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Synthesis of Optically Active, X-Shaped, Conjugated Compounds and Dendrimers Based on Planar Chiral [2.2]Paracyclophane, Leading to Highly Emissive Circularly Polarized Luminescence

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Abstract: Optically active, Fréchet-type dendrimers containing an emissive X-shaped π-electron system as the core unit were synthesized. Gram-scale optical resolution and transformations of 4,7,12,15-tetrasubstituted [2.2]paracyclophanes were also carried out. The high-generation dendrons effectively absorbed UV light and transferred energy to the core, resulting in high photoluminescence (PL) from the core. In addition, the dendrons sufficiently isolated the emissive X-shaped conjugated core and bright emission was observed from both thin films and solutions. Intense circularly polarized luminescence (CPL) was observed from the thin film. The dendrimer films exhibited excellent optical properties, such as large molar extinction coefficients, high fluorescence quantum efficiencies, intense PL and CPL, and large CPL dissymmetry factors.

Introduction

Optically active, emissive, conjugated compounds exhibit a potential difference between their left- and right-handed circularly polarized luminescence (CPL[1]) intensities. Recently, the development of optically active CPL-emitting organic compounds[2–11] for applications in 3D organic light-emitting devices has received much attention. CPL characteristics are evaluated from the photoluminescence (PL) intensity and the luminescence dissymmetry factor (g_{lum}), defined as $2(I_{\mathrm{left}}-I_{\mathrm{right}})/(I_{\mathrm{left}}+I_{\mathrm{right}})$, in which I_{left} and I_{right} represent the left- and right-handed CPL intensities, respectively. The molar absorption coefficient (ε), PL quantum efficiency (Φ_{lum}), and large g_{lum} value are therefore important factors in CPL materials. However, it is generally difficult to achieve large PL intensities in combination with large g_{lum} values due to the existing challenges in obtaining large g_{lum} values in organic compounds.

We recently suggested that a second-ordered structure created from the rigid and conformationally stable [2.2]paracyclophane[12] structure was effective for achieving CPL.[9a,13] Despite the stacked structure of the π-electron systems, [2.2]paracyclophane-based conjugated compounds exhibit good Φ_{lum} values in addition to a large ε. Furthermore, the optically active, second-ordered structures obtained from planar, chiral [2.2]paracyclophane, including V-shaped,[13b] helical,[13b] triangular,[9a,13b] and propeller-shaped structures[13a,c] in the excited state provided large g_{lum} values in the order of 10^{-2} to 10^{-3}. The CPL profiles of the optically active [2.2]paracyclophane compounds have been observed in dilute solutions, whereas the PL performance in the solid state, in particular, the PL intensity and Φ_{lum}, decreased dramatically due to typical aggregation-caused quenching.

We report herein the synthesis of a simple X-shaped compound that contains two stacked π-electron systems. We focused on the dendritic structure[14] to investigate the optical and chiroptical properties of its thin film. In addition to the film-forming ability, the Fréchet-type dendrimer was selected to overcome aggregation-caused quenching, and to take advantage of its light-harvesting effect; dendrons protect the emissive core unit from aggregation and the benzene rings in the dendrons effectively absorb UV light. The dendrimers exhibited excellent CPL properties both in dilute solution and in the film state, which led to highly emissive CPL materials with large g_{lum} values. Gram-scale syntheses of enantiopure 4,7,12,15-tetrasubstituted [2.2]paracyclophanes are also disclosed.

Results and Discussion

The reported synthetic procedure to obtain *rac*-4,7,12,15-tetrabromo[2.2]paracyclophane was modified as outlined in the Supporting Information.[15] The method reported by Chow et al. selectively produces 4,7,12,15-tetrasubstituted [2.2]paracyclophane compounds,[15] as shown in Scheme 1; however, polymeric compounds are mainly obtained as byproducts. We successfully prepared *rac*-4,7,12,15-tetrabromo[2.2]paracyclophane in 68 % yield under more dilute reaction conditions. The

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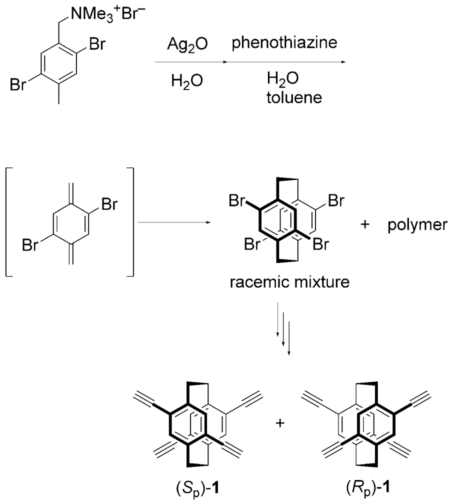


Scheme 1. Synthetic route to *rac*-4,7,12,15-tetrabromo[2.2]paracyclophane,[15] and structures of planar chiral 4,7,12,15-tetraethynyl[2.2]paracyclophanes ((S_p)- and (R_p)-**1**.[13a]

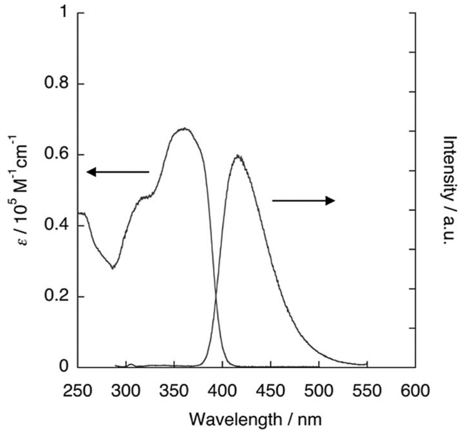


Figure 1. UV/Vis absorption and PL spectra of (S_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M for UV and 1.0×10^{-7} M for PL). Excitation wavelength: 365 nm.

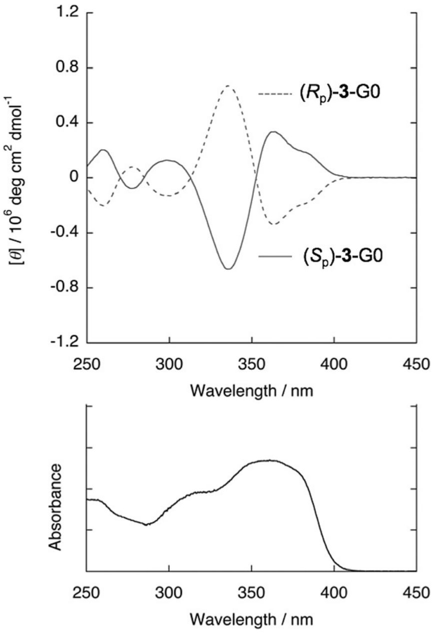
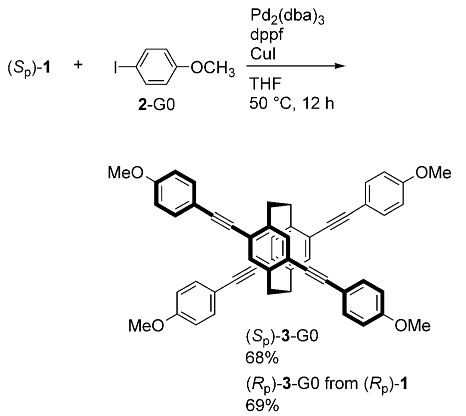


Figure 2. CD spectra of (S_p)- and (R_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M) and UV/Vis absorption spectrum of (S_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M).

gram-scale optical resolution of planar chiral 4,7,12,15-tetrasubstituted [2.2]paracyclophane,[16] and the successive transformations to enantiopure (S_p)- and (R_p)-**1** (see Scheme 1) are also described in the Supporting Information.

The X-shaped conjugated compound (S_p)-**3**-G0, in which two *p*-phenylene–ethynylenes were stacked at the central phenylene units,[17,18] was prepared from the reaction of (S_p)-**1** with commercially available *p*-iodoanisole (**2**-G0; Scheme 2). In addition, the enantiomer (R_p)-**3**-G0 was prepared from the corresponding (R_p) isomer.

The UV/Vis absorption and PL spectra of dilute solutions of (S_p)- and (R_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M) were recorded.[18] Figure 1 shows the spectra for the (S_p) isomer. The absorption bands derived from the π–π* transition of *p*-phenylene–ethynylene were observed with band maxima at $\lambda=361$ and around 315 nm. Photoexcitation of (S_p)-**3**-G0 at $\lambda=365$ nm gave an emission band at $\lambda=416$ nm with an absolute PL efficiency (Φ_{lum}) of 0.66. Figure 2 shows the circular dichroism (CD) spectra of dilute solutions of (S_p)- and (R_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M). A clearly bisignate mirror-image Cotton effects was observed along with a relatively high [θ] of 6.7×10^5 deg cm^2 dmol^{-1}, which suggested that the light-absorbing units involved were chirally perturbed by the planar chiral [2.2]paracyclophane. As expected, CPL was also observed. The CPL and g_{lum} spectra of a dilute solution of (S_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M) are shown in Figure 3. Mirror-image CPL signals were observed in the PL region, and the absolute g_{lum} value was estimated to be 1.4×10^{-3}. The X-shaped compound of planar, chiral [2.2]paracyclophane is an excellent CPL emitter, that is, it has good Φ_{lum}, intense CPL, and large g_{lum} properties. However, due to crystallization, thin films of (S_p)- and (R_p)-**3**-G0 were not obtained, and the PL intensity and Φ_{lum} observed in the solid state decreased due to typical aggregation-caused quenching.



Scheme 2. Synthesis of (S_p)-**3**-G0; dba = dibenzylideneacetone, dppf = 1,1′-bis(diphenylphosphino)ferrocene.

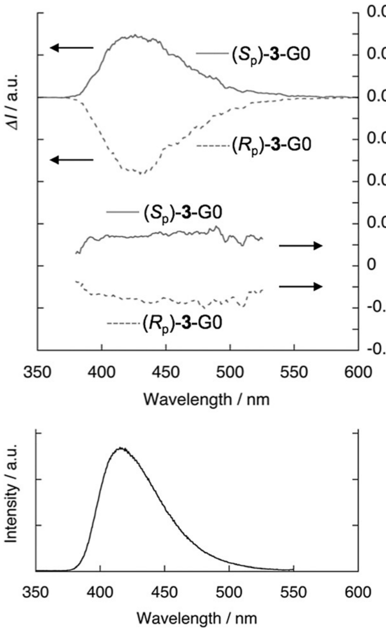
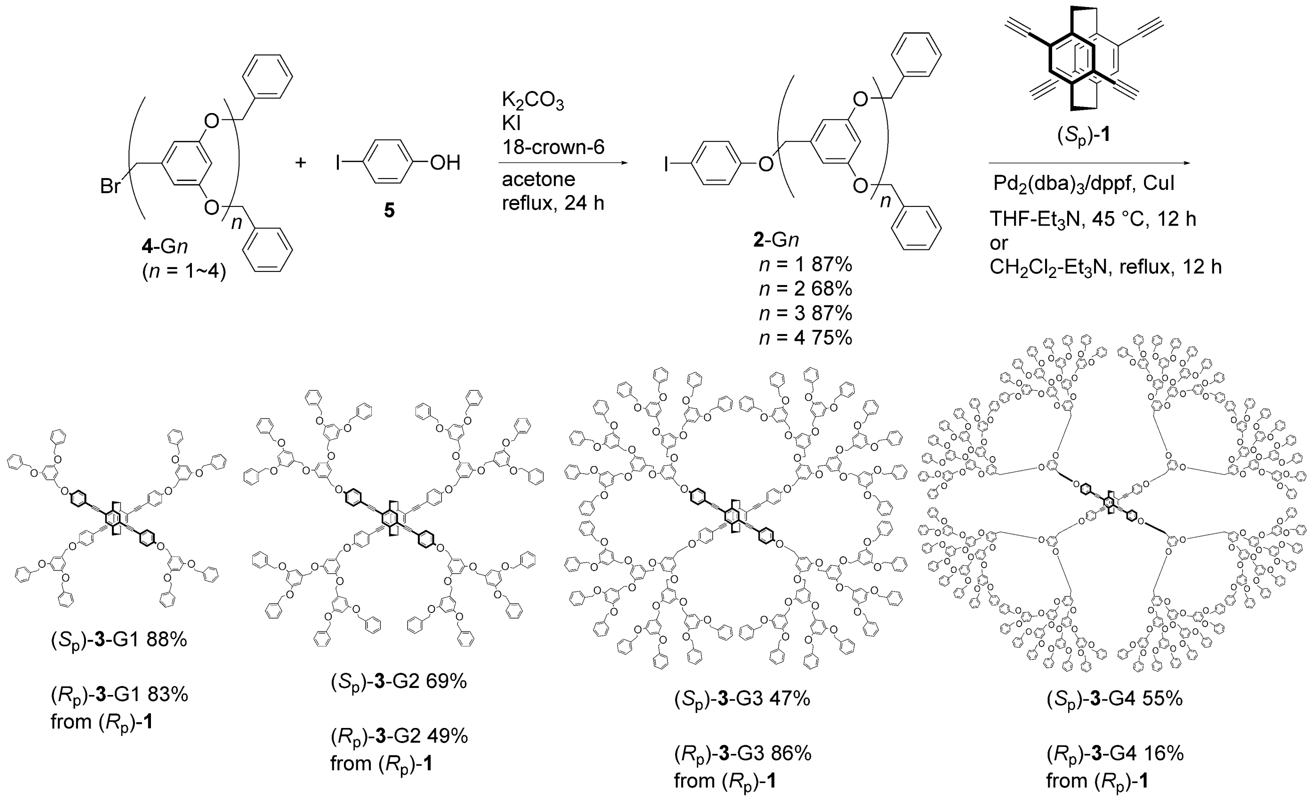


Figure 3. CPL and g_{lum} spectra of (S_p)- and (R_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M) and the PL spectrum of (S_p)-**3**-G0 in $CHCl_3$ (1.0×10^{-5} M). Excitation wavelength: 279 nm.

From the viewpoint of film formation for the X-shaped compound, we focused on the dendritic structure.[14,19,20] Fréchet-type[20] dendrons were introduced into the X-shaped compound to take advantage of the light-harvesting effect[21,22] of the benzene rings on the dendrons to enhance the PL performance of the system. Fréchet-type bromo-substituted dendrons **4**-G*n* (*n* = 1–4) were prepared and treated with *p*-iodophenol (**5**) to obtain dendrons **2**-G*n* (Scheme 3). Sonogashira–Hagihara coupling[23] of (S_p)-**1** with **2**-G*n* afforded the target dendrimers (S_p)-**3**-G*n* (*n* = 1–4), which contained the X-shaped conjugated moiety as the core unit (Scheme 3). The yields of different enantiomers varied according to experimental error because of difficulties in handling as a result of increased hygroscopicity with increasing generations. The dendrimers were highly soluble in common organic solvents, including THF, toluene, CH_2Cl_2, and $CHCl_3$. In addition, they possessed film-forming abilities through spin coating of solutions in $CHCl_3$ (2.0×10^{-3} M).

The optical and chiroptical properties of (S_p)- and (R_p)-**3**-G*n* (*n* = 1–4) were evaluated by means of UV/Vis absorption, PL, CD, and CPL spectroscopy. The optical and chiroptical data are summarized in Tables 1 and 2, respectively. Figures 4A and 4B show the UV/Vis absorption spectra of dilute solutions of all compounds in $CHCl_3$ (1.0×10^{-5} M) and spin-coated films, respectively. Absorption bands at $\lambda\approx275$ and 300–400 nm were assigned to the π–π* bands of the benzene rings in the dendrons and *p*-phenylene–ethynylene moieties of the core unit, respectively. The absorption bands at $\lambda\approx275$ nm increased with increasing dendrimer generation (i.e., the number of benzene rings). As shown in Figure 4B, the absorption edges of the (S_p)-**3**-G1 and G2 films were redshifted relative to those of the G3 and G4 dendrimers because of core unit aggregation in the solid state.



Scheme 3. Synthesis of dendrimers (S_p)-**3**-G*n* (*n* = 1–4).

Table 1. Spectroscopic data for the optical properties of the (S_p) isomers.

	λ_{abs}[a] [nm] ($\varepsilon \times 10^{-5}$ [$\text{M}^{-1}\,\text{cm}^{-1}$])	λ_{abs}[b] [nm]	λ_{lum}[c] [nm]	λ_{lum}[d] [nm]	Φ_{lum}[e]	Φ_{lum}[f]
(S_p)-**G0**	361 (0.68)	–	416	–	0.66	–
(S_p)-**G1**	279 (0.40), 363 (0.67)	368	415	425, 445	0.63	0.20
(S_p)-**G2**	279 (0.61), 364 (0.69)	278, 367	416	423, 435	0.66	0.54
(S_p)-**G3**	279 (1.00), 365 (0.68)	279, 369	417	421, 438	0.66	0.65
(S_p)-**G4**	279 (1.76), 363 (0.68)	283, 368	416	420, 435	0.67	0.58

[a] In $CHCl_3$ (1.0×10^{-5} M). [b] Thin film prepared by the spin-coating method from solutions in $CHCl_3$ (1.0×10^{-3} M). [c] In $CHCl_3$ (1.0×10^{-7} M), excited at $\lambda=279$ nm. [d] Thin film, excited at $\lambda=279$ nm. [e] Absolute PL quantum efficiency in $CHCl_3$ (1.0×10^{-7} M) excited at the band maximum of the core unit ($\lambda=365$ nm). [f] Absolute PL quantum efficiency of the film prepared by the spin-coating method from solutions in $CHCl_3$ (1.0×10^{-3} M), excited at the band maximum of the core unit ($\lambda=370$ nm).

Table 2. Spectroscopic data for the chiroptical properties of the (S_p) isomers.

	g_{abs}[a] $\times 10^3$		g_{lum}[d] $\times 10^3$	
	Solution[b]	Film[c]	Solution[b]	Film[c]
(S_p)-**G0**	+1.3	–	+1.4	–
(S_p)-**G1**	+1.3	+1.6	+1.4	+2.1
(S_p)-**G2**	+1.3	+1.6	+1.4	+2.0
(S_p)-**G3**	+1.6	+1.6	+1.4	+1.8
(S_p)-**G4**	+1.3	+1.5	+1.4	+2.0

[a] $g_{abs}=2\Delta\varepsilon/\varepsilon$, in which $\Delta\varepsilon$ indicates differences in absorbance between left- and right-handed circularly polarized light, respectively. The g_{abs} value of the band maximum at $\lambda\approx360$ nm was estimated. [b] In $CHCl_3$ (1.0×10^{-5} M). [c] Film prepared by the spin-coating method from solutions in $CHCl_3$ (5.0×10^{-3} M). [d] $g_{lum}=2(I_{left}-I_{right})/(I_{left}+I_{right})$, in which I_{left} and I_{right} indicate the luminescence intensities of left- and right-handed CPL, respectively. The excitation wavelength was 279 nm in the CPL spectra. The g_{lum} value of the PL band maximum at $\lambda\approx415$ nm was estimated.

The PL spectra of dilute solutions of (S_p)-**3**-G*n* in $CHCl_3$ (1.0×10^{-7} M) and the spin-coated films are shown in Figure 5A and B, respectively. Excitation was carried out at $\lambda=279$ nm to ensure excitation of the benzene rings in the dendrons. In Figure 5A, emission bands of the dendrimers (S_p)-**3**-G*n* appeared at $\lambda\approx415$ nm, which was comparable to the spectrum of the dendron-free (S_p)-**3**-G0; thus indicating that emission occurred from the *p*-phenylene–ethynylene moieties in the core unit. Because the emitting species of (S_p)-**3**-G*n* ($n=0$–4) were identical (i.e., the same core unit), their Φ_{lum} values were also comparable and calculated to be approximately 0.65 (Table 1). The band intensity of the dendrimers increased with an increasing number of benzene rings in the dendrons because of the light-harvesting effect and energy transfer from the dendrimer surface to the core. The PL intensity of the films also increased with increasing dendrimer generation (Figure 5B). In contrast with the observations in solution, the Φ_{lum} of the dendrimer film increased with increasing dendrimer generation. The Φ_{lum} values of **3**-G3 and -G4 were different, despite both cores being well protected by dendrons (see Figure 8, below). It is considered that, in the films, the conformations of the core units are slightly different in the excited states due to the restricted mobility of the cores by the congested dendrons. Aggregation of the core phenylene–ethynylene moieties is inhibited by the dendrons, and emission occurs from the isolated phenylene–ethynylene moieties, despite their film state. As the result, the intense blue emission derived from large ε and good Φ_{lum} values was obtained from the higher generation dendrimers.

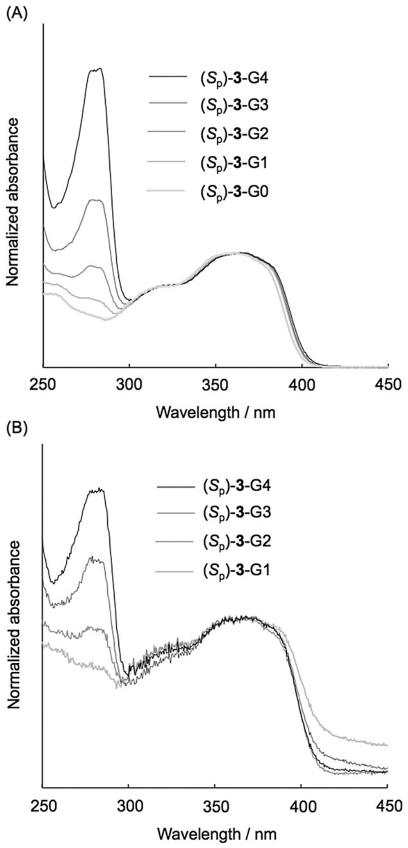


Figure 4. A) UV/Vis absorption spectra of solutions (1.0×10^{-5} M) of (S_p)-dendrimers in $CHCl_3$. B) UV/Vis absorption spectra of (S_p)-dendrimer thin films. The spectra were normalized at $\lambda\approx365$ nm.

The CD spectra of dendrimers (S_p)- and (R_p)-**3**-G*n* in $CHCl_3$ (1.0×10^{-5} M) and as films are shown in Figure 6A and B, respectively. In all cases, mirror-image Cotton effects with large $\Delta\varepsilon$ values were observed in the CD spectra. The dissymmetry factors of absorbance ($g_{abs}=\Delta\varepsilon/\varepsilon$) are also plotted in Figure 6. The g_{abs} values of the π–π* transition bands of the benzene rings at $\lambda=250$–300 nm decreased with increasing dendrimer generation (insets in Figure 6A and B). Because the Cotton

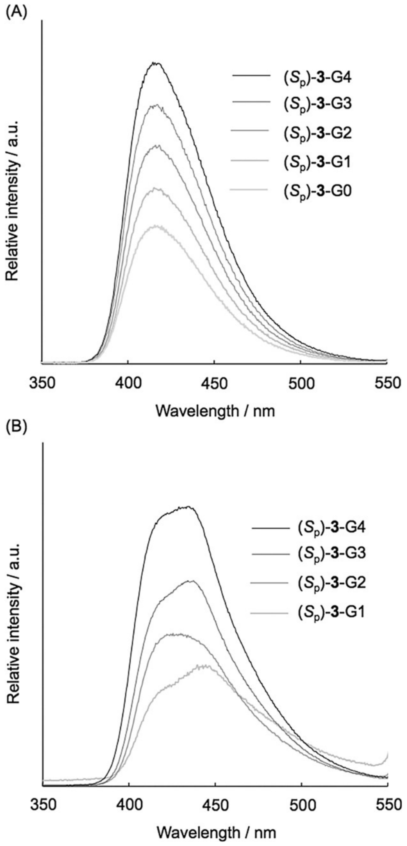


Figure 5. A) PL spectra of solutions (1.0×10^{-7} M) of (S_p)-dendrimers in $CHCl_3$. B) PL spectra of (S_p)-dendrimer thin films. Excitation wavelength: 279 nm.

effect of the benzene rings is induced by the optically active [2.2]paracyclophane core, the planar chirality of the core is not effective for benzene rings on the dendron surface. In contrast, the g_{abs} values in the π–π* transition bands of the phenylene–ethynylene moieties were identical.

The X-shaped, second-order structure of the π-electron systems of planar chiral [2.2]paracyclophane was CPL active, as previously shown in Figure 3. Intense CPL signals were therefore observed for the dendrimers in $CHCl_3$ (1.0×10^{-5} M) and the spin-coated films (Figure 7 A and B, respectively). All dendrimers exhibited high g_{lum} values in the order of 10^{-3}. Thus, the Fréchet-type dendron provided planar, chiral, [2.2]paracyclophane-based π-electron systems with unprecedented PL and CPL properties such as large ε, good Φ_{lum}, and excellent g_{lum} values both in solution and as films. Figure 8 shows the simulated structures of the dendrimers (S_p)-**3**-G*n* ($n=1$–4) obtained by using PM3[24] with MOPAC2012.[25] The dendrons of (S_p)-**3**-G1 and -G2 do not sufficiently protect the core unit, whereas those of (S_p)-**3**-G3 and -G4 isolate the core unit; thus inhibiting aggregation-caused quenching.

To investigate the dendritic effect on PL, X-shaped (S_p)-**3**-G0 was dispersed in a polystyrene (PS; $M_n=8.1\times10^4$, $M_w=2.1\times10^5$) matrix. The PL spectra of 5 and 10 wt% (S_p)-**3**-G0 in PS were compared with those of (S_p)-**3**-G3 and (S_p)-**3**-G4 spin-coated films (Figure 9 A). The PL intensities of 5 and 10 wt% (S_p)-**3**-G0 in PS were clearly lower than those of the dendrimer films, despite the benzene-rich environment. As shown in the excitation spectra (Figure 9 B), only weak bands derived from the PS phenylene moieties were observed at $\lambda\approx270$ nm, which implied that the benzene rings of PS did not participate significantly in emission from the core unit. On the other hand, as shown in Figure 9 B, bands appeared at $\lambda\approx275$ nm in the excitation spectra of the (S_p)-**3**-G3 and (S_p)-**3**-G4 dendrimer films. Figures S13A and S13B in the Supporting Information show the excitation spectra of (S_p)-**3**-G*n* ($n=1$–4) in $CHCl_3$ and as spin-coated films, respectively. The band intensity derived

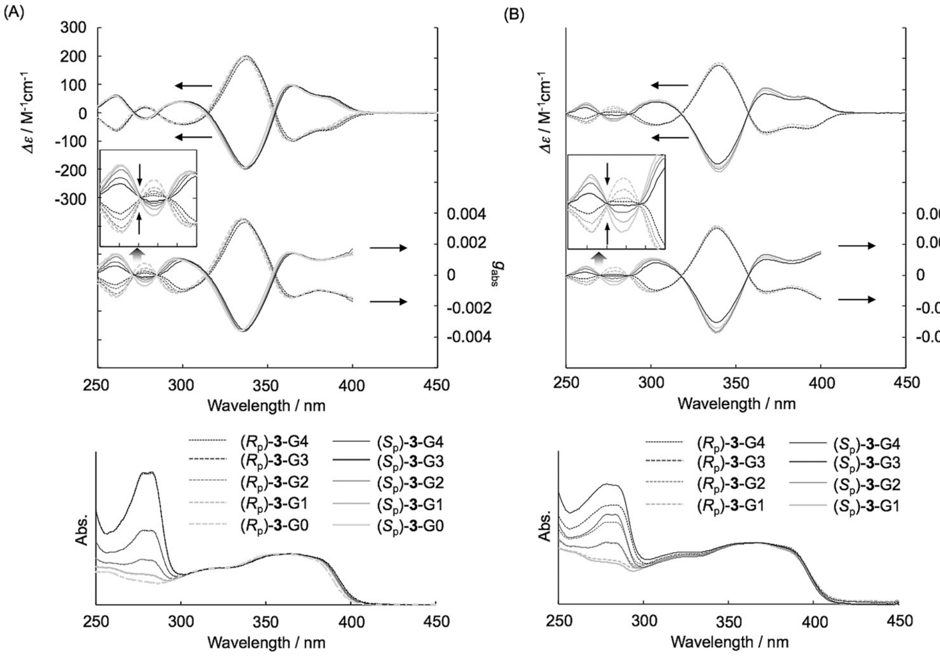


Figure 6. A) CD, g_{abs}, and UV/Vis absorption spectra of solutions (1.0×10^{-5} M) of dendrimers in $CHCl_3$. B) CD, g_{abs}, and UV/Vis absorption spectra of the thin films. Expanded g_{abs} spectra (from $\lambda=250$ to 300 nm) are shown in the insets.

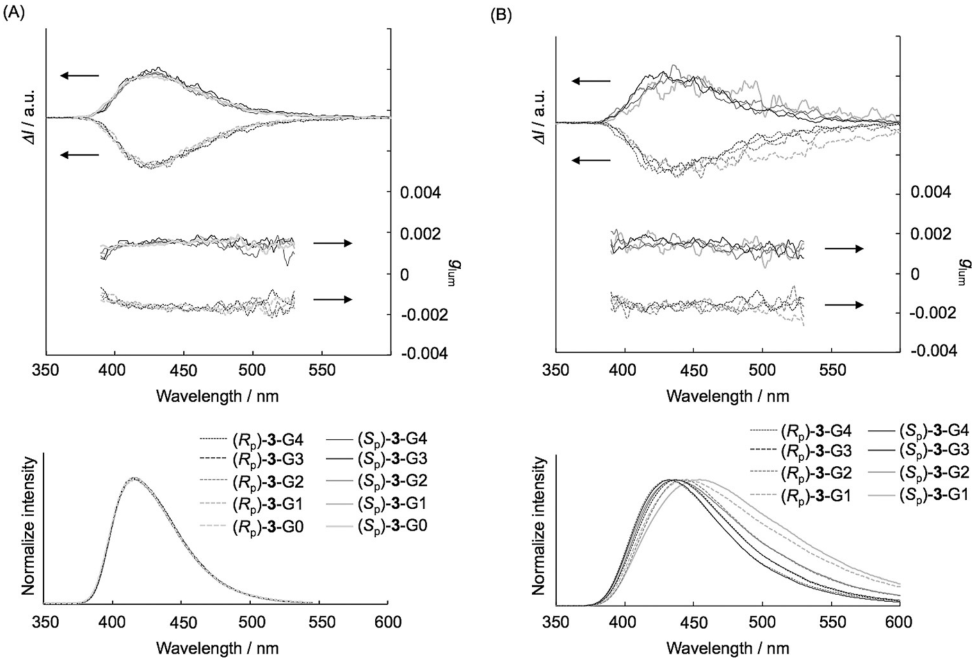


Figure 7. A) CPL, g_{lum}, and PL spectra of solutions (1.0×10^{-5} M) of dendrimers in $CHCl_3$. B) CPL, g_{lum}, and PL spectra of dendrimer thin films. Excitation wavelength: 279 nm.

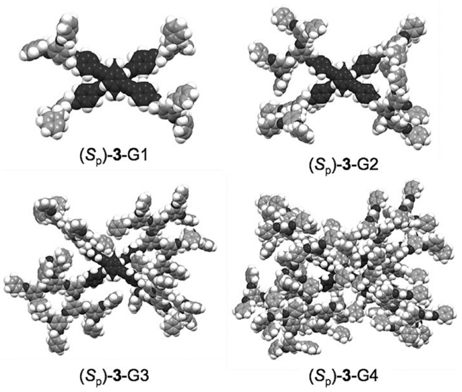


Figure 8. Space-filling model of the dendrimers simulated by means of PM3.[24] The conjugated core units are shown in dark gray.

from the benzene units in the dendrons increased as the dendrimer generation increased. These results clearly indicate the contribution of the benzene rings to emission from the core unit in the dendrimers through the light-harvesting effect.

Conclusion

We achieved the gram-scale optical resolution and transformations of planar, chiral, 4,7,12,15-tetrasubstituted [2.2]paracyclophanes. Optically active Fréchet-type dendrimers containing an X-shaped conjugated core with the planar chiral [2.2]paracyclophane moiety were prepared. The dendrons effectively absorbed UV light and transferred energy to the core. In addition, the dendrons sufficiently isolated the emissive X-shaped conju-

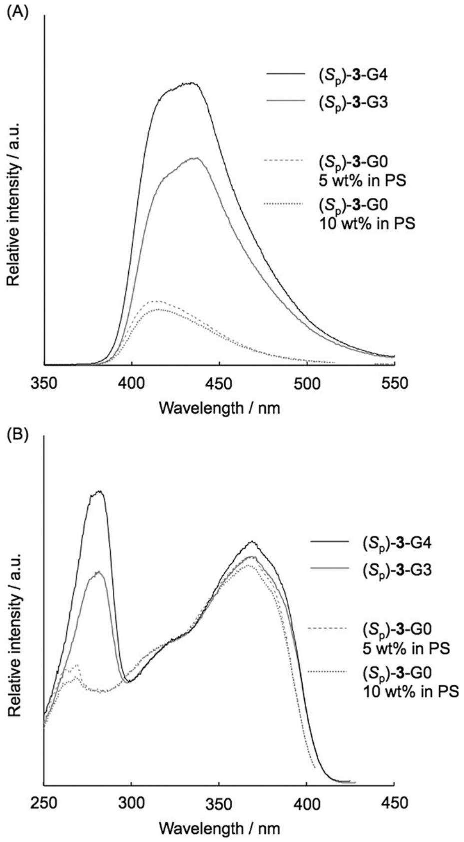


Figure 9. A) PL spectra of (S_p)-**3**-G3 and -G4 films. PL spectra of PS films containing 5 and 10 wt% (S_p)-**3**-G0. B) Excitation spectra of (S_p)-**3**-G3 and -G4 films. Excitation spectra of PS films containing 5 and 10 wt% (S_p)-**3**-G0. Excitation spectra were obtained at the PL band maximum wavelength.

gated core, which resulted in high emission from the thin films. Intense CPL by the planar chiral [2.2]paracyclophane was observed with a high dissymmetry factor in the order of 10^{-3}. The combination of Fréchet-type dendrons with planar chiral [2.2]paracyclophane provided emissive conjugated compounds with large ε and $\Delta\varepsilon$ values, good Φ_{lum} values, intense PL and CPL, and large g_{lum} factors. This strategy is promising for the design of organic CPL materials.

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Keywords: chirality · conjugation · dendrimers · luminescence · paracyclophanes

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