

NOTE

Synthesis of optically active through-space conjugated polymers consisting of planar chiral [2.2]paracyclophane and quaterthiophene

Yasuhiro Morisaki, Kenichi Inoshita, Shotaro Shibata and Yoshiki Chujo

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INTRODUCTION

Some [2.2]paracyclophane compounds^{1,2} exhibit planar chirality, a unique feature derived from suppressed rotary motion in the two fixed phenylene units.^{2–4} Various [2.2]paracyclophanes have been optically resolved,^{3–7} and optically active [2.2] paracyclophane compounds have been used mainly as chiral auxiliaries in the fields of organic and organometallic chemistry. Recently, we studied planar chiral [2.2] paracyclophanes and developed a novel approach to obtain enantiopure 4,12-disubstituted⁶ and 4,7,12,15-tetrasubstituted [2.2] paracyclophanes.⁸ These molecules were employed as chiral building blocks to construct optically active through-space-conjugated systems in an effort to apply planar chirality in the fields of polymer and materials chemistry. Here, we report the synthesis of optically active through-space-conjugated copolymers consisting of enantiopure 4,12-disubstituted [2.2]paracyclophane and quaterthiophene to expand the substrate scope. In a single polymer chain, 2,2''-dixylyl-2,2':5',2'':5' ',2''-quaterthiophenes are stacked by the [2.2]paracyclophane skeleton.^{9,10} In addition to the previously reported optical resolutions by the diastereomer method,⁶ chromatographic optical resolutions of key compounds with chiral columns were successfully carried out. The obtained polymers exhibited beneficial chiroptical properties such as circularly polarized luminescence (CPL) with a relatively large CPL dissymmetry factor (g_{lum}). We disclose herein that the optically active through-space-conjugated polyarylenes, instead of poly(*p*-arylene-ethynylene)s, emit clear CPL due to the planar chiral [2.2] paracyclophane.

EXPERIMENTAL PROCEDURE

Synthesis of polymer (R_p)-P1

The mixture of Pd₂(dba)₃ (3.7 mg, 0.004 mmol), P(*t*-Bu)₃·HBF₄ (5.8 mg, 0.020 mmol), K₃PO₄ (42.5 mg, 0.200 mmol), compound (R_p)-4 (10.6 mg, 0.020 mmol), and compound 5 (15.1 mg, 0.020 mmol) was dissolved in tetrahydrofuran (1.0 ml) and H₂O (1.0 ml) at room temperature under Ar atmosphere. The reaction mixture was stirred at 70 °C (oil bath temperature) under Ar atmosphere for 48 h. After cooling to room temperature, H₂O and CHCl₃ were

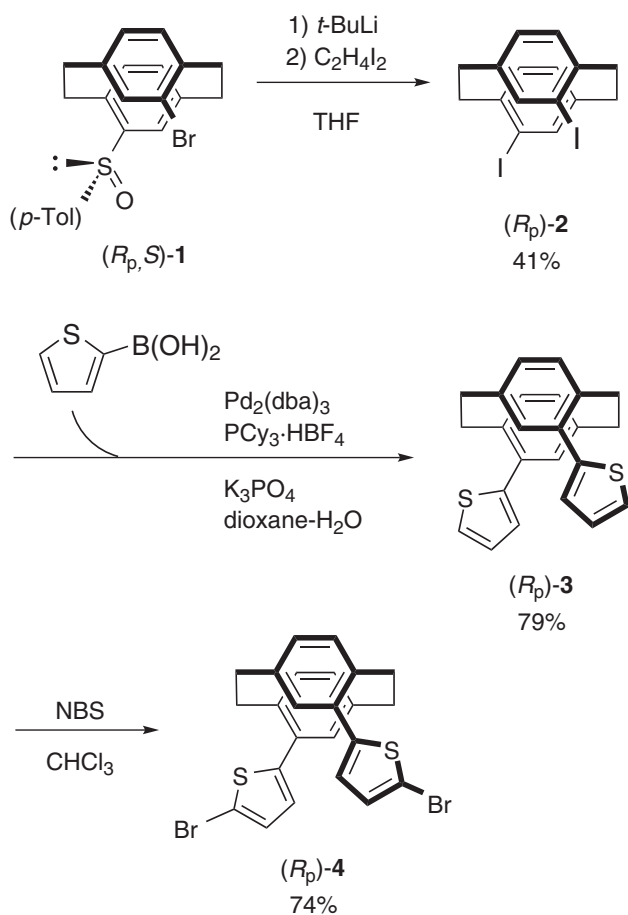
added, and the organic species were extracted with CHCl₃. The organic layer was dried over MgSO₄. After MgSO₄ was removed, the solvent was evaporated. The residue was purified by high performance liquid chromatography with CHCl₃ as an eluent to obtain polymer (R_p)-P1 as an orange powder (10.3 mg, 0.012 mmol, 59%).

Polymer (S_p)-P1 was obtained by the same procedure (8.7 mg, 0.010 mmol, 50%).

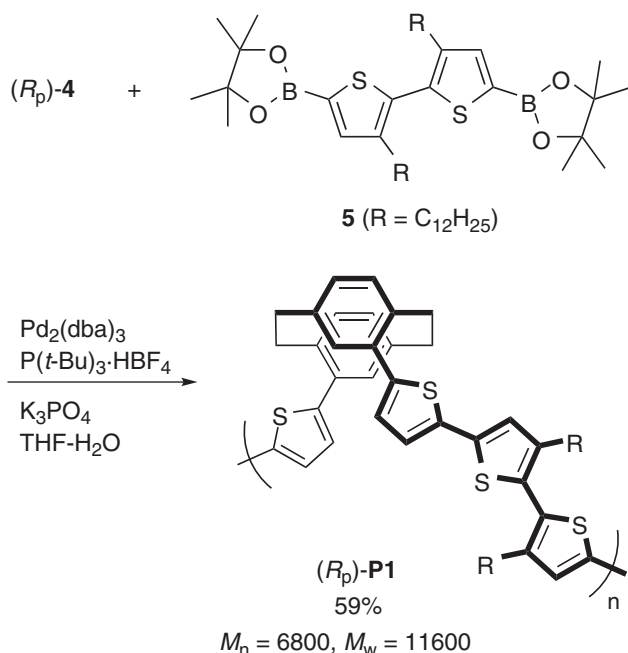
In Supplementary Information, the detailed synthetic procedures and data of compounds 3 and 4, and the ¹H and ¹³C NMR spectra of (R_p)-isomers 3 (Supplementary Figures S2 and S3), 4 (Supplementary Figures S5 and S6) and P1 (Supplementary Figures S7 and S8) are shown. Chromatograms of compounds 3 and 4 with a Chiralpak IA column (Daicel Corporation, Osaka, Japan) are also shown in Supplementary Figures S1 and S4, respectively. Fluorescence decay curves with the data of polymers (R_p)- and (S_p)-P1 are shown in Supplementary Figures S9 and S10. The optimized structure of the model compound in the excited state is shown in Supplementary Figure S11.

RESULTS AND DISCUSSIONS

The synthetic route toward the enantiopure planar chiral [2.2] paracyclophane monomer is shown in Scheme 1, in which reactions of only (R_p)-isomers are shown. (R_p)-4,12-Diiodo[2.2]paracyclophane,^{7,11} (R_p)-2, was prepared from the corresponding (R_p,S)-isomer, (R_p,S)-1,⁶ by lithiation and successive iodination. However, when a Suzuki–Miyaura cross-coupling¹² polymerization of (R_p)-2 with bithiophene monomer 5 was carried out, the molecular weight of the obtained polymer was quite low. Therefore, thiophene-substituted [2.2]paracyclophane was synthesized and used as a co-monomer. As shown in Scheme 1, the Suzuki–Miyaura cross-coupling of (R_p)-2 with 2-thienylboronic acid produced (R_p)-4,12-di(2-thienyl)[2.2]paracyclophane (R_p)-3 with a 79% isolated yield. After several attempts to obtain (R_p)-3, we found that the Suzuki–Miyaura cross-coupling provided the best results, in accordance with a report by Lützen and coworkers⁷ on successful Suzuki–Miyaura cross-coupling between *rac*-2 and 4-methoxyphenylboronic acid. Brominations at the fifth position of both thiophene units in (R_p)-3 using *N*-bromosuccinimide was carried out to obtain the target monomer (R_p)-4 with a 74%



Scheme 1 Synthesis of the monomer.



Scheme 2 Synthesis of the polymer.

isolated yield. Chromatographic optical resolutions of racemic compounds *rac*-3 and *rac*-4 were successfully performed by using Chiralpak IA as a stationary phase, as shown in Supplementary Figures S1 and S4 in the Supplementary Information.

As shown in Scheme 2, the treatment of (*R*_p)-4 with bithiophene monomer 5 in the presence of Pd₂(dba)₃/P(*t*-Bu)₃·HBF₄ (dba = dibenzylideneacetone) afforded the corresponding polymer (*R*_p)-P1 with a 59% isolated yield after work-up. The number-average and weight-average molecular weights (*M*_n and *M*_w, respectively) of (*R*_p)-P1 were estimated to be 6800 and 11600, respectively, by gel permeation chromatography. In our previous study, a cyclic compound (cyclic trimer) was obtained as a byproduct;¹³ however, with the present reaction conditions and substrates, the polymerization proceeded to yield a polymer with a relatively high *M*_n and no detectable cyclic byproducts. The obtained polymers (*R*_p)- and (*S*_p)-P1 were well-soluble in organic solvents, such as CHCl₃, CH₂Cl₂, tetrahydrofuran and toluene. Thus, this enabled the structure elucidation by NMR spectroscopy and the characterization of the optical and chiroptical properties by ultraviolet–visible (UV–vis), circular dichroism (CD), photoluminescence (PL) and CPL spectroscopy.

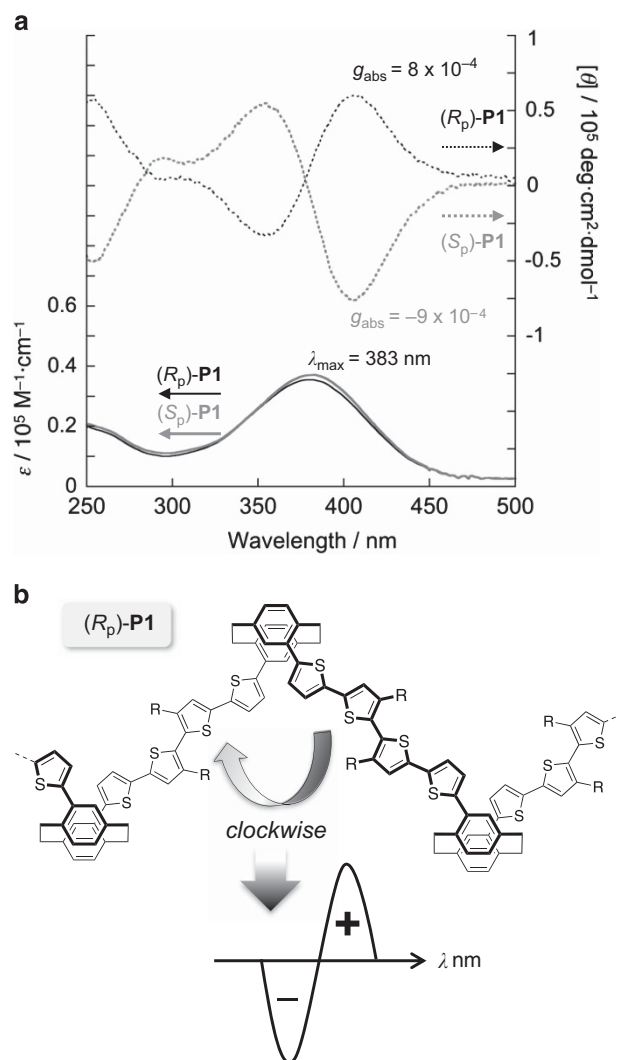


Figure 1 (a) Ultraviolet and circular dichroism (CD) spectra of (*R*_p)- and (*S*_p)-P1 in CHCl₃ (1.0 × 10⁻⁵ M). (b) Explanation of the bisignate exciton-coupled CD spectrum.

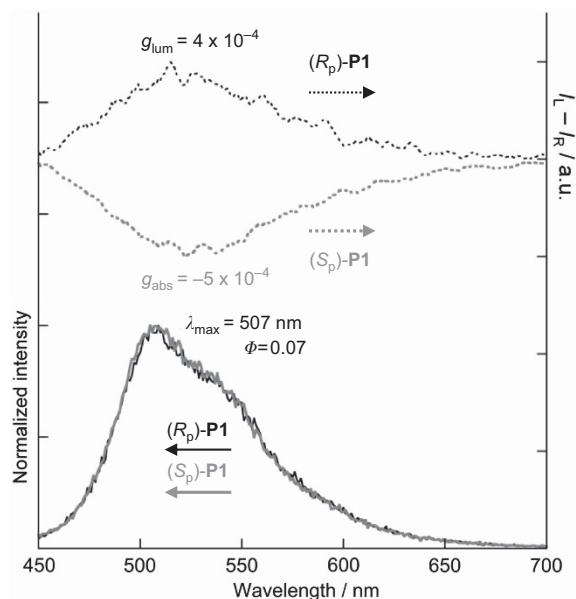


Figure 2 Photoluminescence (PL) and circularly polarized luminescence (CPL) spectra of (*R_p*)- and (*S_p*)-**P1** in CHCl₃ (1.0×10^{-5} M, excitation at 380 nm). Φ = PL absolute quantum efficiency (average of both (*R_p*)- and (*S_p*)-isomers).

Figure 1a shows the UV-vis and CD spectra of (*R_p*)- and (*S_p*)-**P1** in CHCl₃ (1.0×10^{-5} M). In the UV-vis spectra, (*R_p*)- and (*S_p*)-**P1** exhibited a maximum absorbance at 383 nm. The spectra were almost identical to the spectrum of 2,2'''-di[2.2]cyclophanyl-2,2':5',2'':5'',2'''-quaterthiophene prepared by Guyard and Audebert.¹⁴ This similarity indicates that the spectra of (*R_p*)- and (*S_p*)-**P1** resulted from the π - π^* transition in the 2,2'''-dixylyl-2,2':5',2'':5'',2'''-quaterthiophene moiety. The CD spectra of (*R_p*)- and (*S_p*)-**P1** exhibited clear Cotton effects and were mirror images. In each spectrum, the CD signal was split, and the signal pattern was consistent with the predictions of the exciton chirality method¹⁵ that was based on the orientation of the two adjacent 2,2'''-dixylyl-2,2':5',2'':5'',2'''-quaterthiophene chromophores (Figure 1b). The absorbance dissymmetry factors g_{abs} of the peak tops are given in Figure 1 ($g_{\text{abs}} = \Delta\epsilon/\epsilon$, where $\Delta\epsilon$ is the difference in molar absorptivity between left and right circularly polarized light). The maximum g_{abs} values of (*R_p*)- and (*S_p*)-**P1** at ~ 410 nm were calculated to be 8×10^{-4} and -9×10^{-4} , respectively, which were relatively large for dilute solutions. This implies that in the dilute solution, chirality is strongly induced in stacked 2,2'''-dixylyl-2,2':5',2'':5'',2'''-quaterthiophenes in the ground state as a result of the planar chiral [2.2]paracyclophane skeleton.

Polymers (*R_p*)- and (*S_p*)-**P1** emitted green PL (Figure 2) in their CHCl₃ solution (1.0×10^{-6} M) with an absolute PL quantum efficiency

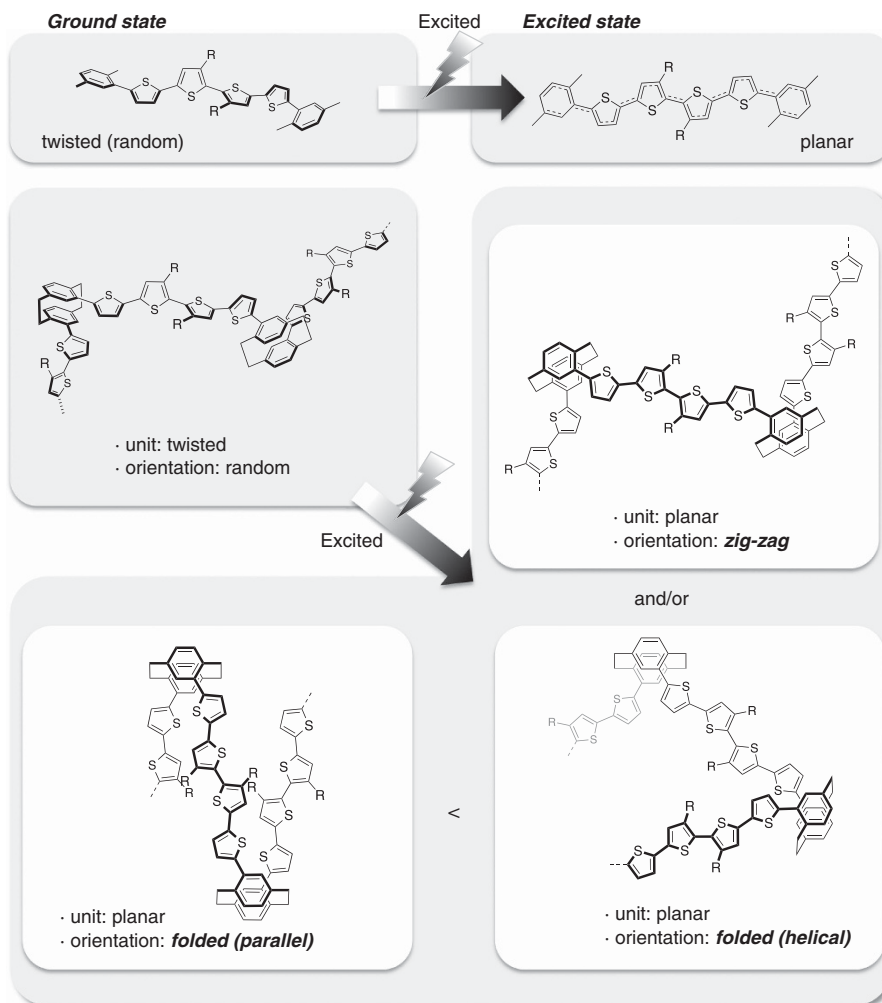


Figure 3 Plausible structures of the polymer in the ground and excited states.

(Φ_{lum}) of 0.07 (average value of both isomers). The emission likely arose from the chromophore state rather than the planar state,¹⁶ judging from the short PL lifetime (τ) of 0.63 ns (average value of both isomers) by a single exponential curve fitting (Supplementary Figures S8 and S9). Figure 2 shows the CPL spectra of (*R*_p)- and (*S*_p)-**P1** in CHCl₃ solution (1.0×10^{-5} M); mirror-image CPL signals were observed. The g_{lum} values of (*R*_p)- and (*S*_p)-**P1** were found to be 4×10^{-4} and -5×10^{-4} , respectively ($g_{\text{lum}} = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R are left- and right-handed CPL signals, respectively). It is rare that a monodisperse optically active polymer in solution exhibits a clear CPL.¹³ Generally, CPL signals of optically active polymers appear in their films or aggregates (representative examples^{17–19} are listed in the reference and notes section), indicating the chiral orientation of the emitting species. In other words, a higher-ordered structure is essential for an intense CPL. The π -electron systems in the [2.2]paracyclophane-based through-space-conjugated polymer were stacked in the polymer chain, and each stacked 2,2''-dixylyl-2,2':5',2'':5''-quaterthiophene formed planar and quinoid structures in the excited state.²⁰ Therefore, both isomers of polymer **P1** should form optically active higher-ordered structures, such as zigzag, helical or parallel structures in the excited state (Figure 3).¹¹ The PL spectrum and τ (0.63 ns, single exponential decay) of **P1** suggested an absence of intramolecular π - π interactions of the π -electron systems in **P1**; it was unlikely to form the parallel structure (Figure 3). An optimized structure of the model oligomer comprising three stacked π -electron systems in the excited state was examined by time-dependent density functional theory. The helical conformation was obtained, as shown in Supplementary Figure S11 in Supplementary Information. However, it is not the result of preventing the formation of the other structures. At present, it is difficult to conclude the conformation of the whole molecule in the excited state, such as zigzag, helical or both. In any case, it is noted that the neighboring π -electron systems in **P1** should form the optically active, V-shaped structure by a conformationally stable planar chiral [2.2]paracyclophane. Such a chiral orientation of the emitting π -electron systems achieved in the **P1** chains should result in the observed intense CPL with relatively large g_{lum} values in the monodisperse state.

In conclusion, we have demonstrated the synthesis of optically active, through-space-conjugated polymers consisting of enantiopure planar chiral 4,12-disubstituted [2.2]paracyclophane and quaterthiophene. The chromatographic optical resolutions of key compounds were also achieved. The obtained optically active polymers exhibited a mirror-image Cotton effect, and the split in the CD signal was predicted by the exciton chirality method. A solution-based mirror-image CPL response was also observed with a g_{lum} value in the order of 10^{-4} . The next target in this research is to achieve an intense CPL with large g_{lum} values from the polymer films for practical use in CPL materials. The dibromo[2.2]paracyclophane monomer prepared in this study is highly active in Suzuki–Miyaura cross-coupling and leads to copolymerizations with various diboronic acid and ester derivatives. Additional syntheses of planar chiral [2.2]paracyclophane-based copolymers with oligothiophenes or oligofluorenes are in progress, with the

goal of producing intense CPL from their films and aggregates through the formation of higher-ordered structures.

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Supplementary Information accompanies the paper on Polymer Journal website (<http://www.nature.com/pj>)