Chirality

Planar-Chiral Through-Space Conjugated Oligomers: Synthesis and Characterization of Chiroptical Properties

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Abstract: Optically active through-space conjugated oligomers, namely, a dimer, trimer, tetramer, and cyclic trimer, consisting of a planar-chiral [2.2]paracyclophane skeleton were synthesized. In the ground state, observed similarities in the chiroptical properties of the oligomers were attributed to the equivalent orientations of two adjacent chromophores. In the excited state, the oligomers were folded into a form analogous to a one-handed helix by photoexcitation. All the compounds in dispersed solution exhibited intense circularly polarized luminescence with relatively large anisotropy factors on the order of 10^{-3}.

Introduction

Planar chirality is one of the distinguishing physical characteristics of [2.2]paracyclophane derivatives and arises from the proximally fixed face-to-face phenylene moieties.[1] Unlike the planar chirality of metal complexes such as ferrocene and (η^6-arene)chromium complexes, the planar chirality of [2.2]paracyclophane compounds is conformationally stable due to the suppression of axial rotation. Various methods for the optical resolution of planar chiral [2.2]paracyclophanes have been developed so far to afford the corresponding enantiopure derivatives,[2–4] thus leading to their primary use as chiral auxiliaries in the field of organic chemistry. Considering their conformational stability, planar-chiral [2.2]paracyclophanes can be used as chiral scaffolds to construct a variety of optically active structures. From this viewpoint, we have recently developed a practical method for the optical resolution of disubstituted [2.2]paracyclophane compounds[3i] and synthesized optically active through-space conjugated polymers[3j] in contribution to the fields of polymer and materials chemistry.[1c] The resulting optically active polymers exhibited circularly polarized luminescence (CPL) with large dissymmetry factors (g_{lum}), even in dilute solutions. To discuss the chiroptical properties in detail, it is desirable to understand the properties of well-defined optically active through-space conjugated oligomers rather than polymers. Thus, we report herein detailed studies on the syntheses and properties of optically active through-space conjugated [2.2]paracyclophane oligomers, in which 2–4 π-electron systems are partly stacked (Figure 1). Important findings on the mechanism for the intense CPL were obtained in this study.

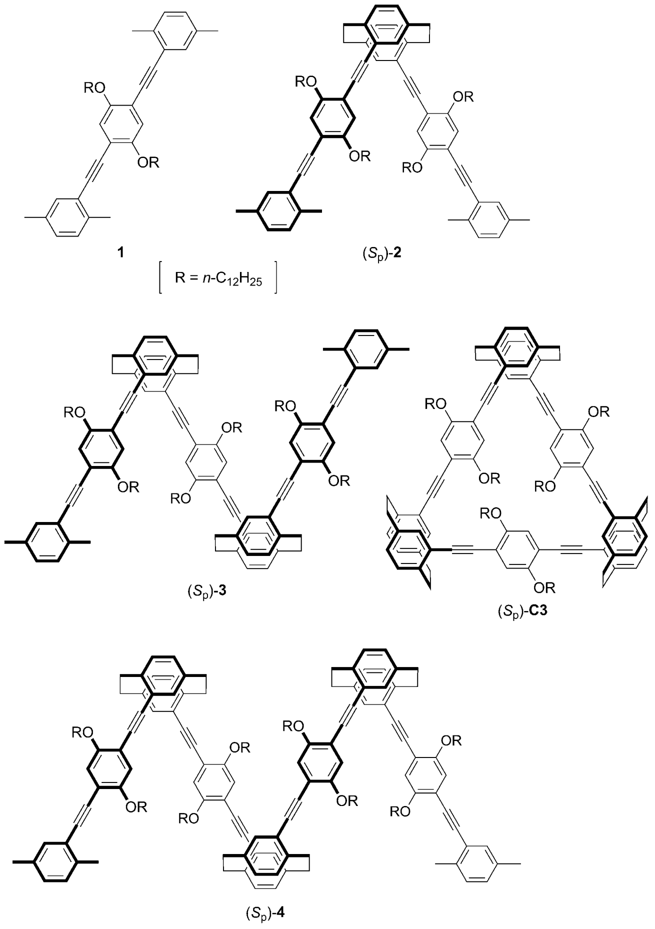

Figure 1. Compounds prepared in this study. The S_p isomers are shown.

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Results and Discussion

Optical and chiroptical properties in the ground state

Figure 1 shows monomeric compound **1** and S_p enantiomers (S_p)-**2**–**4** prepared by using the Sonogashira–Hagihara coupling (see Schemes S1–S3 in the Supporting Information).[5] Cyclic compound (S_p)-**C3** was obtained as a byproduct of polymerization[3j] (see the Supporting Information for the synthetic procedures and spectral data).

The absorption (UV) spectra and circular dichroism (CD) spectra of (S_p)-**2**–**4** and (R_p)-**2**–**4** were measured in dilute $CHCl_3$ (1.0×10^{-5} M) and are shown in Figure 2 A with the UV spectrum of **1**. The obtained UV spectra were bathochromically shifted as the number of the stacked π-electron systems increased as a result of the through-space conjugation.[6,7] The effect of the through-space conjugation of the pseudo-*ortho*-oligomer was slightly smaller than that of the corresponding pseudo-*para*-oligomer; for example, the absorption maxima of **2** and **3** were $\lambda_{max}=374.5$ and 375.5 nm, respectively, whereas those of the corresponding pseudo-*para*-dimer and trimer were $\lambda_{max}=378$ and 381 nm, respectively.[7] DFT calculations for the pseudo-*ortho*- and pseudo-*para*-dimers supported the results of the UV spectroscopic analysis (see Figure S17 in the Supporting Information). The uniformity of the phases and overlap of the orbitals between the face-to-face aromatic rings of the [2.2]paracyclophane moiety decreased the energy band gap of the pseudo-*para*-dimer relative to the pseudo-*ortho*-dimer.

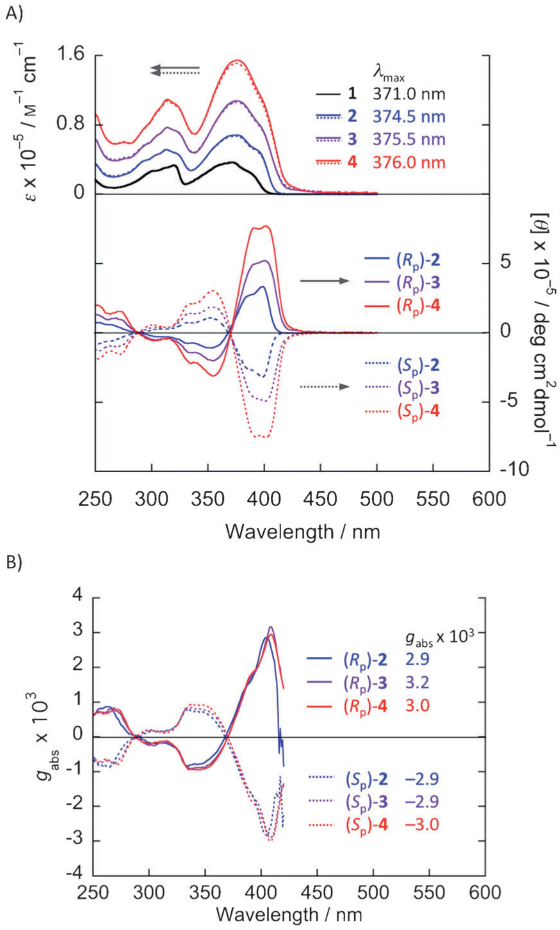

Figure 2. A) UV and CD spectra of **1**, (S_p)-**2**–**4**, and (R_p)-**2**–**4** in $CHCl_3$ (1.0×10^{-5} M) and B) their g_{abs} plots.

The CD spectra of (S_p)-**2**–**4** and (R_p)-**2**–**4** exhibited mirror image Cotton effects in the π–π* transition region of the π-electron systems with relatively large molar ellipticity ([θ]) values on the order of 10^5 (Figure 2 A). Bisignate exciton-coupled CD signals[8] were observed owing to the rigidly stacked π-electron systems at an angle of 60°. The [θ] values became larger with the increase in the number of the stacked π-electron systems.

In contrast, their absorption anisotropy factors (g_{abs}, defined as $g_{abs}=\Delta\varepsilon/\varepsilon$) were almost identical (Figure 2 B). Orientations of the electric transition moments of two adjacent interacting π-electron systems were fixed in a V-shape by the planar chiral [2.2]paracyclophane scaffold,[8,9] whereas higher-ordered structures of each compound were not formed through molecular motions (discussed later in Figure 4); therefore, the chirality of the whole molecule was intrinsically equivalent in the ground state and resulted in the almost constant g_{abs} values.

Figure 3 shows the UV spectra, CD spectra, and g_{abs} plots of the linear trimers (S_p)-**3** and (R_p)-**3** and the cyclic trimers (S_p)-**C3**

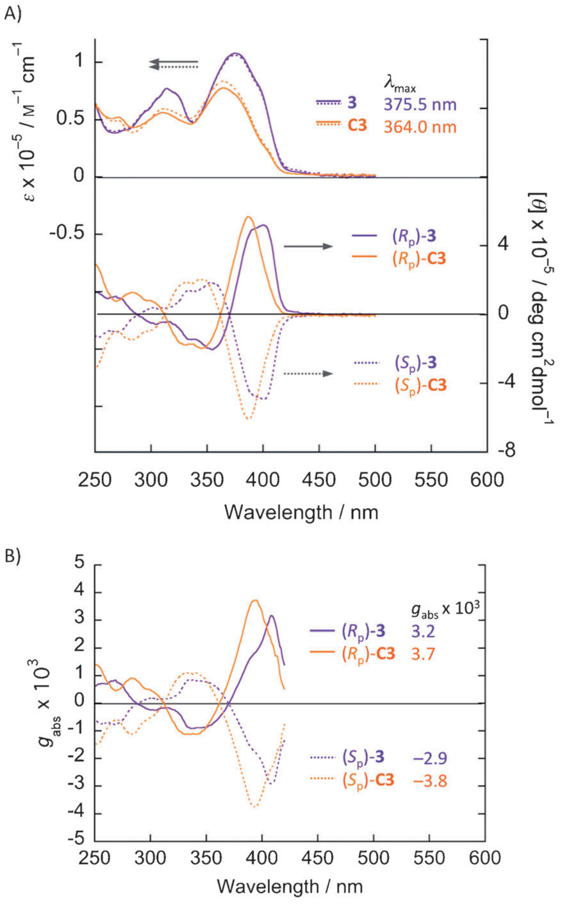

Figure 3. A) UV and CD spectra of (S_p)-**3**, (R_p)-**3**, (S_p)-**C3**, and (R_p)-**C3** in $CHCl_3$ (1.0×10^{-5} M) and B) their g_{abs} plots.

and (R_p)-**C3**. The UV spectra of (S_p)-**C3** and (R_p)-**C3** were hypsochromically and hypochromically shifted relative to (S_p)-**3** and (R_p)-**3** (Figure 3 A). A twist in the didodecyloxyphenylene unit of the stacked π-electron system in (S_p)-**C3** and (R_p)-**C3** suppressed the extension of π conjugation due to steric hindrance. The Cotton effects exhibited by (S_p)-**C3** and (R_p)-C3 were slightly larger than those of (S_p)-**3** and (R_p)-**3** (Figure 3 A); in addition, the g_{abs} values of (S_p)-**C3** and (R_p)-C3 were larger than those of (S_p)-**3** and (R_p)-**3** (Figure 3 B). In the cyclic trimer, the orientation of the electric transition moments of two adjacent π-electron systems was the same as that of the linear trimer (Figure 4). The chain ends of each stacked π-electron system were completely fixed by the [2.2]paracyclophane to construct an optically active higher-ordered structure. Thus, noticeable changes in the [θ] and g_{abs} values were observed between **3** and **C3**; particularly, a clear enhancement in the g_{abs} value was observed (Figure 3 A, B).

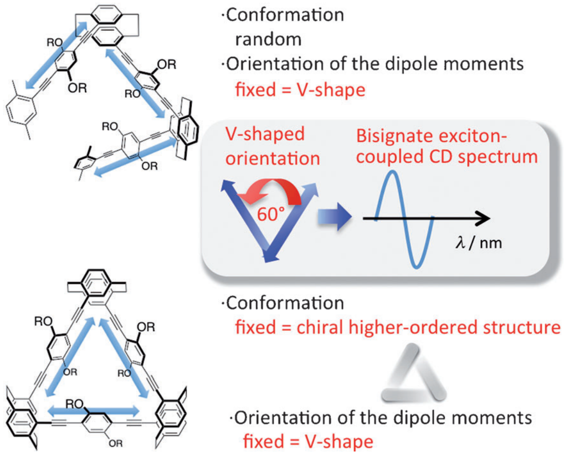

Figure 4. Plausible structures of (S_p)-**3** and (S_p)-**C3** in the ground state.

Optical and chiroptical properties in the excited state

Photoluminescence (PL) spectra of **1**, (S_p)-**2**–**4**, and (R_p)-**2**–**4** in dilute $CHCl_3$ (1.0×10^{-6} M) are shown in Figure 5 A. The PL spectra of oligomers were also gradually red-shifted in accordance with the number of stacked π-electron systems. Vibronic structures were observed in all the PL spectra, and their decay curves were fitted with a single exponential relation.[10] Pseudo-*ortho*-linked through-space conjugated oligomers emitted from the chromophore state rather than from the phane state,[6] a behavior similar to that of the pseudo-*para*-linked compounds.[6,7]

CPL measurements for (S_p)-**2**–**4** and (R_p)-**2**–**4** in dilute $CHCl_3$ (1.0×10^{-5} M) were carried out. Intense CPL signals of I_L-I_R,

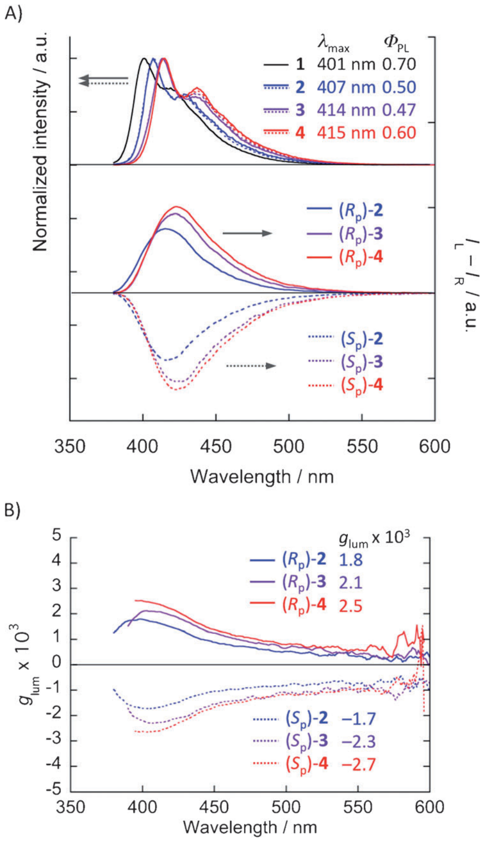

Figure 5. A) PL and CPL spectra of **1**, (S_p)-**2**–**4**, and (R_p)-**2**–**4** in $CHCl_3$ (1.0×10^{-6} M, excitation at UV λ_{max} for PL; 1.0×10^{-5} M, $\lambda_{ex}=320$ nm for CPL). Φ_{PL} = PL absolute quantum efficiency (average of the S_p and R_p isomers). B) The g_{lum} plots of (S_p)-**2**–**4** and (R_p)-**2**–**4**.

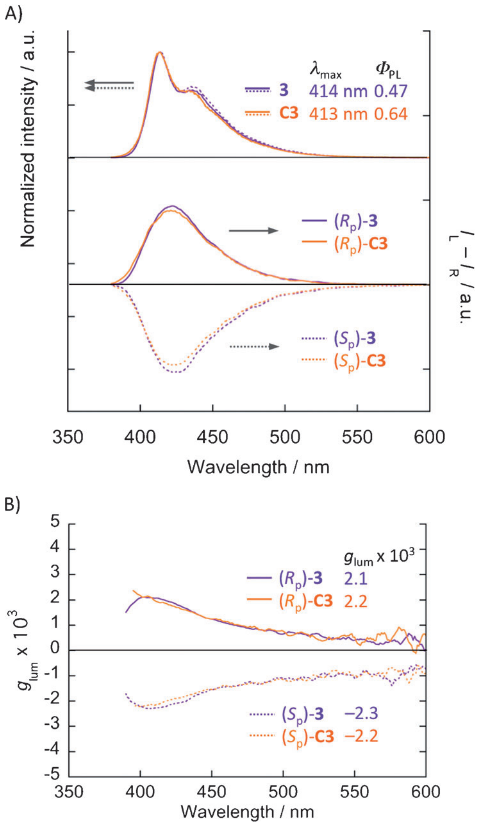

Figure 6. A) PL and CPL spectra of (S_p)-**3**, (R_p)-**3**, (S_p)-**C3**, and (R_p)-**C3** in $CHCl_3$ (1.0×10^{-6} M, excitation at UV λ_{max} for PL; 1.0×10^{-5} M, $\lambda_{ex}=320$ nm for CPL). Φ_{PL} = absolute PL quantum efficiency. B) The g_{lum} plots of (S_p)-**3**, (R_p)-**3**, (S_p)-**C3**, and (R_p)-**C3**.

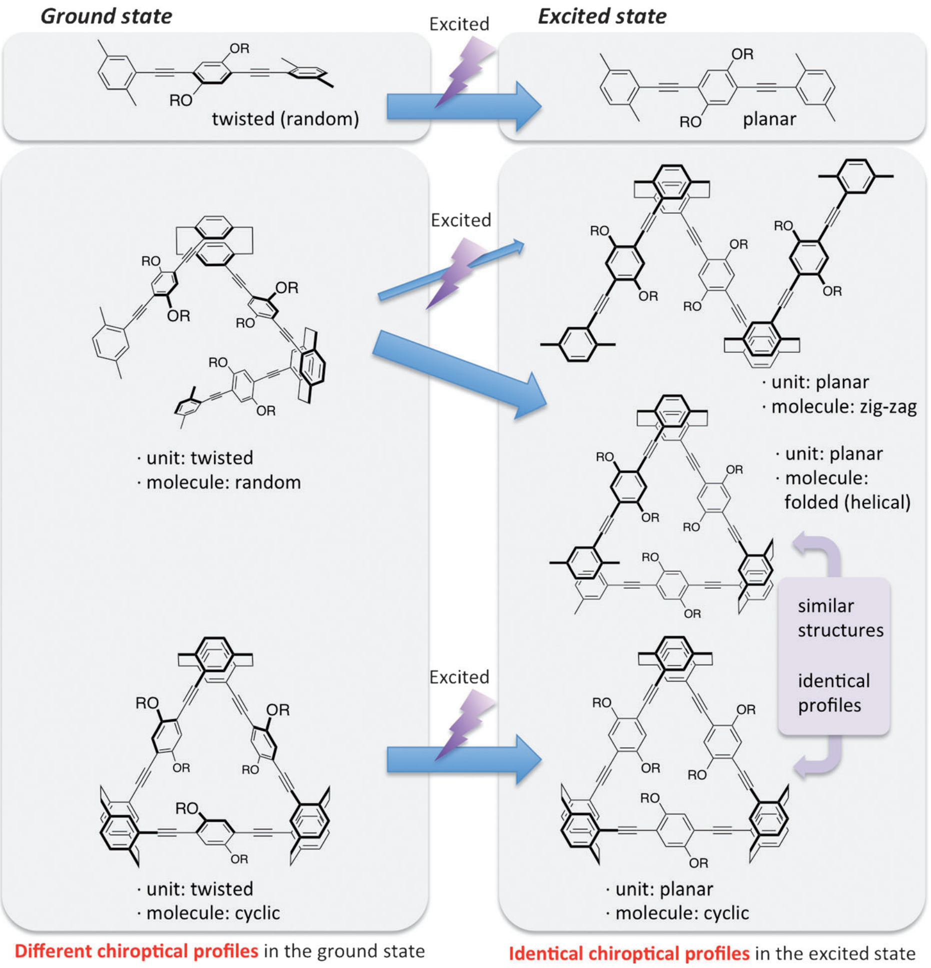

Figure 7. Plausible structures of the oligomers: The linear trimer versus the cyclic trimer in the ground and excited states.

where I_L and I_R are intensities of the left- and right-handed luminescence, respectively, appeared with mirror images in the PL peak ranges (Figure 5A). Intensities of the CPL peak tops and CPL dissymmetry factors $g_{lum}=2(I_L-I_R)/(I_L+I_R)$ increased gradually as the number of π-electron systems increased, in contrast to the constant g_{abs} values.

Figure 6 illustrates the PL spectra, CPL spectra, and g_{lum} plots of the linear trimers (S_p)-**3** and (R_p)-**3** and the cyclic trimers (S_p)-**C3** and (R_p)-**C3**. Interestingly, there were negligible spectral differences between the linear and cyclic compounds. In particular, the almost identical CPL spectra and g_{lum} values suggest that the linear and cyclic compounds form similar optically active higher-ordered structures in the excited state.

It is expected that the *para*-phenylene ethynylenes form a planar quinoid-like structure in the excited state (Figure 7);[11] consequently, trimer **3** and tetramer **4** adopt optically active higher-ordered structures, that is, zigzag and/or helical structures in the excited state (Figure 7). The change in g_{lum} values arises from this higher-ordered structural contribution. Considering the completely fixed cyclic structure of (S_p)-**C3** and (R_p)-**C3**, it is speculated that the linear trimers (S_p)-**3** and (R_p)-**3** are folded to form a one-handed helix rather than a zigzag structure in the case of excitation (Figure 7).

It should be noted that, as discussed above, all the optically active compounds (S_p)-**2**–**4**, (R_p)-**2**–**4**, (S_p)-**C3**, and (R_p)-**C3** exhibited intense CPL with relatively high PL quantum efficiencies and large g_{lum} values on the order of 10^{-3}. Monodispersed CPL-active organic molecules reported to date consist of helical or axial chirality.[12–15] To achieve the intense CPL, a chiral orientation of the emitting species in the excited state is required. The present study suggests that planar chirality of [2.2]paracyclophane is a promising option for chiral scaffolds to produce CPL materials.

Conclusion

We have investigated the chiroptical properties of planar-chiral [2.2]paracyclophane-based through-space conjugated oligomers. In the ground state, observed similarities in the chiroptical properties of these oligomers were attributed to the equivalent orientations of two adjacent chromophores. In the excited state, the chiroptical properties of the oligomers were gradually enhanced as the number of the stacked π-electron systems increased, thus implying that the oligomers were folded into a form analogous to a one-handed helix by photoexcitation. Moreover, an intense CPL response was observed from the oligomers; this property, attributed to the planar chirality of the [2.2]paracyclophane skeleton, holds potential for their use in practical CPL materials.

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Keywords: circular dichroism · cyclophanes · luminescence · higher-ordered structure · planar chirality

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