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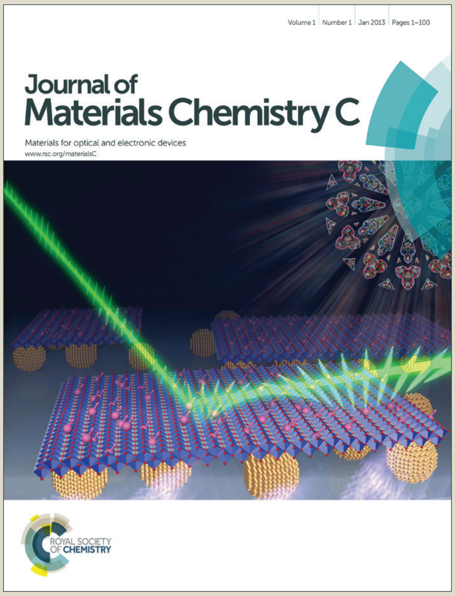

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Optically Active Cyclic Compounds Based on Planar Chiral [2.2]Paracyclophane: Extension of the Conjugated Systems and Chiroptical Properties †

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A series of optically active cyclic compounds based on the planar chiral tetrasubstituted [2.2]paracyclophane core were synthesized to obtain luminescent materials with excellent chiroptical properties in both the ground and excited states. The optical resolution of tetrasubstituted [2.2]paracyclophane was carried out using our previously reported method. The obtained cyclic compounds were composed of the optically active propeller-shaped structures created by the [2.2]paracyclophane core with *p*-phynylene-ethynylne moieties. The compounds exhibited good optical profiles, with a large molar extinction coefficient (ε) and photoluminescence quantum efficiency (Φ_{lum}). The emission occurred mainly from the propeller-shaped cyclic structures. This optically active higher-ordered structure provided chiroptical properties of high performance, such as a large specific rotation ($[\alpha]_D$) and molar ellipticity ($[\theta]$) in the ground state and intense circularly polarized luminescence (CPL) with large dissymmetry factors (g_{lum}) in the exited state. The results suggest that planar chiral [2.2]paracyclophane-based optically active higher-ordered structures, such as the propeller-shaped cyclic structure, are promising scaffolds for obtaining CPL and that appropriate modifications can enhance the CPL characteristics.

Introduction

The importance of conjugated compounds has been increasing owing to their conductive, luminescent, and charge transfer properties, leading to their potential application in various opto-electronic devices.[1] Both industrial and academic researchers have extensively studied the design and construction of novel conjugated systems. For the past decade, we have focused on a [2.2]paracyclophane skeleton[2] as a building block for conjugated polymers[3] and oligomers.[4] [2.2]Paracyclophane is a typical cyclophane compound containing two stacked phenylenes in close proximity. This compound was first prepared by Brown and Farthing in 1949 by pyrolysis of *p*-xylene.[5] In 1951, Cram and Steinberg reported its direct synthesis by a Wurtz-type intramolecular cyclization of 1,4-bis(bromomethyl)benzene.[6] Since then, considerable attention has been paid in the field of organic chemistry to the synthesis, reactivity, and opto-electronic properties of this unique conjugated system.[2]

One of the interesting features of [2.2]paracyclophane compounds is undoubtedly the π-π interactions between the stacked aromatic rings, as well as the resulting stacked π-electron systems. Bazan, Mukamel, and co-workers reported the characteristic optical properties of 4,12-disubstituted and 4,7,12,15-tetrasubstituted [2.2]paracyclophane compounds.[7] They disclosed that the stacked position of the two π-electron systems affects the conjugation system in the ground and excited states. In particular, the two stacked π-electron systems found in the 4,7,12,15-tetrasubstituted [2.2]paracyclophane skeleton, i.e. interchromophore interactions between the two π-electron systems, exhibit strong through-space conjugation in addition to the common through-bond conjugation.[7b,d,e,i,j] Hopf, Haley, and co-workers synthesized cyclic compounds that have an propeller-shaped structure based on the 4,7,12,15-tetrasubstituted [2.2]paracyclophane unit.[8]

The stacked structures of [2.2]paracyclophanes result in the three-dimensional molecules. Very recently, inspired by the synthesis of the propeller-shaped cyclic compounds based on 4,7,12,15-tetrasubstituted [2.2]paracyclophane and its unique π-conjugation system, we attempted to introduce chirality into this cyclic structure.[9] Some [2.2]paracyclophanes with substituents are planar chiral compounds due to the suppression of the rotary motion of the phenylenes.[10] We achieved optical resolution of 4,7,12,15-tetrasubstituted [2.2]paracyclophane compounds[9,11] using the diastereomer method, followed by a transformation to obtain the enantiopure precursors (R_p)- and (S_p)-**3Ph** and the propeller-shaped cyclic compounds (R_p)- and (S_p)-**3PhC** (Figure 1).[9] It should be noted that the obtained optically active cyclic compounds exhibited intense circularly polarized luminescence (CPL)[12] with a large dissymmetry factor (g_{lum}) on the order of 10^{-2}.

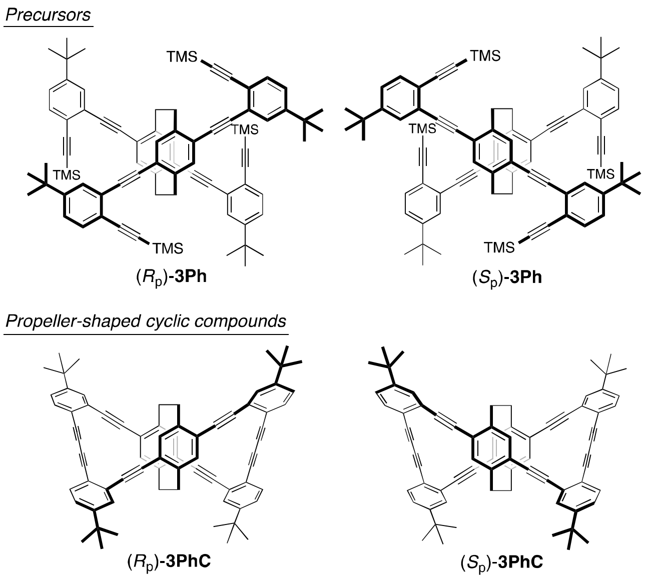
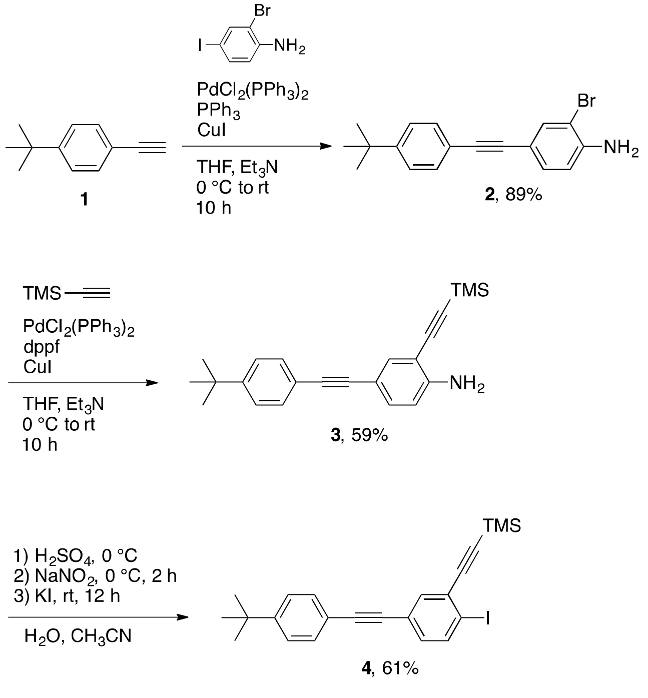


Fig. 1 Precursors and the corresponding propeller-shaped cyclic compounds we prepared previously.

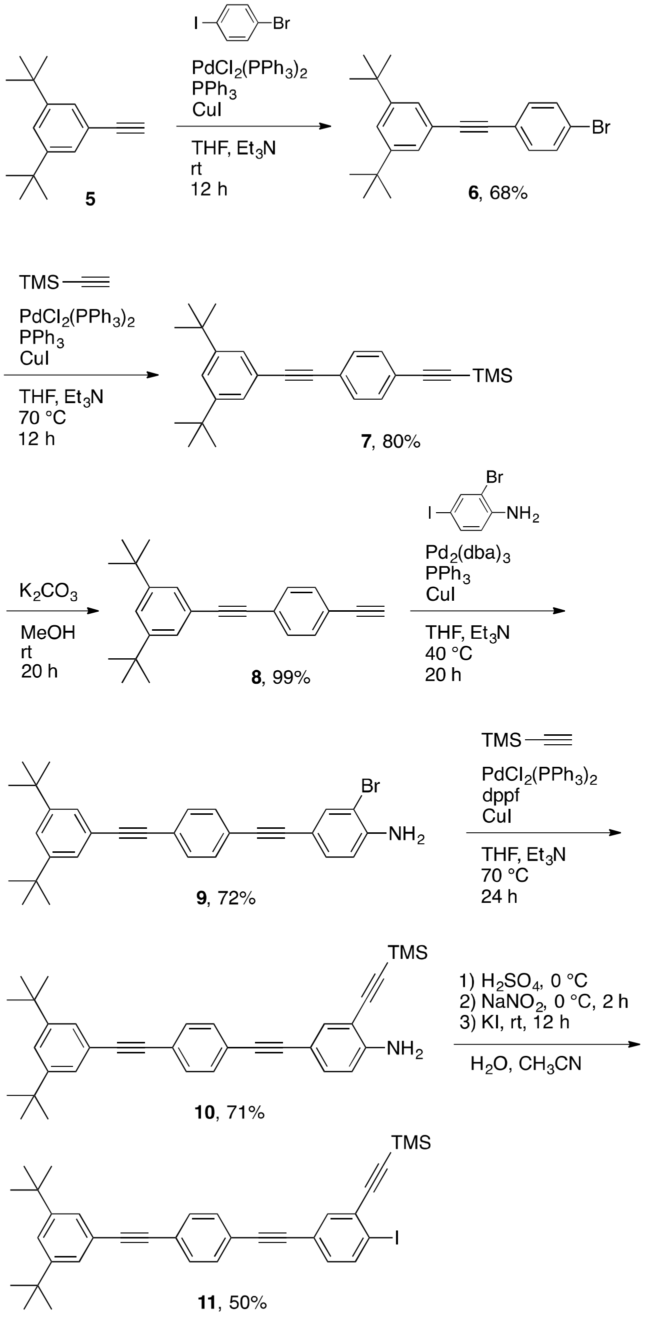
Further development of planar chiral [2.2]paracyclophane-based optically active compounds is expected to afford luminescent materials with excellent chiroptical properties in both the ground and excited states. In this study, we focused our attention on the propeller-shaped skeleton containing the planar chiral tetrasubstituted [2.2]paracyclophane core. To obtain superior CPL emitters, we designed cyclic compounds with extended π-conjugation moieties; herein, the synthesis and optical properties of these compounds are discussed.

Results and discussion

Synthesis



Scheme 1 Synthesis of compound **4** (arm unit for **5PhC**).

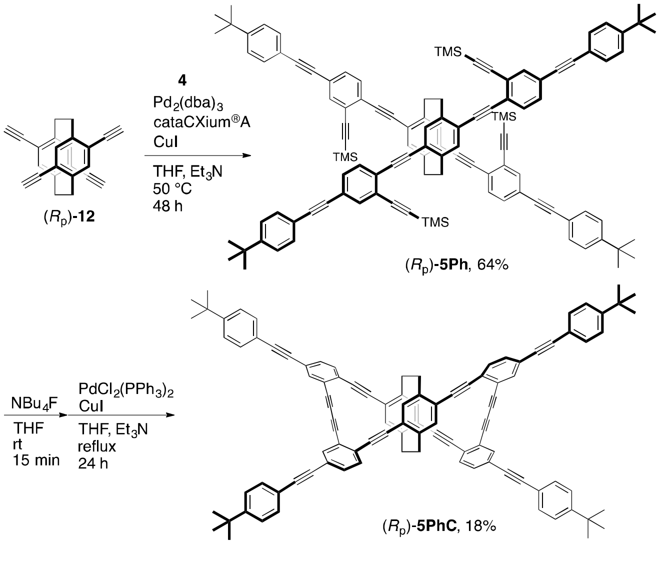


Scheme 2 Synthesis of compound **11** (arm unit for **7PhC**).

The optical resolution of planar chiral 4,7,12,15-tetrasubstituted [2.2]paracyclophane was carried out using the diastereomer method we previously developed, and the obtained enantiopure compounds were converted to the corresponding (R_p)- and (S_p)-4,7,12,15-tetraethynyl[2.2]paracyclophanes.[9] The synthetic routes to the target optically active cyclic compounds are shown in Schemes 1–4. Initially, we prepared phenylene-ethynylene compounds **4** and **11** as arm units for light-harvesting moieties (Schemes 1 and 2, respectively). The *tert*-butyl groups in **4** and **11** were introduced to provide the target compounds with solubility in organic solvents, such as THF, $CHCl_3$, CH_2Cl_2, and toluene; in particular, two *tert*-butyl groups were required in **11** to dissolve the extended π-conjugation system of this cyclic compound in these solvents.

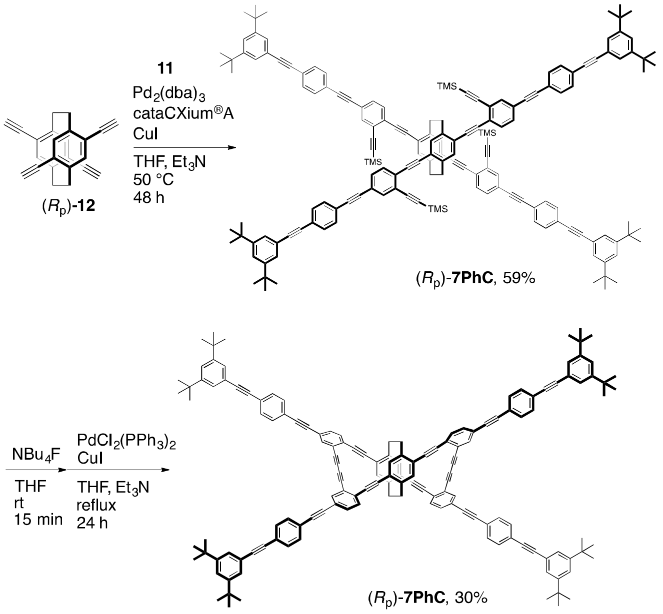
As shown in Scheme 1, 4-*tert*-butylethynylbenzene **1** was reacted with 2-bromo-4-iodoaniline in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ to obtain compound **2** in 89% isolated yield; this reaction occurred chemoselectively at the iodine substituent of **2**. Sonogashira-Hagihara coupling[13] of **2** with trimethylsilylacetylene (TMS-acetylene) afforded compound **3** in 59% isolated yield. The amino group in **3** was converted to an iodo group using the Sandmeyer reaction[14] to obtain compound **4** in 61% isolated yield.

The chemoselective Sonogashira-Hagihara coupling of 3,5-di(*tert*-butyl)ethynylbenzene **5** with *p*-iodobromobenzene afforded compound **6** in 68% isolated yield (Scheme 2). The successive Sonogashira-Hagihara coupling of **6** with TMS-acetylene gave compound **7** in 80% isolated yield. The TMS group in **7** was readily removed by reaction with K_2CO_3/MeOH to prepare compound **8** quantitatively. Compound **8** was reacted with 2-bromo-4-iodoaniline in the same manner as described for compound **1** (Scheme 1); successive Sonogashira-Hagihara coupling with TMS-acetylene to obtain compound **10** in 71% isolated yield and the Sandmeyer reaction afforded the corresponding compound **11** in 50% isolated yield.



Scheme 3 Synthesis of (R_p)-**5Ph** and (R_p)-**5PhC**.

Schemes 3 and 4 show the syntheses of the target cyclic compounds **5PhC** and **7PhC**, respectively. In these Schemes, only the reactions of the (R_p)-isomers are shown in these reactions; the (S_p)-isomers where prepared under identical conditions from (S_p)-**12**. The treatment of (R_p)-4,7,12,15-tetraethynyl[2.2]paracyclophane (R_p)-**12** with compound **4** in the presence of the $Pd_2(dba)_3$/CuI catalytic system using di(1-adamantyl)-*n*-butylphosphine[15] (cataCXium® A) as a phosphine ligand afforded compound (R_p)-**5Ph** in 64% isolated yield (Scheme 3). After deprotection of the four TMS groups in (R_p)-**5Ph** using NBu_4F, a Pd-mediated alkyne coupling was carried out in situ to obtain cyclic compound (R_p)-**5PhC** in 18% isolated yield. Under the same reaction conditions, compounds (R_p)-**7Ph** and (R_p)-**7PhC** with the extended phenylene-ethynylene units were prepared by the reaction of **11** with (R_p)-**12**, as shown in Scheme 4. When cyclization was carried out, unidentified impurities such as oligomeric products by intermolecular reactions were formed. They could be readily removed by column chromatography on SiO_2, resulting in low isolated yields (18% and 30% for (R_p)-**5PhC** and (R_p)-**7PhC**, respectively). The structures of all new compounds in this study were confirmed by ^1H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis; the detailed synthetic procedures and NMR spectra are shown in Electronic Supplementary Information (ESI).



Scheme 4 Synthesis of (R_p)-**7Ph** and (R_p)-**7PhC**.

Optical properties

The optical properties of both enantiomers of cyclic compounds **3PhC**, **5PhC**, and **7PhC** as well as their precursors **3Ph**, **5Ph**, and (S_p)-**7Ph** were evaluated. The data are summarized in Table 1. Although the optical and chiroptical properties of **3Ph** and **3PhC** were previously reported, they are included herein for comparison.

Figures 2A and 2B show the UV-vis absorption spectra and photoluminescence (PL) spectra of the (R_p)-precursors in dilute $CHCl_3$ solutions (1.0×10^{-5} M for UV and 1.0×10^{-6} M for PL), respectively. The absorption spectra exhibited a hyperchromic effect and bathochromic shift with extension of the π-conjugation length (Figure 2A). In the PL spectra (Figure 2B), a similar bathochromic shift was observed. The PL spectra of (R_p)-**5Ph** and (R_p)-**7Ph** exhibited vibrational structure, whereas that of (R_p)-**3Ph** was relatively broad; the same phenomena were observed in the case of *p*-phenylenevinylene-stacked [2.2]paracyclophane compounds reported previously by Bazan and co-workers.[7b,d,e,i,j] This result suggests that the excited energy migrates to the phane state[7] in (R_p)-**3Ph**; however, it is localized on the extended phenylene-ethynylene chromophores in (R_p)-**5Ph** and (R_p)-**7Ph**. Table 1 includes the PL decay data (PL lifetime (τ□) and χ^2 parameters) for all compounds, and the decay curves are shown in ESI. Thus, it was supported by the shorter PL lifetimes of (R_p)-**5Ph** (τ = 1.05 ns) and (R_p)-**7Ph** (τ = 0.87 ns) than that of (R_p)-**3Ph** (τ = 2.16 ns); in other words, the PL of (R_p)-**5Ph** and

(R_p)-**7Ph** occurred from the chromophore states[7] rather than the phane states.

Table 1 Optical properties: spectroscopic data of (R_p)-isomers.

	$\lambda_{abs}{}^{a}$ / nm ($\varepsilon \times 10^{-5}$ / □$^{-□}$□□$^{-□}$)	$\lambda_{\lambda um}{}^{b}$	τ^{c}/ ns (χ^2)	$\Phi_{lum}{}^{d}$
(R_p)-**3Ph**	372 (0.44)	418	2.16 (1.04)	0.46
(R_p)-**5Ph**	398 (1.41)	438	1.05 (1.00)	0.80
(R_p)-**7Ph**	403 (1.79)	443	0.87 (1.00)	0.88
(R_p)-**3PhC**	314 (2.60), 391 (0.46)	453	3.75 (1.06)	0.41
(R_p)-**5PhC**	329 (2.16), 419 (1.06)	471	2.07 (1.01)	0.60
(R_p)-**7PhC**	355 (2.58), 422 (1.27)	474	2.00 (1.08)	0.70

[a] In CHCl$_3$ (1.0 × 10^{-5} □). [b] In CHCl$_3$ (1.0 × 10^{-6} □), excited at absorption maxima. [c] Emission life time at λ_{lum}.
[d] Absolute PL quantum efficiency.

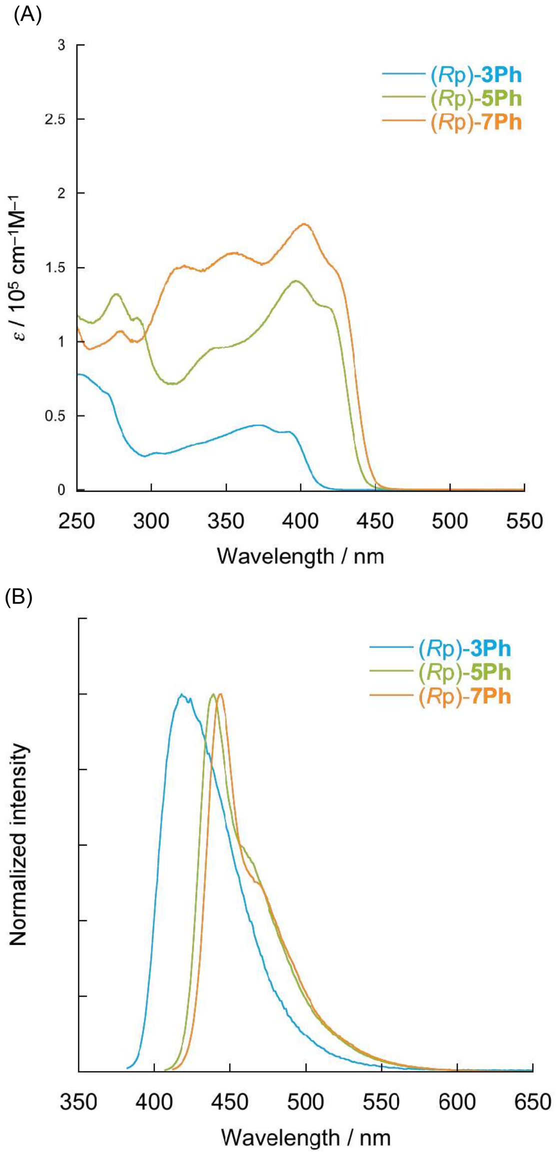


Fig. 2 (A) UV-vis absorption spectra in dilute CHCl$_3$ (1.0 × 10^{-5} M) and (B) PL spectra in dilute CHCl$_3$ (1.0 × 10^{-6} M; excited at absorption maximum) of (R_p)-**3Ph**, (R_p)-**5Ph**, and (R_p)-**7Ph**.

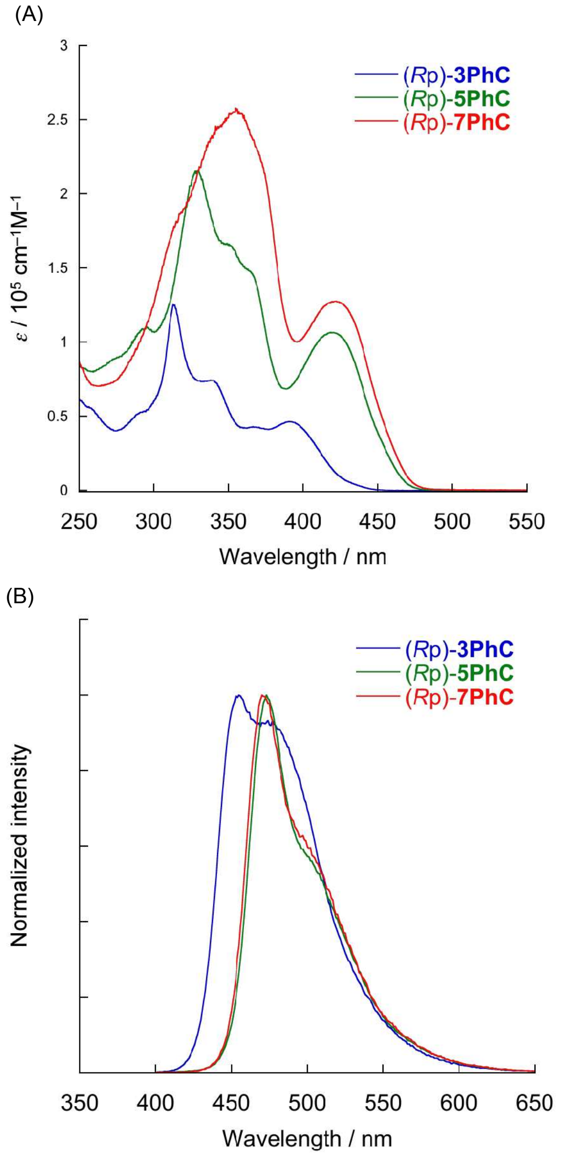


Fig. 3 (A) UV-vis absorption spectra in dilute CHCl$_3$ (1.0 × 10^{-5} M) and (B) PL spectra in dilute CHCl$_3$ (1.0 × 10^{-6} M; excited at absorption maximum) of (R_p)-**3PhC**, (R_p)-**5PhC**, and (R_p)-**7PhC**.

As shown in Figures 3A and 3B, the same tendencies were observed in the absorption and PL spectra of cyclic compounds (R_p)-**3PhC**, (R_p)-**5PhC**, and (R_p)-**7PhC**. The absorption spectrum of (R_p)-**5PhC** exhibited a hyperchromic effect and was bathochromically shifted in comparison with that of (R_p)-**3PhC** (Figure 3A). Although the absorption spectrum of (R_p)-**7PhC** also showed a hyperchromic effect and was bathochromically shifted, the absorption bands of (R_p)-**5PhC** and (R_p)-**7PhC** near 425 nm were almost identical. As shown in Figure 3B, the PL spectra of (R_p)-**5PhC** and (R_p)-**7PhC** were identical and both exhibited vibrational structures. The absolute PL quantum efficiencies (Φ_{lum}) of (R_p)-**5PhC** and (R_p)-**7PhC** were determined to be 0.60 and 0.70, respectively. The lifetimes were lengthened by cyclization of the compounds and shortened by elongation of the conjugated systems. All compounds exhibited single exponential decay curves. The τ of (R_p)-**3PhC** was estimated to be 3.75 ns, which were longer than those of (R_p)-**5PhC** (τ = 2.07 ns) and (R_p)-**7PhC** (τ = 2.00 ns). In addition, the τ of (R_p)-**5PhC** and (R_p)-**7PhC** were identical, suggesting that the PL of (R_p)-**5PhC** and (R_p)-**7PhC** arose from similar emitting species.

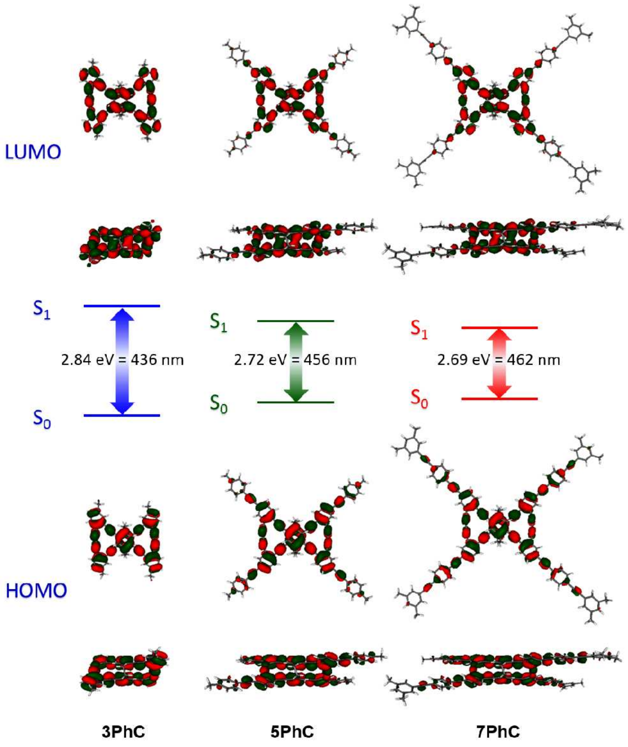


Fig. 4 HOMOs and LUMOs of (R_p)-**3PhC**, (R_p)-**5PhC**, and (R_p)-**7PhC** obtained by density functional theory (DFT) at the TD-BHandHLYP/Def2-TZVPP//BLYP/Def2-TZVPP level.

Figure 4 shows the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of the cyclic compounds (R_p)-**3PhC**, (R_p)-**5PhC**, and (R_p)-**7PhC**; the molecular orbitals were obtained by density functional theory (DFT) at the TD-BHandHLYP/Def2-TZVPP//BLYP/Def2-TZVPP level. The longest wavelength absorption bands observed in the absorption spectra (Figure 3A) were assigned to the S_0 to S_1 transition (Figure 4); both the HOMO and LUMO are located mainly on the cyclic moieties of these compounds. The π-orbitals are somewhat extended to the *p*-phenylene-ethynylene arms in the HOMOs of (R_p)-**5PhC** and (R_p)-**7PhC**, whereas they were localized on the cyclic moieties in the LUMOs. As the π-conjugations of (R_p)-**5PhC** and (R_p)-**7PhC** did not extend to the LUMOs regardless of the length of the π-conjugated *p*-phenylene-ethynylenes, the properties of the cyclic skeleton would predominately affect the absorption and emission, resulting in the similar optical profiles observed for (R_p)-**5PhC** and (R_p)-**7PhC**.

Chiroptical properties

The chiroptical properties of the ground and excited states of **3Ph**, **5Ph**, **7Ph**, **3PhC**, **5PhC**, and **7PhC** were investigated by circular dichroism (CD) and CPL spectroscopy, respectively. The chiroptical data, i.e., the maximum molar ellipticity ([θ]), specific rotation, and CPL dissymmetry factor[16] (g_{lum}) are summarized in Table 2. Figure 5 shows the CD and absorption spectra of both enantiomers of **3Ph**, **5Ph**, and **7Ph** in dilute $CHCl_3$ (1.0×10^{-5} M). In all cases, mirror image Cotton effects were observed in the CD spectra, and the maximum [θ] values were estimated to be approximately $\pm 3.3 \times 10^5$ deg·cm^2·dmol^{-1}. As can be seen in Figure 6, the [θ] values for **3PhC**, **5PhC**, and **7PhC** were larger than those of **3Ph**, **5Ph**, and **7Ph**, with the maximum values on the order of 10^6 deg·cm^2·dmol^{-1}. The specific rotation $[\alpha]^{23}_{\mathrm{D}}$ values for (R_p)-**3PhC**, **5PhC**, and **7PhC** were +1501.0, +855.6, and +467.9, respectively, and were much larger than those for (R_p)-**3Ph**, **5Ph**, and **7Ph** (Table 2). Thus, the construction of optically active higher-ordered (propeller-shaped) structures through cyclization affected the chiroptical properties of the ground state, and greater chirality was induced in the cyclic compounds.

Table 2 Chiroptical properties: specific rotation and spectroscopic data of (R_p)-isomers.

	$[\alpha]^{23}_{\mathrm{D}}$ [a]	$g_{\mathrm{abs}} \times 10^2$ at λ_{abs} [b]	$g_{\mathrm{lum}} \times 10^2$ at $\lambda_{\mathrm{lum,max}}$ [c]
(R_p)-**3Ph**	–45.4	–0.13	–0.14
(R_p)-**5Ph**	–42.5	–0.14	–0.12
(R_p)-**7Ph**	–62.9	–0.10	–0.10
(R_p)-**3PhC**	+1501.0	+0.88	+1.3
(R_p)-**5PhC**	+855.6	+1.0	+1.0
(R_p)-**7PhC**	+467.9	+0.75	+0.75

[a] Specific rotation (c 0.1, $CHCl_3$ at 25 °C). The $[\alpha]^{23}_{\mathrm{D}}$ values of (S_p)-isomers are described in ESI. [b] $g_{\mathrm{abs}} = 2\Delta\varepsilon/\varepsilon$, where $\Delta\varepsilon$ indicates differences of absorbance between left and right handed circularly polarized light, respectively. The g_{abs} value of the first peak top was estimated. [c] $g_{\mathrm{lum}} = 2(I_{\mathrm{left}} - I_{\mathrm{right}})/(I_{\mathrm{left}} + I_{\mathrm{right}})$, where I_{left} and I_{right} indicate luminescence intensities of left and right handed CPL, respectively.

The CPL spectra of the precursors and cyclic compounds in dilute $CHCl_3$ (1.0×10^{-5} M) are shown in Figures 7 and 8, respectively. Intense and mirror image CPL signals were observed in the emission regions for the enantiomers of each compound, as shown in Figures 7 and 8. The g_{lum} values of **3Ph**, **5Ph**, and **7Ph** were very large (-0.14×10^{-2}, -0.12×10^{-2}, and -0.10×10^{-2} for the (R_p)-isomers, respectively; Table 2).

The g_{lum} values for (R_{p})-**3PhC**, **5PhC**, and **7PhC** were calculated to be +1.3 × 10^{-2}, +1.0 × 10^{-2}, and +0.75 × 10^{-2}, respectively (Table 2). As expected, the values for the cyclic compounds were significantly larger than those for the precursors owing to the optically active propeller-shaped structures. Higher-ordered structures of the emitting species in the excited state, such as propeller-shaped,[9] V-shaped,[17] S-shaped,[18] and helical structures,[17–20] are considered to be important for large g_{lum} values on the order of 10^{-2}–10^{-3}.[21,22]

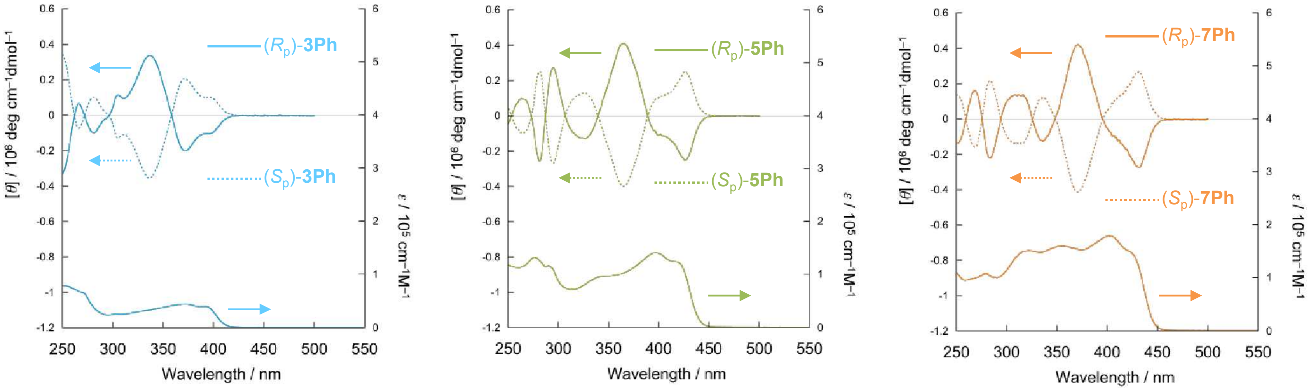


Fig. 5 CD (upper) and absorption (lower) spectra of **3Ph**, **5Ph**, and **7Ph** in $CHCl_3$ (1.0 × 10^{-5} M).

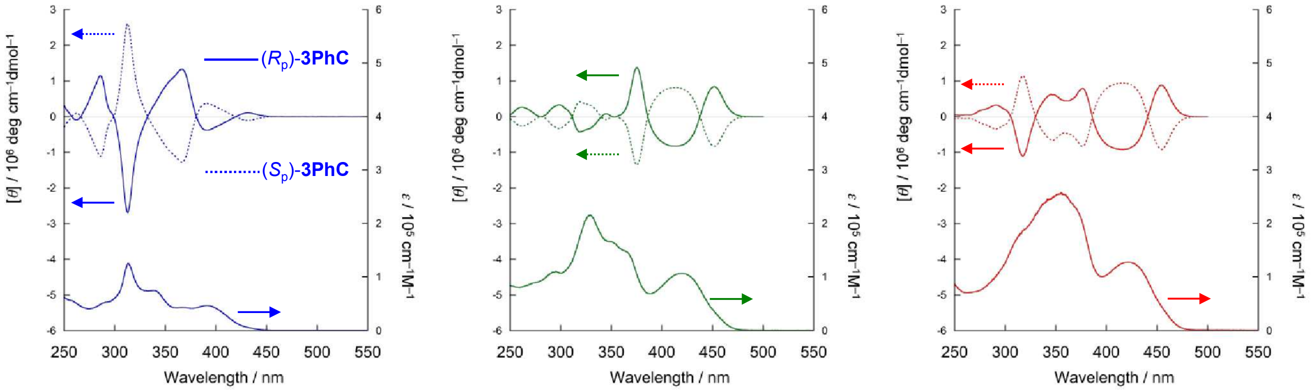


Fig. 6 CD (upper) and absorption (lower) spectra of **3PhC**, **5PhC**, and **7PhC** in $CHCl_3$ (1.0 × 10^{-5} M).

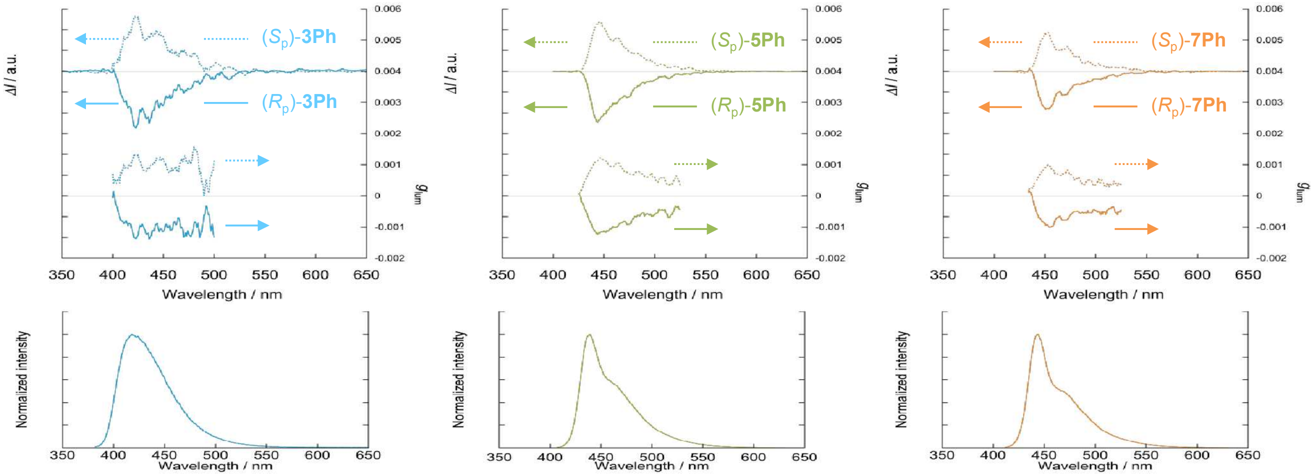


Fig. 7 CPL (top), g_{lum} (middle), and PL (bottom) spectra of **3Ph**, **5Ph**, and **7Ph** in $CHCl_3$ (1.0 × 10^{-5} M for CPL and 1.0 × 10^{-6} M for PL). Excitation wavelength: 300 nm, 350 nm, and 350 nm for **3Ph**, **5Ph**, and **7Ph**, respectively.

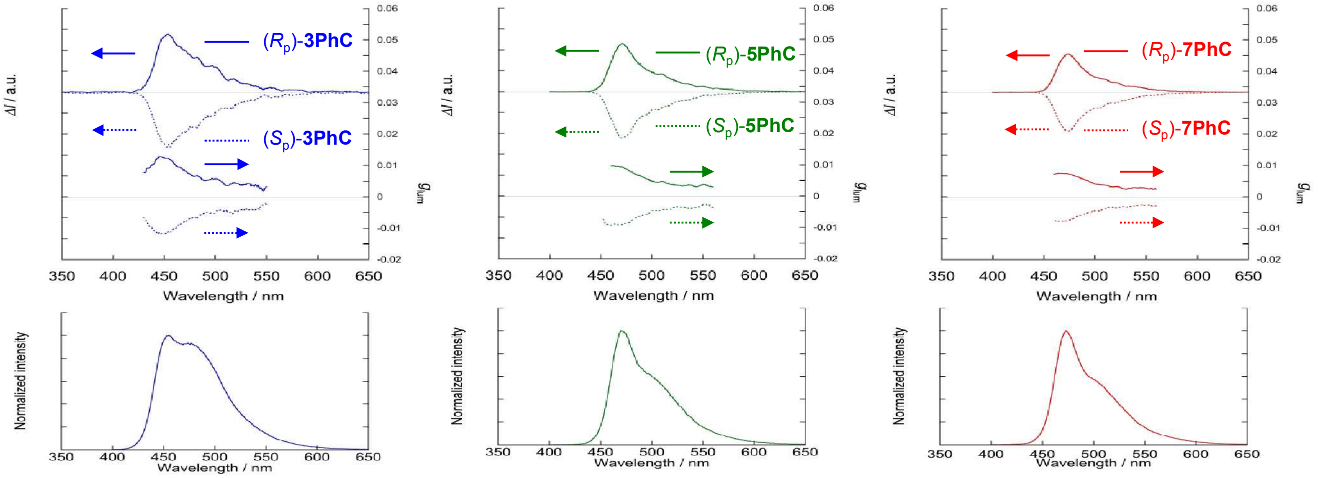


Fig. 8 CPL (top), glum (middle), and PL (bottom) spectra of **3PhC**, **5PhC**, and **7PhC** in $CHCl_3$ (1.0×10^{-6} M). Excitation wavelength: 314 nm, 350 nm, and 355 nm for **3Ph**, **5Ph**, and **7Ph**, respectively.

Concentration effect (from 1.0×10^{-7} M to 1.0×10^{-3} M in $CHCl_3$) on CPL was studied for (R_p)-isomers, and the CPL profiles of their film fabricated by drop-casting from $CHCl_3$ solution (1.0×10^{-3} M) were also investigated. The results are shown in Figures S25–30 in ESI. The CPL spectra were gradually red-shifted and the $g_{\rm lum}$ values decreased slightly, as the concentration increased. In our previous report, the $g_{\rm lum}$ value of **3PhC** was estimated to be 1.1×10^{-2} in $CHCl_3$ (1.0×10^{-5} M),[9] whereas the $g_{\rm lum}$ values in more diluted $CHCl_3$ solutions (1.0×10^{-6} and 10^{-7} M) were 1.3×10^{-2}. Solvent effect on CPL using good solvents such as CH_2Cl_2, toluene, and THF was not observed. The films exhibited almost the same $g_{\rm lum}$ values as those in solution, although the $\Phi_{\rm lum}$ decreased, as shown in Figures S26, S28, and S30.

The $g_{\rm lum}$ values of **3PhC**, **5PhC**, and **7PhC** decreased as the $\Phi_{\rm lum}$ values increased with the extension of the *p*-phenylene-ethynylene substituents; however, the $g_{\rm lum}$ values were sufficiently large in comparison with the values reported till now.[21,17–22] Generally, the achievement of both high $\Phi_{\rm lum}$ and large $g_{\rm lum}$ values is challenging, because orientation of fluorophores tends to decrease the PL performance because of excimer-like emission. Helicene derivatives are considered to be one of the promising candidates for organic CPL materials, and many of them exhibit large $g_{\rm lum}$ values;[19] however, the $\Phi_{\rm lum}$ values of helicene derivatives are by no means satisfactory.[23] Considering the applications of organic emitters, large ε, high $\Phi_{\rm lum}$, and large $g_{\rm lum}$ values are required. From this viewpoint, **5PhC** and **7PhC** possess well-balanced optical profiles (large ε values of $2.16–2.58 \times 10^5$ $M^{-1}cm^{-1}$, good $\Phi_{\rm lum}$ values of 0.60–0.70, and large $g_{\rm lum}$ values of $0.75–1.0 \times 10^{-2}$), and these compounds show good potential for application in organic CPL materials.

Conclusions

In summary, planar chiral [2.2]paracyclophane-based cyclic compounds with extended π-conjugated systems were synthesized. Cyclization resulted in a significant enhancement of the optical and chiroptical properties compared with those of the non-cyclic precursors. The HOMOs of the cyclic compounds were mainly located on the cyclic skeletons, whereas the LUMOs were localized on the cyclic skeletons. Thus, the absorption and emission occurred from the propeller-shaped cyclic structures, resulting in similar optical profiles for both **5PhC** and **7PhC**. The optically active higher-ordered structure of these compounds provided chiroptical properties of high performance, and both large $[\alpha]_{\rm D}$ and $[\theta]$ values were derived from the optically active propeller-shaped structure. The rigid propeller-shaped cyclic structures are maintained in the exited state unless carbon-carbon bonds are cleaved; hence, intense CPL with large $g_{\rm lum}$ values was observed for these compounds. The *p*-phenylene-ethynylene substituents introduced onto the propeller-shaped structure acted as light-harvesting antenna and improved the optical properties, leading to the large ε values and relatively high $\Phi_{\rm lum}$ values for the cyclic compounds. Compound **5PhC** was, in particular, an outstanding CPL emitter, possessing well-balanced optical and chiroptical properties. The results of the present work suggest that planar chiral [2.2]paracyclophane-based optically active higher-ordered structures, such as the propeller-shaped cyclic structure, are promising scaffolds for emergent CPL materials and that appropriate modifications, e.g. extension of the π-conjugated system, can enhance the CPL characteristics.

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Notes and references

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† Electronic supplementary information (ESI) available: Experimental details including synthetic procedures, characterizations, and NMR spectra. Fluorescence decay curves and excitation spectra are also included. See DOI: 10.1039/b000000x/

1 For example, (a) *Handbook of Conducting Polymers, 3rd ed.*, ed. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Marcel Dekker, New York, 2006; (b) *Organic Light Emitting Devices: Synthesis, Properties and Application*, ed. K. Müellen and U. Scherf, Wiley-VCH, Weinheim, Germany, 2006; (c) *Organic Field-Effect Transistors*, ed. J. R. Groza and J. J. Locklin, CRC Press Taylor & Francis Group, New York, 2007; (d) *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*, ed. C. Brabec, V. Dyakonov and U. Scherf, Wiley-VCH, Weinheim, Germany, 2008.

2 (a) *Cyclophane Chemistry: Synthesis, Structures and Reactions*, F. Vögtle, John Wiley & Sons, Chichester, 1993. (b) *Modern Cyclophane Chemistry*, R. Gleiter and H. Hopf, Eds., Wiley-VCH: Weinheim, Germany, 2004.

3 For example, (a) Y. Morisaki and Y. Chujo Y, *Angew. Chem. Int. Ed.*, 2006, **45**, 6430–6437; (b) Y. Morisaki and Y. Chujo Y, *Polym. Chem.*, 2011, **2**, 1249-1257; (c) Y. Morisaki and Y. Chujo Y, *Chem. Lett.*, 2012, **41**, 840-846; (d) Y. Morisaki, S. Ueno, A. Saeki, A. Asano, S. Seki and Y. Chujo, *Chem.–Eur. J.*, 2012, **18**, 4216-4224.

4 Y. Morisaki, N. Kawakami, S. Shibata and Y. Chujo, *Chem.–Asian J.*, 2014, **9**, 2891-2895.

5 C. J. Brown and A. C. Farthing, *Nature*, 1949, **164**, 915–916.

6 D. J. Cram and H. Steinberg, *J. Am. Chem. Soc.*, 1951, **73**, 5691–5704.

7 (a) G. C. Bazan, W. J. Oldham Jr., R. J. Lachicotte, S. Tretiak, V. Chernyak and S. Mukamel, *J. Am. Chem. Soc.*, 1998, **120**, 9188–9204; (b) S. Wang, G. C. Bazan, S. Tretiak and S. Mukamel, *J. Am. Chem. Soc.*, 2000, **122**, 1289–1297; (c) J. Zyss, I. Ledoux, S. Volkov, V. Chernyak, S. Mukamel, G. P. Bartholomew and G. C. Bazan, *J. Am. Chem. Soc.*, 2000, **122**, 11956–11962; (d) Bartholomew, G. P.; Bazan, G. C. *Acc. Chem. Res.* 2001, **34**, 30–39; (e) Bartholomew, G. P.; Bazan, G. C. *Synthesis* 2002, 1245–1255.; (f) G. P. Bartholomew and G. C. Bazan, *J. Am. Chem. Soc.*, 2002, **124**, 5183–5196; (g) D. S. Seferos, D. A. Banach, N. A. Alcantar, J. N. Israelachvili and G. C. Bazan, *J. Org. Chem.*, 2004, **69**, 1110–1119; (h) G. P. Bartholomew, M. Rumi, S. J. K. Pond, J. W. Perry, S. Tretiak and G. C. Bazan, *J. Am. Chem. Soc.*, 2004, **126**, 11529–11542; (i) Hong, J. W.; Woo, H. Y.; Bazan, G. C. *J. Am. Chem. Soc.* 2005, **127**, 7435–7443; (j) G. C. Bazan, *J. Org. Chem.* 2007, **72**, 8615–8635.

8 H. Hinrichs, A. J. Boydston, P. G. Jones, K. Hess, R. Herges, M. M. Haley and H. Hopf, *Chem. Eur. J.*, 2006, **12**, 7103–7115.

9 Y. Morisaki, M. Gon, T. Sasamori, N. Tokitoh and Y. Chujo, *J. Am. Chem. Soc.*, 2014, **136**, 3350-3353.

10 (a) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 1955, **77**, 6289–6294; (b) V. Rozenberg, E. Sergeeva and H. Hopf, In *Modern Cyclophane Chemistry*, R. Gleiter and H. Hopf, Eds.; Wiley-VCH: Weinheim, Germany, 2004, pp. 435–462; (c) G. J. Rowlands, *Org. Biomol. Chem.*, 2008, **6**, 1527–1534; (d) S. E. Gibson and J. D. Knight, *Org. Biomol. Chem.*, 2003, **1**, 1256–1269; (e) A. A. Aly and A. B. Brown, *Tetrahedron*, 2009, **65**, 8055–8089; (f) J. Paradies, *Synthesis*, 2011, 3749–3766.

11 Optical resolution of *rac*-4,5,15,16-tetrasubstituted [2.2]paracyclophane has already been achieved: N. V. Vorontsova, V. I. Rozenberg, E. V. Sergeeva, E. V. Vorontsov, Z. A. Starikova, K. A. Lyssenko and H. Hopf, *Chem. Eur. J.*, 2008, **14**, 4600–4617.

12 (a) J. P. Riehl and F. S. Richardson, *Chem. Rev.*, 1986, **86**, 1–16; (b) J. P. Riehl and F. Muller, *Comprehensive Chiroptical Spectroscopy*, Wiley and Sons, New York, 2012.

13 (a) Y. Tohda, K. Sonogashira and N. Hagihara, *Tetrahedron Lett.*, 1975, **16**, 4467–4470; (b) K. Sonogashira, In *Handbook of Organopalladium Chemistry for Organic Synthesis*; E. Negishi, Ed., Wiley-Interscience, New York, 2002, pp 493–529.

14 (a) T, Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 1633–1635; (b) T, Sandmeyer, *Ber. Dtsch. Chem. Ges.*, 1884, **17**, 2650–2653.

15 A. Zapf, A. Ehrentraut and M. Beller, *Angew. Chem. Int. Ed.*, 2000, **39**, 4153–4155.

16 CPL dissymmetry factor is defined as $g_{\mathrm{lum}} = 2(I_{\mathrm{left}} - I_{\mathrm{right}})/(I_{\mathrm{left}} + I_{\mathrm{right}})$, where I_{left} and I_{right} indicate luminescence intensities of left and right handed CPL, respectively.

17 Y. Morisaki, K. Inoshita and Y. Chujo Y. *Chem.–Eur. J.*, 2014, **20**, 8386–8390.

18 K. Nakamura, S. Furumi, M. Takeuchi, T. Shibuya and K. Tanaka, *J. Am. Chem. Soc.*, 2014, **136**, 5555–5558.

19 (a) J. E. Field, G. Muller, J. P. Riehl and D. Venkataraman, *J. Am. Chem. Soc.*, 2003, **125**, 11808–11809; (b) T. Kaseyama, S. Furumi, X. Zhang, K. Tanaka and M. Takeuchi, *Angew. Chem. Int. Ed.*, 2011, **50**, 3684–3687; (c) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi and K. Tanaka, *J. Am. Chem. Soc.*, 2012, **134**, 4080–4083; (d) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa and K. Nozaki, *Org. Lett.*, 2013, **15**, 2104–2107.

20 (a) H. Maeda, Y. Bando, K. Shimomura, I. Yamada, M. Naito, K. Nobusawa, H. Tsumatori and T. Kawai, *J. Am. Chem. Soc.*, 2011, **133**, 9266–9269; (b) Y. Haketa, Y. Bando, K. Takaishi, M. Uchiyama, A. Muranaka, M. Naito, H. Shibaguchi, T. Kawai and H. Maeda, *Angew. Chem. Int. Ed.*, 2012, **51**, 7967–7971.

21 Review, see: (a) H. Maeda and Y. Bando, *Pure Appl. Chem.*, 2013, **85**, 1967–1978. CPL was observed from chiral orientation of flurophores. Based on axially chiral scaffolds: (b) T. Kawai, K. Kawamura, H. Tsumatori, M. Ishikawa, M. Naito, M. Fujiki and T. Nakashima, *ChemPhysChem*, 2007, **8**, 1465–1468; (c) H. Tsumatori, T. Nakashima and T. Kawai, *Org. Lett.*, 2010, **12**, 2362–2365; (d) T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *Chem.–Asian J.*, 2012, **7**, 2836–2841; (e) T. Amako, T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *RSC Adv.*, 2013, **3**, 6939–6944; (f) T. Amako, T. Kimoto, N. Tajima, M. Fujiki and Y. Imai, *Tetrahedron*, 2013, **69**, 2753–2757; (g) T. Kimoto, T. Amako, N. Tajima. R. Kuroda, M. Fujiki and Y. Imai, *Asian. J. Org. Chem.*, 2013, **2**, 404–410; (h) J. Kumar, T. Nakashima, H. Tsumatori and T. Kawai, *J. Phys. Chem. Lett.*, 2014, **5**, 316–321; (i) Y. Kitayama, T. Amako, N. Suzuki, M. Fujiki and Y. Imai, *Org. Biomol. Chem.*, 2014, **12**, 4342–4346. Based on centrally chiral scaffold: (j) J. Kumar, T. Nakashima, H. Tsumatori, M. Mori, M. Naito and T. Kawai, *Chem.–Eur. J.*, 2013, **19**, 14090–14097. CPL from inherently achiral monochromophore systems is recently reported: (k) E. M. Sánchez-Carnerero, F. Moreno, B. L. Maroto, A.

R. Agarrabeitia, M. J. Ortiz, B. G. Vo, G. Muller and S. de la Moya, *J. Am. Chem. Soc.*, 2014, **136**, 3346–3349.

22 Some optically active conjugated polymers exhibit CPL. For polymers emitting CPL in their film or aggregation states: (a) E. Peeters, M. P. T. Christiaans, R. A. J. Janssen, H. F. M. Schoo, H. P. J. M. Dekkers and E. W. Meijer, *J. Am. Chem. Soc.,* 1997, **119**, 9909–9910. (b) A. Satrijio, S. C. J. Meskers and T. M. Swager, *J. Am. Chem. Soc.,* 2006, **128**, 9030–9031.; (c) J. N. Wilson, W. Steffen, T. G. McKenzie, G. Lieser, M. Oda, D. Neher and U. H. F. Bunz, *J. Am. Chem. Soc.,* 2002, **124**, 6830–6831; (d) B. M. W. Langeveld-Voss, R. A. Janssen, M. P. T. Christiaans, S. C. J. Meskers, H. P. J. M. Dekkers and E. W. Meijer, *J. Am. Chem. Soc.,* 1996, **118**, 4908–4909; (e) M. Oda, H.-G. Nothofer, G. Lieser, U. Scherf, S. C. J. Meskers and D. Neher, *Adv. Mater.,* 2000, **12**, 362–365; (f) M. Oda, H.-G. Nothofer, U. Scherf, V. Šunjić, D. Richter, W. Regenstein, S. C. J. Meskers and D. Neher, *Macromolecules,* 2002, **35**, 6792–6798; (g) H. Goto and K. Akagi, *Angew. Chem. Int. Ed.,* 2005, **44**, 4322–4328; (h) H. Hayasaka, T. Miyashita, K. Tamura and K. Akagi, *Adv. Funct. Mater.,* 2010, **20**, 1243–1250; (i) S. Fukao and M. Fujiki, *Macromolecules,* 2009, **42**, 8062–8067; (j) J.-M. Yu, T. Sakamoto, K. Watanabe, S. Furumi, N. Tamaoki, Y. Chen and T. Nakano, *Chem. Commun.,* 2011, **47**, 3799–3801; (k) K. Watanabe, T. Sakamoto, M. Taguchi, M. Fujiki and T. Nakano, *Chem. Commun.,* 2011, **47**, 10996–10998; (l) T. Hirahara, M. Yoshizawa-Fujita, Y. Takeoka and M. Rikukawa, *Chem. Lett.*, 2012, **41**, 905–907; (m) K. Watanabe, Y. Koyama, N. Suzuki, M. Fujiki and T. Nakano, *Polym. Chem.*, 2014, **5**, 712–717. For polymer aggregates in optically active solvents: (n) Y. Nakano, Y. Liu and M. Fujiki, *Polym. Chem.,* 2010, **1**, 460–469; (o) Y. Kawagoe, M. Fujiki and Y. Nakano, *New J. Chem.,* 2010, **34**, 637–647. For polymers emitting CPL in solution: (p) Y. Morisaki, R. Hifumi, L. Lin, K. Inoshita, Y. Chujo, *Polym. Chem.*, 2012, **3**, 2727–2730; (q) Y. Nagata, T. Nishikawa and M. Suginome, *Chem. Commun.*, 2014, **50**, 9951–9953. For CPL created by polymer-polymer complexation: (r) T. Shiraki, Y. Tsuchiya, T. Noguchi, S. Tamaru, N. Suzuki, M. Taguchi, M. Fujiki and S. Shinkai, *Chem.–Asian J.*, 2014, **9**, 218–222.

23 Optically active helicene can be used as a chiral dopant for a conjugated polymer film, resulting in induced circularly polarized electroluminescence (CPEL): Y. Yang, R. C. da Costa, D-M. Smilgies, A. J. Campbell and M. J. Fuchter, *Adv. Mater.*, 2013, **25**, 2624–2628.

Graphical Abstract

Optically active propeller-shaped cyclic compounds based on planar chiral [2.2]paracyclophane emit intense and bright circularly polarized luminescence (CPL).