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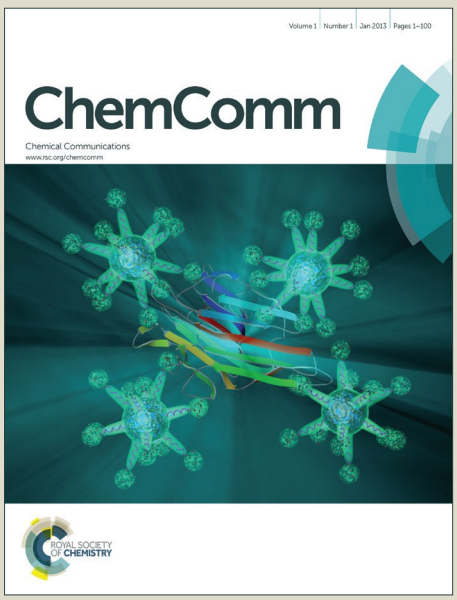

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Exact helical polymer synthesis by two-point-covalent-linking protocol between C_2-chiral spirobifluorene and C_2- or C_s-symmetric anthraquinone monomers

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Two types of one-handed exact helical polymers, coil- and screw-shaped polymers, were synthesized by the two-point-covalent-linking protocol using C_2-chiral spirobifluorene (SBF) and C_2- or C_s-symmetric anthraquinone spacer. Central to this protocol is a new aromatic ring-forming reaction based on the stepwise reductive cyclization of bis(aryloxy group)-substituted anthraquinone derivatives. The helical structures of the polymers annulated by aromatic skeletons exhibited high thermal stability attributed to the rigid C_2-chiral SBF units and the covalently two-point-connected structure.

Helical polymer architectures have attracted considerable attention because of their applications as chiral sensors,[1] chiral catalysts,[2] and other various uses.[3] Precise control of the higher-order-structure of helical polymers is required for acquiring excellent properties. Therefore, a variety of synthetic methods producing helical polymers have been extensively studied. The representative synthetic methods of rigid and one-handed helical polymers are the asymmetric chirogenic polymerization of prochiral monomers and the asymmetric enantiomer-differentiating polymerization of racemic monomers.[4] However, it remains a challenge to construct a perfectly controlled helical structure, because such asymmetric polymerizations are comprised of sequential asymmetric reactions, and even a barely detectable decrease of the stereoselectivity may lead to significant structural defects in the higher-order-structure of the helix.

To manipulate the higher-order-structure of helical polymers, we have developed strategic approaches exploiting rigid C_2-chiral repeating units for synthesizing helical polymers.[5–8] The synthetic method of helical polymers is based on polymerization of optically active C_2-chiral biaryl derivatives as twisted units with a rigid spacer unit. The resulting polymers form one-handed helical structures, whose helix senses can be *a priori* determined by the chirality of the C_2-chiral unit.

9,9'-Spirobifluorene (SBF) has a rigid and bulky skeleton where two fluorene moieties are orthogonally connected at a spiro center. Because of the rigidity, SBF is an ideal C_2-chiral unit as a building block of well-defined helical structures. Recently, we devised a rational synthetic strategy for helical polymers based on the two-point-linking of SBF units,[9] in which C_2-chiral SBF units are directionally fixed by a rigid planar spacer through a metal coordinated structure. This strategy can selectively afford two types of exact helical polymers, coil- and screw-shaped, by selecting the proper spacer (Fig 1). The coil-shaped helical polymer could be prepared by integrating *cis*-type latticeworks consisting of a C_2-symmetric spacer and C_2-chiral SBF. Alternatively, the screw-shaped helical polymer could be prepared by *trans*-type latticeworks consisting of a C_s-symmetric spacer and C_2-chiral SBF. Although this strategy has first provided the tailor-made synthetic method of exact helical polymers, the polymers include chemically labile coordination bonds in the spacer moieties to restrict the further applications of the polymers.

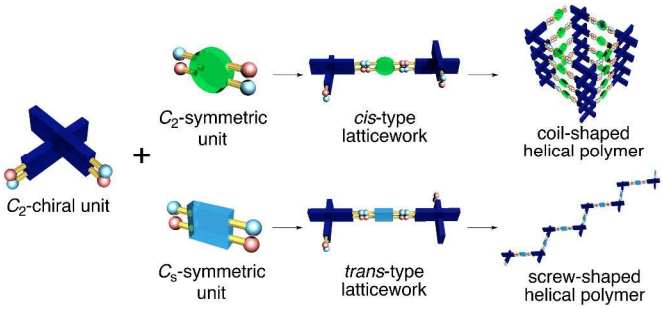
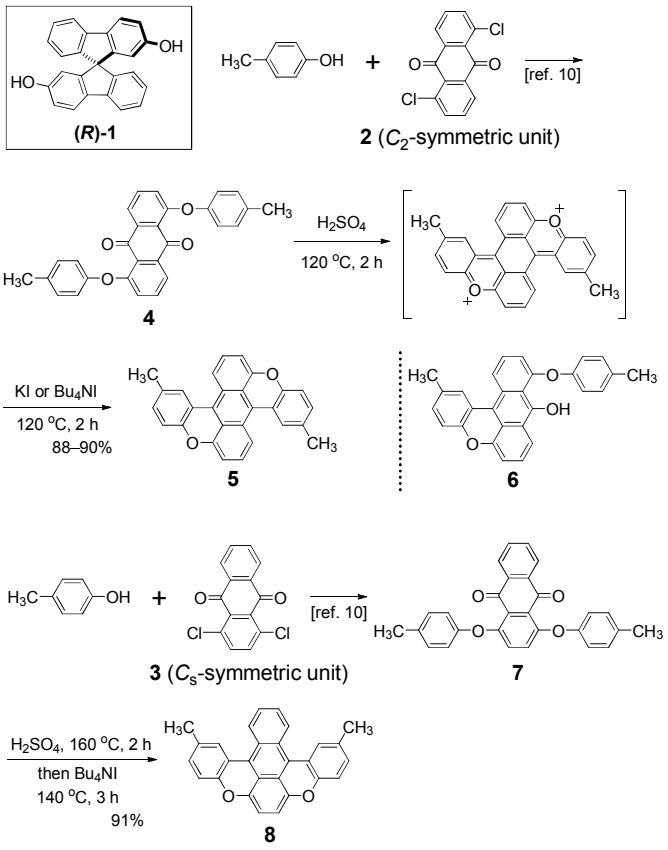


Fig 1. Strategy for the synthesis of exact helical polymers based on a two-point-covalent-linking protocol to afford a selectively coil- and a screw-shaped helical polymer.

We describe herein a novel synthesis of exact helical polymers annulated by aromatic skeletons between optically active C_2-chiral SBF repeating units **(*R*)-1**. As a key reaction for the annulation, we developed a new reliable aromatic ring-forming reaction via S_NAr reactions between two phenols and commercially available dichloroanthraquinones, C_2-symmetric **2** and C_s-symmetric **3** (Scheme 1).



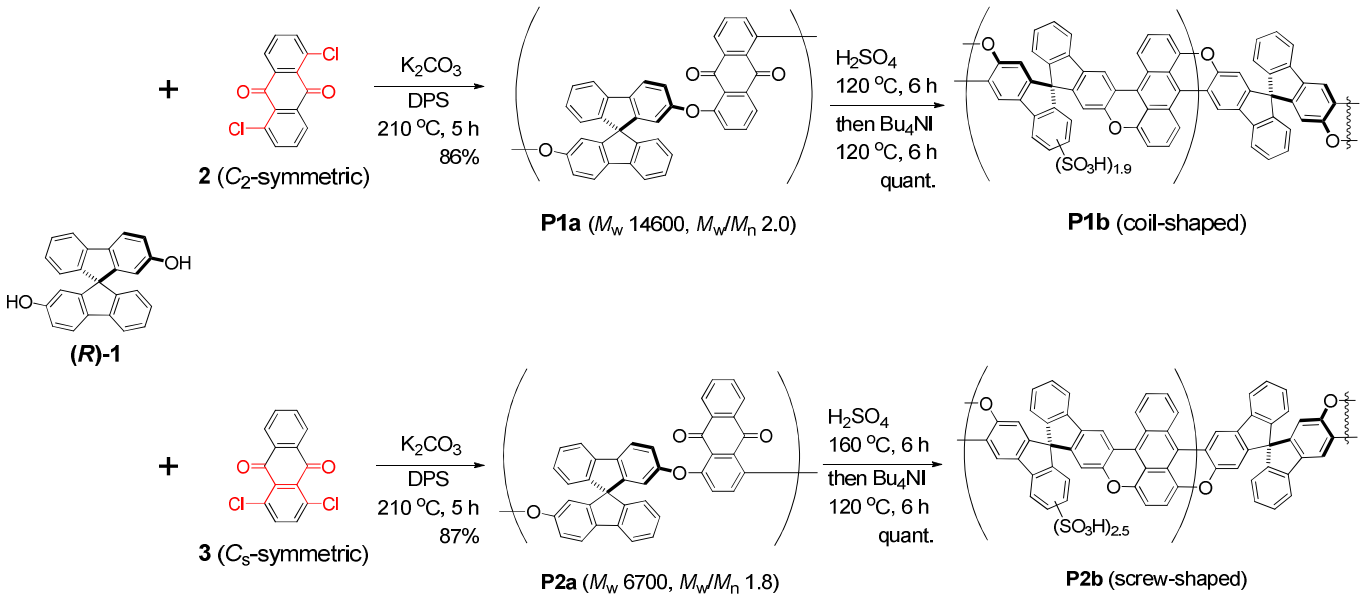
Scheme 1. Synthesis of **5** and **8**.

The aromatic ring-forming reaction was optimized using model compounds **4** and **7**, which were prepared from **2** or **3** with two *p*-cresols via S_NAr reactions, respectively (Scheme 1).[10] We first attempted the reductive cyclization reaction using $AlCl_3$ and NaCl as a solid state reaction in accordance with the literature,[10] which resulted in only 37% yield of **5** along with the generation of phenol **6** (Table S1).[12] We considered that the byproduct **6** would be generated by reduction of an intermediate with the chloride anion[11] before the intermediary formation of dication (Scheme S1).[12] Thus, we examined a stepwise reaction including treatment with conc H_2SO_4 as a halide-free acid followed by the addition of iodide salts as a reducing agent. After heating a solution of **4** in conc H_2SO_4 at 120°C for 2 h, KI solids were directly added to the reaction mixture to afford a 90% yield of **5** as a single product without the formation of **6**. The generation of dark purple I_2 solids was confirmed during the reaction, clearly supporting that iodide worked as the reducing agent of the intermediary dication as shown in Scheme 1. Tetrabutylammonium iodide (Bu_4NI) was also available for the reduction to give 88% yield of **5**.[12] The aromatic ring-forming reaction of **7** was performed at a similar manner to obtain **8** as a single product in 91% yield, although the cyclization step required a higher temperature (160 °C).

Based on the model experiments described above, we synthesized rigid coil- and screw-shaped helical polymers containing the SBF repeating units. We first obtained the poly(aryl ether) **P1a** as a precursor of the coil-shaped helical polymer through polycondensation of optically pure **(*R*)-1** and C_2-symmetric spacer **2** (Scheme 2). After considerable efforts (Table S2),[12] we found that the reaction at 210 °C in diphenylsulfone (DPS) afforded a sufficiently high-molecular-weight polymer. The structure of **P1a** was characterized by IR and ^{1}H NMR measurements.[12] The characteristic carbonyl absorption at 1674 cm^{-1} in the IR spectra and sharp ^{1}H NMR signals support the formation of **P1a** with a high molecular weight. Thermal properties of **P1a** and **P2a** were evaluated by thermo gravimetric analyses (TGA, Figures S21 and S26).[12] Six % weight loss of **P1a** in a range of 200–400 °C and 3% weight loss of **P2a** in a range of 160–460 °C were observed. The results might be attributed to the occurrence of di- or mono-dehydration per a repeating unit as a result of the cyclization.

Reductive cyclization of **P1a** was investigated to synthesize the well-defined coil-shaped helix **P1b**. Based on the model reactions (Schemes 1 and S2[12]), we first used KI as a reducing agent. The appearance of I_2 during the reaction supported that the reductive cyclization took place as in the model reactions. Surprisingly, the obtained polymer was highly soluble in water in contrast to the related polymers with rigid structures, likely due to the introduction of sulfonyl groups into the polymer backbone. Because the separation of sulfonated **P1b** from inorganic salts was very difficult, we next used Bu_4NI instead of KI. Removal of the ammonium salts and H_2SO_4 by repeated wash with Et_2O, CH_3CN, acetone, and CH_2Cl_2 gave pure **P1b** in a quantitative yield. The conversion of the reductive cyclization reaction was estimated by the IR spectrum.[12] The complete disappearance of the absorption peak of the carbonyl stretching band clearly supports a quantitative conversion to the coil-shaped helical polymer structure. On the other hand, the broad absorption peak around 3500 cm^{-1} and the high solubility in water are consistent with the sulfonation of the polymer backbone. Since no sulfonation of **5** was observed in the model reaction, the sulfonation may mainly occur on the fluorene moieties of **P1b**. The sulfonation ratio was estimated to be 1.9 per one repeating unit by the elemental analysis of **P1b**.[12] It should be noted that the good solubility of **P1b** in water and DMSO can facilitate evaluation of the optical properties in solution. Next, we synthesized the screw-shaped helical polymer. As with the protocol for **P1b**, the polycondensation of **(*R*)-1** with C_s-symmetric spacer **3** efficiently gave **P2a** (Scheme 2). A subsequent intramolecular cyclization reaction of **P2a** afforded the well-defined screw-shaped helical polymer **P2b** with a partially sulfonated backbone; the sulfonation ratio was estimated as described above to be 2.5.[12]

The chiroptical properties of the helical polymers were investigated by means of UV-vis and CD spectra (Fig 2). **P1a** and **P2a** showed absorption peaks and corresponding positive Cotton effects near 400 nm, derived from the anthraquinone moieties. After cyclization, these peaks disappeared, and new absorption peaks appeared at approximately 560 nm, originating from the expanded π-conjugated plane, which strongly support the effective conversions of **P1a** and **P2a** to **P1b** and **P2b**, respectively.



Scheme 2. Synthesis of exact helical polymers based on a two-point-covalent-linking protocol to afford a selectively coil-shaped **P1b** and a screw-shaped **P2b**.

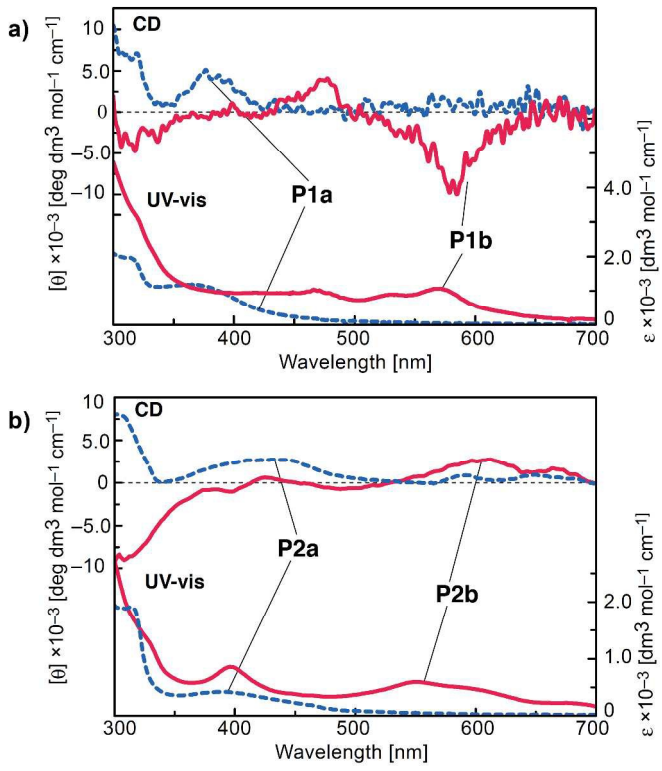


Fig 2. UV-vis and CD spectra (DMSO, 293 K) of a) **P1a** and **P1b** (50 μM) and b) **P2a** and **P2b** (100 μM).

The Cotton effects of **P1b** and **P2b** observed in this region support the formation of a chiral polymer, whereas the CD pattern of **P2b** was inverse to that of **P1b** in spite of the same chiral sense of their helicity. This inversion could be ascribed to the different directions of their conjugated spacer moieties: the directions of the spacer moieties on the screw-shaped helical polymer **P2b** alternate inversely, as shown in Scheme 3, whereas in the case of the coil-shaped polymer **P1b**, every spacer lines up unidirectionally. The g_{CD} values of ***(R)*-1** and the polymers were 3.2×10^{-5} for ***(R)*-1** (320 nm), 2.4×10^{-4} for **P1a** (382 nm), 2.7×10^{-4} for **P2a** (423 nm), 4.9×10^{-4} for **P1b** (581 nm), and 2.0×10^{-4} for **P2b** (612 nm). The increasing g_{CD} order of all polymers compared with that of ***(R)*-1** also ensures the inductions of chiral higher-order-structures to the main chains.

To estimate the effect of the sulfonation on the UV-vis and CD spectra, we obtained the simulated UV-vis and CD spectra of sulfonate-free **P1b** and **P2b** in the presence of DMSO using time-dependent molecular orbital (MO) calculations with a semi-empirical Zerner's intermediate neglect of differential overlap (ZINDO) method in Gaussian 09 (Figure S31).[12,13] In all cases, Gaussian-type functions based on wavelength were employed to draw the UV-vis and CD spectra from oscillator strength (*f*) and rotatory strength (R_{vel}) values and their positions, where a half Gaussian (1/e) bandwidth ($\Delta/2$) was set to be 40 nm. Through the comparison of the observed spectrum with the simulated one, we found that the sulfonation of the polymer backbone resulted in the CD Cotton effect change from bisignate to monosignate along with the blue-shifts of absorption maxima attributed to the conjugated moieties.

The UV-vis and CD spectra of **P1b** and **P2b** at various temperatures exhibited little change (Figure 3),[12] highlighting the rigidity and the high thermal stability of the higher-order-structures in these exact helical polymers bearing covalently two-point-connected skeletons.

Meanwhile, exposure of the solution to air led to a color change from purple to yellow, accompanied by the disappearance of characteristic absorption bands to the π-conjugated moieties (Figures S29 and S30).[12] This observation could be explained by a Diels-Alder reaction of the spacer moiety with a singlet oxygen.[14] In fact, the spacer models **5** and **7** were highly reactive to oxygen to afford the corresponding endo-peroxides.[12]

The structures of **P1a**, **P2a**, **P1b**, and **P2b** have further been estimated by force-field calculations of the 8-mer models (Figures S32–S35).[12] From the optimized structures of **P1a** and **P2a**, it was found that the polymers adopt one-handed helices originating from the rigid C_2-chiral SBF structure, although the higher-order-structures of the polymers are not completely defined due to the one-point-connection between SBF units and the spacers. The helical structures of **P1a** and **P2a** were roughly estimated to be a 4/1-helix with a pitch of 23 Å in size for **P1a** and a 2/1-helix with a pitch of 25 Å in size for **P2a**. On the other hand, the structures of **P1b** and **P2b** exhibited exact helical conformations without defect for both models. The optimized model for **P1b** has a 5/1-helical coil-shaped structure with a large helical groove of 15 Å in size, while that of **P2b** features 2/1-helical screw-shaped conformation with a pitch of 25 Å in size.[12]

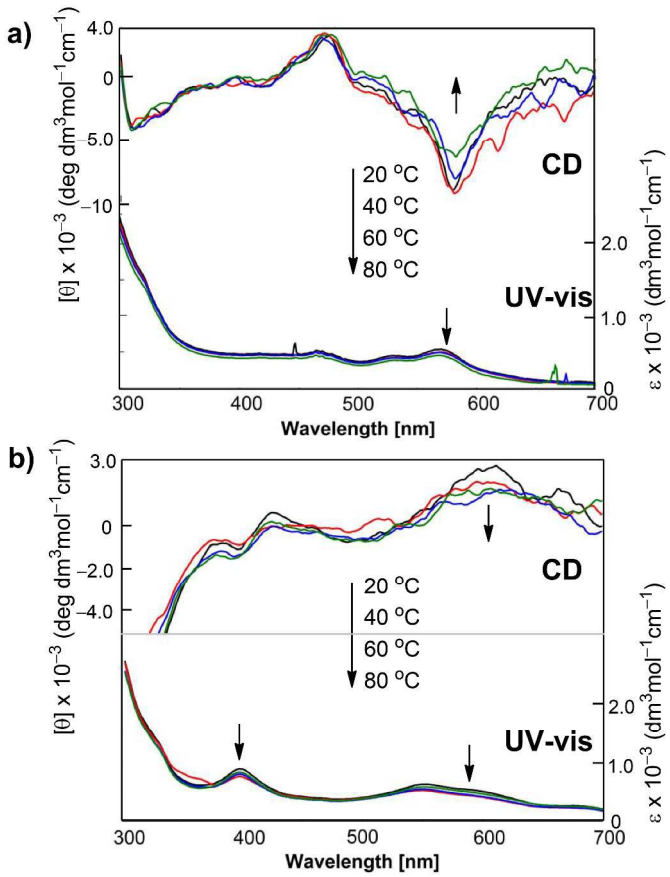


Fig 3. UV-vis and CD spectra (DMSO) of a) **P1b** (50 μM) and b) **P2b** (100 μM) at various temperatures.

In conclusion, we accomplished the synthesis of two types of exact helical polymers based on a new stepwise reductive annulation between C_2-chiral spirobifluorene and C_2- or C_s-symmetric anthraquinone spacers. The resulting helical polymers showed well-defined and thermally stable structures attributed to stiffly locking the rotational movements between the monomer units. The present two-point-covalent-linking protocol would also be applicable to other aromatic polymers with an exact higher-order-structure. Further investigations on applications using the helically ordered π-conjugated plane for devices or catalysts are currently underway.

Notes and references

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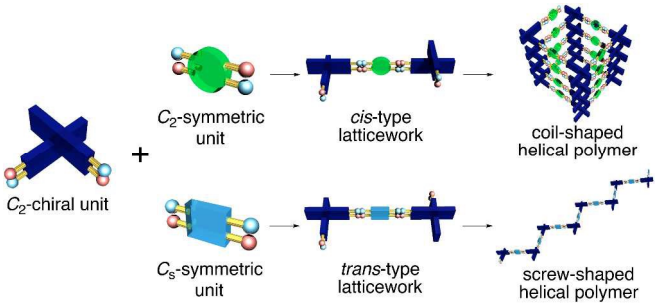
Graphical Abstract



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