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# Reversible Transformation of a One-Handed Helical Foldamer Utilizing a Planarity-Switchable Spacer and $C_2$-Chiral Spirobifluorene Units

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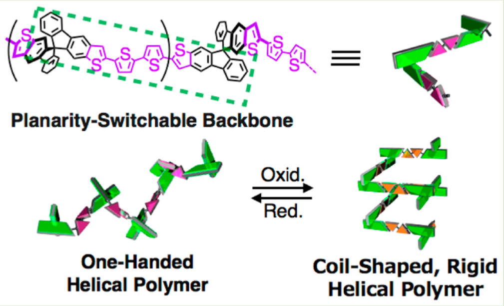
Supporting Information

**ABSTRACT:** Polymeric quaterthiophenes containing optically active $C_2$-chiral spirobifluorene skeletons were synthesized as a new type of helical foldamers, and their higher-order structures were investigated. Oxidization of quaterthiophene moieties caused the spacer units to be in planar structure, leading the conformation of the polymer to be a coil-shaped, rigid helix. This transformation was reversibly performed.



Helical architectures in biological systems such as RNA, proteins, and polysaccharides show specific functions originating from precisely controlled higher-order structures.[1] By their structural analogy, a variety of helically folded polymers, i.e., helical foldamers, have been designed and synthesized in an effort to develop unique applications for chiral sensors,[2] chiral catalysts,[3] optical materials,[4] and other various uses.[5] To control folding behavior, intra- and intermolecular interactions,[6] such as hydrogen bonding, coordination bonding, $\pi-\pi$ interactions, and lyophobic effects, are often employed. These interactions are weak or omnidirectional,[6c] leading to the difficulty in controlling the folded macromolecular structure. Therefore, important challenges still remain concerning the arbitrary design of one-handed helical foldamers and the need for strict structural control.

We have previously reported the tailor-made synthesis of helical ladder polymers with well-defined pitch, cavity, and helicity, by the combination of two building blocks of a $C_2$-chiral unit and a rigid planar unit.[7] In this way the helix sense is perfectly defined by the chirality of the $C_2$-chiral unit, and the macromolecular structures are simply controllable by selecting the proper spacer unit. Katz et al. and Pu et al. have also reported the synthesis of helical ladder polymers using a similar concept.[8]

Inspired by such reports, we designed a new folding system utilizing a $C_2$-chiral unit and a planarity-switchable spacer to regulate the planarity (Figure 1), which offers a straightforward method toward the precise structural control of the helical foldamer. The external stimulus, e.g., redox reaction, changes the planarity of spacer units in the main chain, providing a rational redox-driven conformational switch of the helical foldamer. Therefore, we focused our attention on the use of oligothiophenes, which are one of the well-studied, redox-active $\pi$-conjugated structures.[9]

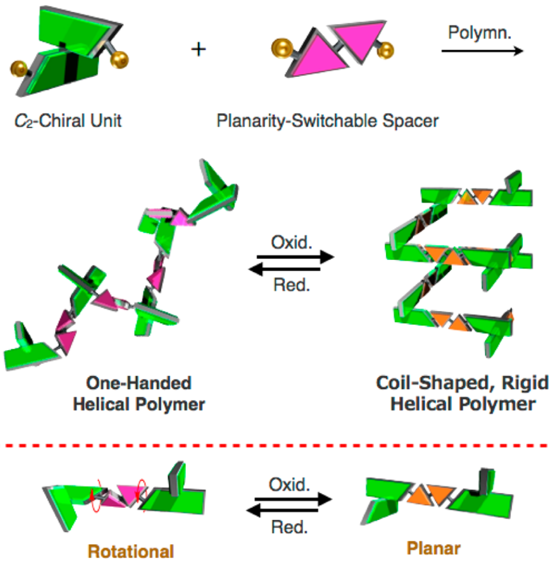


**Figure 1.** Concept of the folding system with the spacer unit having switchable planarity.

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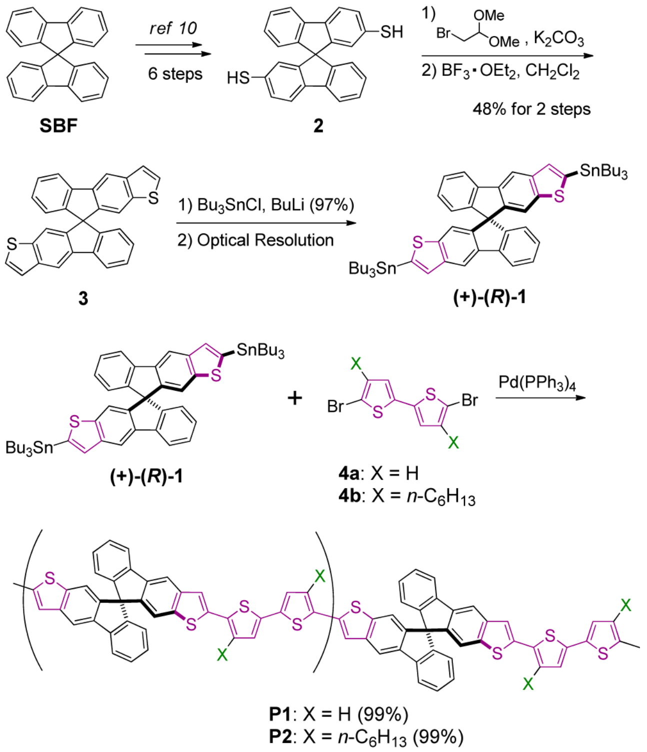
The oligothiophene at the ground state is capable of twisting with relatively low energy, whereas the oxidation of oligothiophene affords the quinoid structure to suppress the bond rotation.[9a] In line with this concept, we designed thiophene-fused 9,9′-spirobifluorene as a right-angled $C_2$-chiral unit and bithiophene as a spacer unit for effective conformational switch of the helical foldamer (Figure 1).

For this purpose, optically active bis(tributylstannyl)-thiophene-fused spirobifluorene (+)-(*R*)-**1** was newly designed and synthesized as the crucial monomer of the redox-driven helical foldamer (Scheme 1).[10,11] 9,9′-Spirobifluorene-2,2′-dithiol **2** was prepared from commercially available 9,9′-spirobifluorene (SBF) according to our previous report.[10] Treatment of **2** with bromoacetaldehyde dimethylacetal in the presence of $K_2CO_3$ produced the corresponding thioether, which was exposed to $BF_3{\cdot}OEt_2$ in $CH_2Cl_2$ to afford thiophene-fused SBF **3** in 48% yield for two steps. Subsequent tributylstannylation of **3** gave (±)-**1**, which was optically resolved with CHIRAL PAK IB.[11] The retention times of the enantiomers (±)-**1** were finely separated, probably because of the large unsymmetric skeleton. The optically pure (+)-(*R*)-**1** showed a positive Cotton effect at approximately 300 nm derived from the π−π* transition[11] and was determined as an (*R*)-isomer in comparison with other spiro-compounds.[12]

**Scheme 1. Synthesis of Spiro-Connected Quaterthiophene-Based Polymers (P1 and P2) Using (+)-(*R*)-1**



Spiro-connected quaterthiophene-based polymers bearing no substituent or hexyl side chains (**P1** and **P2**) were synthesized in quantitative yields via the Still coupling polymerization of (+)-(*R*)-**1** with 5,5′-dibromo-2,2′-bithiophene derivatives (**4a** and **4b**) in the presence of $Pd(PPh_3)_4$. A racemic sample $\mathbf{P1}_{\mathrm{rac}}$ was prepared, for comparison, from racemic (±)-**1** and **4a** in the same manner. The weight-average molecular weights ($M_w$) and their distributions (PDI) of the polymers, estimated by size exclusion chromatography (SEC) analysis based on polystyrene standards, were $M_w$ 11 000, PDI 2.5 for **P1**, $M_w$ 7200, PDI 2.4 for **P2**, and $M_w$ 5200, PDI 1.9 for $\mathbf{P1}_{\mathrm{rac}}$. Through the SEC analysis, we confirmed that no cyclic oligomer was obtained.[11] Their $^1$H NMR spectra, identical to the chemical structures of **P1** and **P2**, have sharp signals, supporting the formation of high-molecular-weight polymers.[11]

Mark−Houwink−Sakurada coefficients (α) of the polymers were estimated by SEC with a viscometric detector to be 0.20 for **P1**, 0.002 for **P2**, and 0.97 for $\mathbf{P1}_{\mathrm{rac}}$, suggesting a contracted structure for **P1** and the more compact spherical conformation for **P2** in solution, which were in good contrast with a stiff rod-like conformation for racemic polymer $\mathbf{P1}_{\mathrm{rac}}$.

To evaluate the conformations of **P1** and **P2** in detail, we also synthesized four model compounds (**M1**, **M2**, **D1**, and **D2**) with comparable conjugated moieties to the corresponding polymers (Figure 2a).[11] Figures 2b and 2c show the UV−vis and CD spectra of the model compounds and the polymers.

The appearance of an absorption band around 400 nm can be assigned to the π−π*-like transition of conjugated moieties. **P2**, **M2**, and **D2**, with hexyl side chains, showed slightly shorter maximum absorption wavelengths ($\lambda_{\max}$) than **P1**, **M1**, and **D1**, because the quaterthiophene moiety in **P2**, **M2**, and **D2** would be twisted by the thermally induced steric interaction between the hexyl group and the spirobifluorene moiety.[9h] On the other hand, the UV−vis spectra of both polymers show broader signals and shorter $\lambda_{\max}$ values than those of the model compounds despite the same spacer structures. This result suggests that the polymers would have nonplanar quaterthiophene moieties, which might be attributed to the entropy-driven conformational change of the polymer chain to adopt an extended structure as well as the steric interaction between the main chains.

Positive Cotton effects in all spectra were observed in the absorption region of the π−π* transition of the quaterthiophene moieties. In the cases of monomer models (**M1** and **M2**), they exhibited the Cotton effects around 360−500 nm originating from the spiro conformation of thiophene-fused fluorenes on the $C_2$-chiral unit (blue arrows in Figure 2a). The CD curves of dimer models **D1** and **M1** were similar in the longer-wavelength region, which might be attributed to the relatively planar structures of **D1** and **M1**. Meanwhile, **D2** exhibited an enhanced Cotton effect at around 410−470 nm and a decreased one at around 300−400 nm relative to that of **M2**. Therefore, it is expected that **D2** could bring about the additional bisignate Cotton effect originating from the exciton coupling between two π-conjugated moieties on both sides of a $C_2$-chiral unit (a red arrow in Figure 2a), which also suggests the twisted quaterthiophene structure of **D2**.[13] On the other hand, the CD spectra of both polymers (**P1** and **P2**) showed remarkably enhanced Cotton effects at around 400−500 nm compared with those of the monomer and dimer models, highlighting that the polymers would have twisted, nonplanar, and rotational quaterthiophene backbones, though the polymers adopt one-handed helices originating from the $C_2$-chiral SBF structure.[7]

It is also noted that the UV−vis and CD spectra of **P1** and **P2** at higher temperature showed almost the same signals as the original spectra at 298 K (Supporting Information, Figure S41),[11] indicating the structural similarity of these neutral polymers at higher temperature.

Oxidizations of polymers (**P1** and **P2**) and model compounds (**M1** and **M2**) were carried out with $FeCl_3$ (Scheme S1, Supporting Information).[9] Upon the addition of

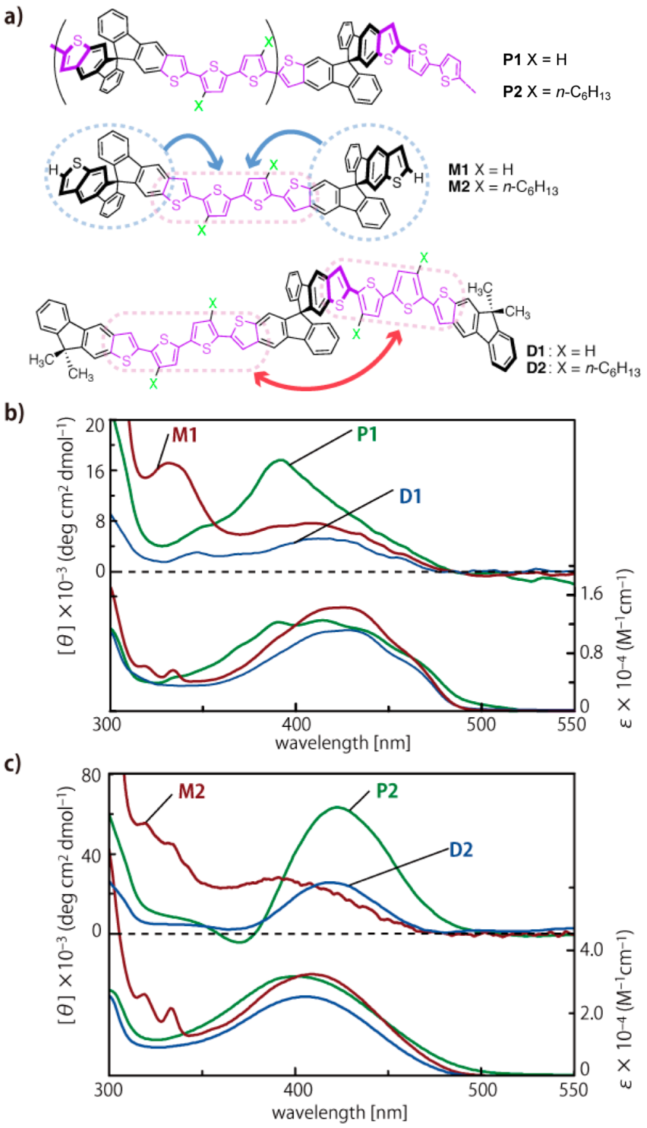


**Figure 2.** (a) Structures of the polymers and model compounds. Cotton effects of the $C_2$-chiral unit on quaterthiophene are indicated by blue arrows, and exciton coupling between two quaterthiophene moieties is indicated by a red arrow. (b) CD and UV−vis spectra of **P1**, **M1**, and **D1**, and (c) **P2**, **M2**, and **D2** ($ClCH_2CH_2Cl$, 25 $\mu$M, 263 K).

$FeCl_3$, the absorption band and Cotton effects were observed at 700 nm in all solutions (Figure 3). The absorption can be assigned to the generation of a radical cation. The disappearance of absorption derived from the neutral quaterthiophene moieties indicates complete oxidation of polymer backbones. No further change was observed upon the addition of over 200 mol % of $FeCl_3$.

UV−vis spectra at various temperatures were measured in order to study the planarity of the neutral (**P1**, **P2**, **M1**, and **M2**) and oxidized species (**P1**$_{ox}$, **P2**$_{ox}$, **M1**$_{ox}$, and **M2**$_{ox}$),[11] and the $\lambda_{max}$ values were summarized in Table 1. Upon heating, the blue shifts of $\lambda_{max}$ values were observed in all the neutral polymers and models,[11] implying that they adopt a random conformation because the decrease of effective conjugation lengths would be ascribed to the increased rotational movements of the quaterthiophene linkages.[9i] The thermochromism was fully reversible, similar to a regioregular polythiophene.[9a] The $\lambda_{max}$ values of the oxidized models (**M1**$_{ox}$ and **M2**$_{ox}$) were almost constant, suggesting a thermal stability of these spacer structures. In contrast, heating of **P1**$_{ox}$ and **P2**$_{ox}$ resulted in a red shift of the $\lambda_{max}$ reaching the values of the corresponding **M1**$_{ox}$ and **M2**$_{ox}$, whose simulated structures have a coplanar conformation.[11] Although the precise reason for the red shift is not clear at the present stage, the red shift of the $\lambda_{max}$ seems to indicate that the spacer moieties in both **P1**$_{ox}$ and **P2**$_{ox}$ adopt a longer conjugation length due to further planarization,[14] accompanied by the removal of solvents and the counteranions around the spacer moieties, because the oxidized polymers with multivalency could tend to aggregate in $ClCH_2CH_2Cl$ as a less polar solvent.

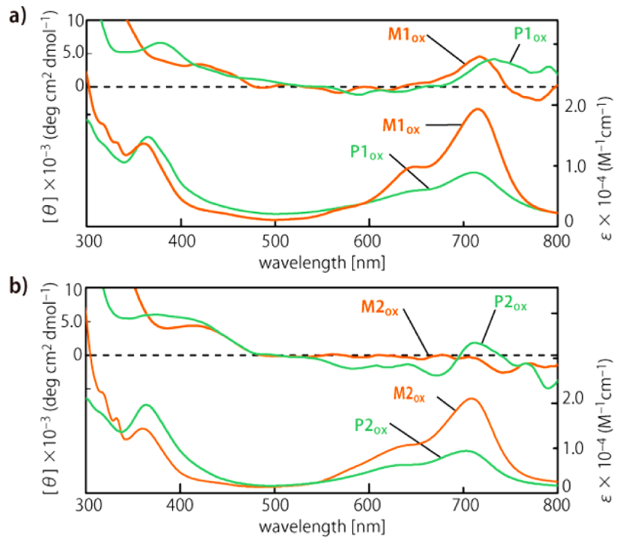


**Figure 3.** CD and UV−vis spectra of the oxidized polymers and model compounds by the addition of $FeCl_3$ (200 mol % relative to the repeating unit) in $ClCH_2CH_2Cl$ (298 K, 50 $\mu$M): (a) **P1**$_{ox}$ and **M1**$_{ox}$ and (b) **P2**$_{ox}$ and **M2**$_{ox}$.

**Table 1. Maximum Absorption Wavelength ($\lambda_{max}$) of the Neutral and Oxidized Species**

| | $\lambda_{max}$ at various temperatures/nm | | |
|---|---|---|---|
| | −10 °C | 20 °C | 50 °C |
| **P1** | 414 | 413 | 411 |
| **M1** | 430 | 426 | 419 |
| **P2** | 400 | 398 | 395 |
| **M2** | 409 | 407 | 404 |
| **P1**$_{ox}$[a] | 710 | 712 | 717 |
| **M1**$_{ox}$[a] | 716 | 716 | 716 |
| **P2**$_{ox}$[a] | 700 | 700 | 704 |
| **M2**$_{ox}$[a] | 709 | 709 | 708 |

[a] The UV spectra were measured in the presence of $FeCl_3$ (600 mol %) in $ClCH_2CH_2Cl$ (5.0 $\mu$M).

Moreover, we also estimated the twisting energies ($\Delta E = E_\phi - E_0$) between the thiophene and thiophene-fused fluorene in **M1** and **M1**$_{ox}$ as a function of the dihedral angle ($\phi$) by a density functional theory (DFT) calculation (B3LYP/6-31G-(d)).[11] The results indicate that the $\Delta E$ strongly depends on $\phi$, and the oxidation from **M1** to **M1**$_{ox}$ remarkably enhances the $\Delta E$.[11] Such propensities are in good accordance with those between the thiophene units of oligo- and polythiophenes reported by Bendikov,[9a] implying that the oxidation of the quaterthiophene moiety of **M1** could lead the moiety to a

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thermally favorable planar structure. From results of both the temperature dependence of UV−vis spectra and the simulated twisting energies, we conclude that the oxidization of **P1** and **P2** immobilizes the structures substantially to give unique coil-shaped helical structures as expected from the rigid chiral structure of the (+)-(*R*)-**1** unit and the fastened planar spacer structure (Figure 1).

To directly prove the conformational change of the polymers triggered by the oxidation, dynamic light scattering (DLS) measurements of the polymers were performed, and we obtained the hydrodynamic diameters of the polymers before and after the oxidation (Table 2). The oxidation of optically active **P1** resulted in a slight contraction of the diameter, while that of $\mathbf{P1}_{rac}$ consisting of racemic SBF units and the same spacer moieties as **P1** afforded the 1.9-fold extended diameter. The results clearly indicate that the oxidations of the polymers induced the structural change depending on the sequences of $C_2$-chiral SBF units in the main chain, also supporting that $\mathbf{P1}_{ox}$ would form the coil-shaped rigid helical structure as illustrated in Figure 1. Contrary to $\mathbf{P1}_{ox}$, the diameter of $\mathbf{P2}_{ox}$ was 7-fold extended in comparison with that of **P2**. Because the $\alpha$ value of **P2** indicated the formation of compact spherical conformation in a neutral state, the planarization of the spacer moieties enforced by the oxidation seems to disentangle the aggregated **P2**, leading to the rather extended coil-shaped helical structure $\mathbf{P2}_{ox}$.

**Table 2. Hydrodynamic Diameters of the Polymers before and after Oxidation Estimated by DLS Measurements**[a]

| polymer | **P1** | $\mathbf{P1}_{ox}$ | $\mathbf{P1}_{rac}$ | $\mathbf{P1}_{rac\text{-}ox}$ | **P2** | $\mathbf{P2}_{ox}$ |
|---|---|---|---|---|---|---|
| hydrodynamic diameter/nm | 24.3 | 23.5 | 51.4 | 97.3 | 11.7 | 79.0 |

[a] DLS measurements were performed in THF (60 $\mu$M) in the absence or presence of $FeCl_3$ (1200 mol %).

The addition of sodium bisulfite as a reducing agent to the mixture of the polymers and $FeCl_3$ restored the original spectra. The SEC profiles of the recovered compounds indicated that no oxidative polymerization or degradation of polymers occurred.[11] Additionally, the cyclic voltammograms (CVs) of **P1** and **P2** showed the quasi-reversible unimodal redox couples.[11] These results could clearly support the efficient reversibility of a redox-driven folding system.

In conclusion, we synthesized one-handed helical foldamers consisting of both quaterthiophene and $C_2$-chiral spirobifluorene skeletons and demonstrated the control over higher-order structure via an unprecedented redox-driven folding system based on the change of rigidity of the main chain. The helix senses can be *a priori* determined by the chirality of the rigid $C_2$-chiral unit. It is also worth noting that our system is able to produce a redox-responsive chiral inner space. This study offers intriguing potentials for chiral materials as hosts, catalysts, or sensors with high selectivity. Further investigations into the applications are currently underway.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details, $^1$H NMR, $^{13}$C NMR, FT-IR, MALDI−TOF MS, UV−vis, and CD spectra, energy-minimized structures and twisting energies of model compounds estimated by DFT calculations, GPC charts, and CVs of polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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