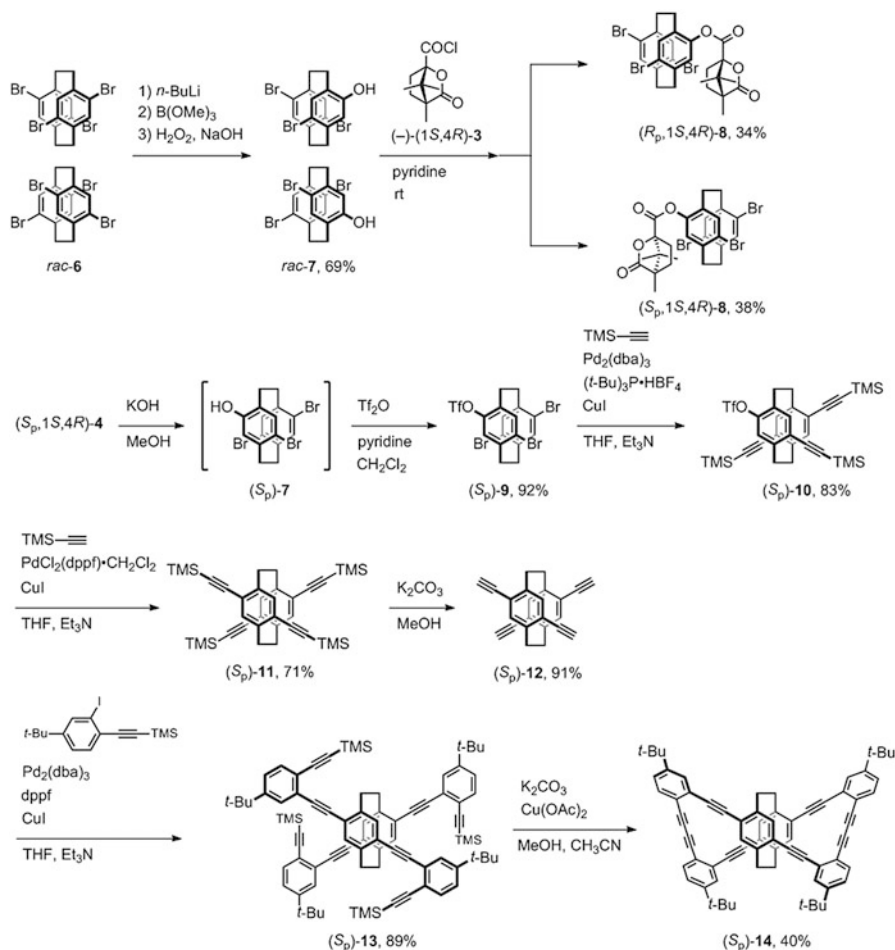
Scheme 1.3 Optical resolution of *rac*-**6** and synthesis of (R_p) and (S_p)-**12**, propeller-shaped macrocycles (S_p)-**14**

$\Phi_{lum} = 0.41$) in the dilute solution condition (Fig. 1.10). It is the first report that planar chirality based on the tetrasubstituted [2.2]paracyclophane has excellent potential to be CPL emitter. Several compounds showing great CPL performances in the diluted solution were reported in these days; however, the compounds showing good Φ_{lum} and g_{lum} with 10^{-2} order were still limited. Following those results, we prepared several derivatives based on a propeller-shaped macrocyclic structure [50, 63], and at the present stage, the CD and CPL performances were modified to be $g_{abs} = 1.0 \times 10^{-2}$, $\varepsilon_{abs} = 216{,}000 \, \text{M}^{-1} \, \text{cm}^{-1}$, $g_{lum} = 1.0 \times 10^{-2}$, and $\Phi_{lum} = 0.60$ (Fig. 1.11) [60].
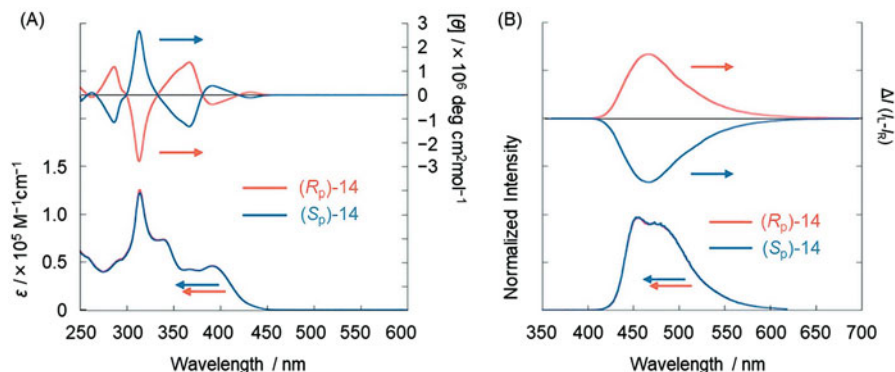
Fig. 1.10 (**a**) UV-vis absorption and CD spectra of (R_p)- and (S_p)-**14** in CHCl$_3$ (1.0×10^{-5} M) at room temperature. (**b**) PL and CPL spectra of (R_p)- and (S_p)-**14** in CHCl$_3$ (1.0×10^{-6} M for PL and 1.0×10^{-5} for CPL) at room temperature, excited at 314 nm. (Reprinted with permission from Ref. [59]. Copyright 2014 American Chemical Society)

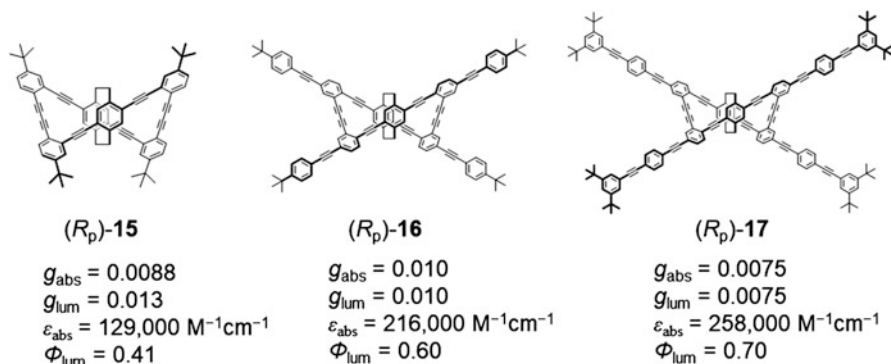(R_p)-**15**
g_{abs} = 0.0088
g_{lum} = 0.013
ε_{abs} = 129,000 M^{-1}cm^{-1}
Φ_{lum} = 0.41

(R_p)-**16**
g_{abs} = 0.010
g_{lum} = 0.010
ε_{abs} = 216,000 M^{-1}cm^{-1}
Φ_{lum} = 0.60

(R_p)-**17**
g_{abs} = 0.0075
g_{lum} = 0.0075
ε_{abs} = 258,000 M^{-1}cm^{-1}
Φ_{lum} = 0.70

Fig. 1.11 The series of macrocycles and the typical chiroptical properties

1.4.5 Development of Chiral Dendrimers

Taking advantage of the unique structure of the tetrasubstituted [2.2] paracyclophane, chiral dendrimers [62] and chiral dimers [61, 65, 66] were synthesized. In addition, self-assembly of the chiral dimers [65] was prepared and investigated the properties. Chiral dendrimer consisted of planar chiral [2.2] paracyclophane core and Fréchet-type dendrimer which is famous as light-harvesting antenna. As a result, the energy absorbed by Fréchet-type dendrimer was transferred to the [2.2]paracyclophane core, and the core emitted high-intense CPL with preservation of chiroptical parameters such as g_{lum}. In addition, the CPL film was easily prepared because of the steric hindrance of the dendrimer (Fig. 1.12).
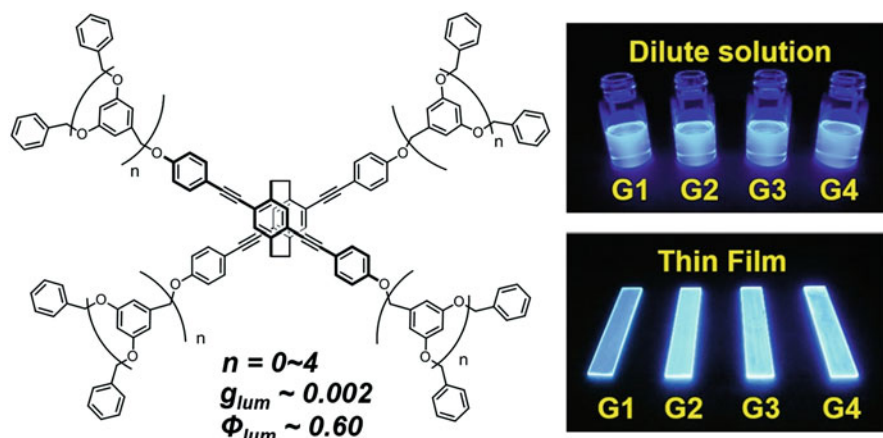
Fig. 1.12 Chemical structures of the dendrimers and photography-irradiated UV lamp (365 nm). (Reprinted with permission from Ref. [62]. Copyright 2016 Wiley-VCH Verlag GmbH & Co. KGaA)

1.4.6   Enhancement of Chiroptical Properties by Molecular Assembly

When the chiral molecules are self-assembled, it is known that the g_{lum} performances are often enhanced [71]. In our case, the self-assembly with oligo-phenylene-ethynylene-based planar chiral tetrasubstituted [2.2]paracyclophane with dodecyl alkyl chains showed dramatic enhancement of g_{lum}; finally the g_{lum} increased in 10^{-1} order after annealing ($g_{lum} = -0.25$ for (R_p)-**CP5** and $g_{lum} = +0.27$ for (S_p)-**CP5**). Those are one of the largest g_{lum} in the assembled systems with organic compounds. In addition, sign inversion was observed corresponding to the difference of preparation method of the films. The high CPL performance and sign inversion should be caused by the easily assembled planar structure of the planar chiral [2.2] paracyclophanes. The proposal mechanism of sign inversion is shown in Fig. 1.13. When the stacking formation of the chromophores changes, inversion of the CD and CPL signs can occur, and the phenomenon was estimated by exciton coupling theory.

1.4.7   Summary

A series of our research based on planar chiral [2.2]paracyclophanes indicated that the combination of the functional units such as planar chiral pseudo-*ortho*-disubstituted [2.2]paracyclophane and 4,7,12,15-tetrasubstituted [2.2]paracyclophane creates unique characteristics and the concept was matched with element-blocks. Recently, we successfully prepared the oligomers showing unidirectional energy
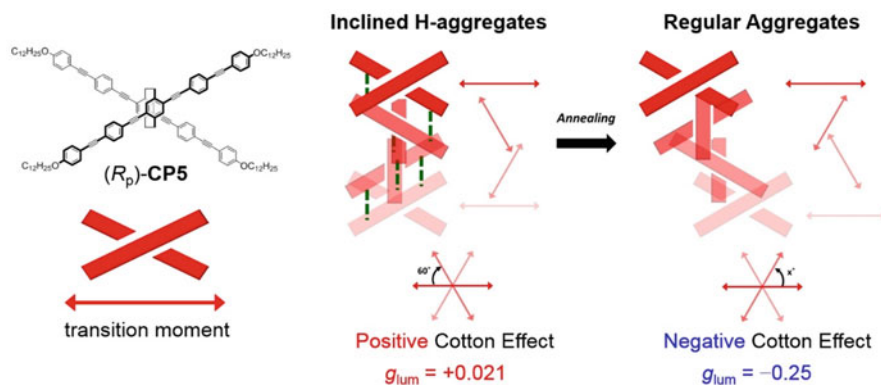
Fig. 1.13 Proposal mechanism of self-assembly of (R_p)-**CP5**. The direction of transition moment was estimated by TD-DFT (B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p))

transfer between chromophores with pseudo-*para*-disubstituted [2.2] paracyclophane as a linker [72–75]. The molecular design was a combination of the functional units, and this is also one of the examples applied with the concept of element-blocks.

1.5 Conclusion

The series of element-blocks involving unique steric structures are reviewed. By employing POSS, thermally stable materials similar to organic-inorganic hybrids can be readily prepared via conventional organic reactions. In particular, by designing the side chains of POSS, various functions can be loaded. Finally, multifunctional element-block materials having combinational properties originated from both organic molecules and POSS were obtained. From these data, we can say that POSS element-blocks contributed to extending applicability of hybrids to various matrices. Finally, the concept of "designable hybrids" was proposed. The possibility of the cardo boron element-blocks as a promising platform for constructing conjugated materials consisting of electronic functional units was demonstrated from the recent studies. By modulating distribution and direction of these functional units at the cardo boron center, energy transfer efficiency and degree of electronic interaction were regulated. As a result, useful optical properties such as solid-state luminescence were obtained. It was demonstrated that [2.2] paracyclophane element-blocks work as the origin for expressing superior CD and CPL signals, and by introducing conjugated system, these optical properties were enhanced and modulated. These results indicate that chiral element-blocks can be a foundation stone for constructing next generation of chiral optical materials. Except for these examples, there are still a numerous number of heteroatom-based steric structures, and these structural units are promised to be individually as a new

element-block. Further exploration of new element-blocks and the discovery of the combination with these element-blocks are exciting for receiving advanced element-block materials.

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