

A Helical Ladder Polymer: Synthesis and Magnetic Circular Dichroism of Poly[phenylene-4,6-bis(methylsulfonio)-1,3-diyl triflate]

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ABSTRACT: A helical ladder polymer composed of a fused-benzothiophenium ring was synthesized *via* the intramolecular ring-closing reaction of the methylsulfoxide-substituted poly(1,3-phenylene). The precursor polymer was prepared by the palladium-catalyzed polymerization of 1,3-dibromobenzene and 1,3-phenylenebisborate and the following quantitative oxidation. The intramolecular ring-closing of the precursor polymer yielded poly[phenylene-4,6-bis(methylsulfonio)-1,3-diyl triflate]. The polymer structure did not involve any structural defects based on NMR analysis, which was supported by the model dimers and the control reaction using the monomeric analogues. The obtained polymer is one of the new poly(thiaheterohelicene)s. Magnetic circular dichroism of the polymer suggested an electron transition ascribed to the fused-ring structure. [DOI 10.1295/polymj.37.592]

KEY WORDS π -Conjugated Polymer / Intramolecular Cyclization / Helical Structure / Helicene / Sulfonium Salt / Magnetic Circular Dichroism /

π -Conjugated polymers containing a thiophene moiety afford a stable doped state due to an excess π -electron conjugation and have a high electrical conductivity among the π -conjugated aromatic polymers.^{1–4} On the other hand, helical polymers have a precisely ordered stereostructure, and they are applied to a chiral separator and a sensor.^{5–20} π -Conjugated helical molecules consisting of aromatic fused-rings are called “helicenes” and have been often characterized by a unique optical activity caused by their π -conjugation with helical structure and by a stiff structure derived from the aromatic fused-rings.^{16–26}

Among them, the “thiaheterohelicenes” consist of fused-benzothiophene rings, and it has been reported that their helical structure and π -conjugation are stable under wide conditions such as in an acidic or basic solvent and even at high temperature.^{27,28} The heterohelicene also showed a second-harmonic generation circular dichroism.¹⁸ Classical methods available for the syntheses of the helicenes and thiaheterohelicenes are the oxidative photo-cyclization of the *cis*-stilbene²⁹ and *cis*-di(2-thienyl)ethylene derivatives,^{22,23} a reaction of benzoquinone and enol esters,¹⁷ a Friedel-Crafts reaction of 9,10-phenanthrenes,²⁰ and the annulation of thiophene rings using lithium di-*iso*-propylamine.^{24–26} However, these synthetic methods required stepwise synthetic routes, and there have been only a few reports^{30,31} of the thiaheterohelicene with a high molecular weight or a sufficient number of repeating units to form a helical structure.

In this study, we designed a new thiaheterohelicene as the target molecule with a helical π -conjugated

structure and described its synthesis using the intramolecular ring-closing reaction of the sulfonium electrophile to form the fused-ring moiety. We have reported an efficient synthetic route to produce “poly(thiaacene)”s which are comprised of fused sulfur-containing aromatic rings and have a planar and ladder-type structure.^{32–35} The key step to form the poly(thiaacene)s is the quantitative ring-closing reaction of the alkyl sulfoxide-substituted aromatic polymers. For example, the ring-closing of poly[1,4-phenylene-*alt*-2,5-bis(methylsulfinyl)-1,4-phenylene] yields poly(phenylene-2,5-dithia-1,4-diyl).³³ This poly(thiaacene) involves the benzothiophene unit that is alternatively linked (or fused) up and down, and gave a significantly developed π -electron conjugation. We extended this poly(thiaacene), in this paper, to design and provide a high molecular weight thiaheterohelicene, *i.e.*, poly[phenylene-4,6-bis(methylsulfonio)-1,3-diyl triflate] (**1** in Chart 1).

Magnetic circular dichroism (MCD) is an electronic spectroscopy used to study the induced optical activity caused by an exterior magnetic field and has been applied to magnetically active, or paramagnetic and ferromagnetic, molecules such as heme-protein and -enzyme.^{36,37} MCD is also effective for estimating the magnetic moments of the ground and excited states of the π -conjugated cyclic compounds.³⁸ In this paper, we applied MCD spectroscopy, for the first time, to the ring-closed polymer and the electron transition based on the molecular structure of poly(thiaheterohelicene).

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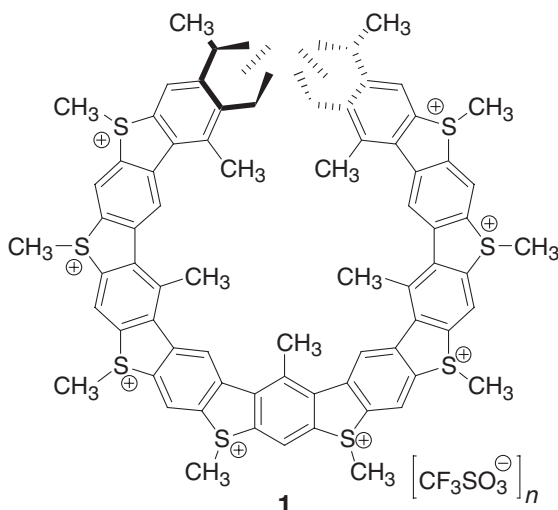


Chart 1.

EXPERIMENTAL

2-(Methylthio)biphenyl (2)

2-Bromothioanisole (4.06 g, 20 mmol) and phenylboronic acid (2.44 g, 20 mmol) were dissolved in THF (200 mL) under argon. Tetrakis(triphenylphosphine)palladium (0) (1.27 g, 1.1 mmol) and a 2 M aqueous sodium carbonate solution (100 mL) were added to the solution, and the mixture was stirred at 70 °C under argon for 18 h. The mixture was cooled to room temperature, the organic phase was extracted with diethyl ether and then washed with water. After drying over anhydrous sodium sulfate followed by evaporation, the residue was purified by silica gel column chromatography with the hexane and chloroform (v/v = 2/1) mixture as the eluent to give a white powder: yield 96%; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 7.64 (d, 2H), 7.61 (t, 2H), 7.54 (t, 1H), 7.49 (t, 1H), 7.45 (d, 1H), 7.41 (d, 1H), 7.36 (t, 1H), 2.49 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 140.7, 140.3, 137.0, 129.8, 129.1, 127.9, 127.7, 127.3, 125.0, 124.5, 15.6; IR (KBr, cm^{-1}): 2923 ($\nu_{\text{C-H}}$); MS (m/z): 200 (M^+), calcd for $\text{M} = 200.3$; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{S}$: C, 78.0; H, 6.0. Found: C, 77.6; H, 5.4.

2-(Methylsulfinyl)biphenyl (3)

A dichloromethane (200 mL) solution of **2** (2.67 g, 13.3 mmol) was stirred at 30 °C. A 30% aqueous hydroxyperoxide solution (53.2 mL) and acetic acid (13.3 mL) were added to the solution, and the mixture was stirred at 30 °C for 4 h. The organic phase was extracted with chloroform and washed with water. The solution was dried over anhydrous sodium sulfate and concentrated, the residue was purified by silica gel column chromatography with the chloroform and methanol (v/v = 5/1) mixture as the eluent to give

a white powder: yield 97%; $^1\text{H NMR}$ (CDCl_3 , 500 MHz): δ 8.13 (d, 1H), 7.63 (t, 1H), 7.54 (t, 1H), 7.48–7.41 (m, 3H), 7.38 (d, 2H), 7.33 (d, 1H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): δ 140.7, 140.3, 136.9, 129.8, 129.1, 127.9, 127.7, 127.3, 125.0, 124.5, 41.5; IR (KBr, cm^{-1}): 2925 ($\nu_{\text{C-H}}$), 1047 ($\nu_{\text{S=O}}$); MS (m/z): 216 (M^+), calcd for $\text{M} = 216.3$; Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{OS}$: C, 72.2; H, 5.6. Found: C, 72.5; H, 5.5.

5-Methyldibenzothiophenium triflate (4)

3 (108 mg, 0.5 mmol) was added to triflic acid (10 mL), and the solution was stirred at room temperature for 72 h in the dark. The mixture was poured into diethyl ether (300 mL) and a white solid was precipitated. The precipitation was filtered and dried under vacuum to give the sulfonium salts **3**: yield 98%; $^1\text{H NMR}$ (CD_3CN , 500 MHz): δ 8.24 (m, 4H), 7.86 (t, 2H), 7.72 (t, 2H), 3.32 (s, 3H). ($\text{CF}_3\text{SO}_3\text{D}$, 500 MHz): δ 7.33 (d, 2H), 7.15 (d, 2H), 7.01 (t, 2H), 6.85, (t, 2H), 2.36 (s, 3H). $^{13}\text{C NMR}$ (CD_3CN , 125 MHz): δ 140.2, 134.9, 132.0, 131.7, 128.7, 125.2, 35.1; IR (KBr, cm^{-1}): 2917 ($\nu_{\text{C-H}}$), 1256 ($\nu_{\text{C-F}}$), 1165 (ν_{SO_2}); ESI-MS (m/z): 198 (M^+), calcd for $\text{M} - \text{CF}_3\text{SO}_3^- = 199.3$; Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{F}_3\text{O}_3\text{S}_2$: C, 48.3; H, 3.2. Found: C, 48.0; H, 3.4.

Poly[4,6-bis(methylthio)-1,3-phenylene-alt-2-methyl-1,3-phenylene] (7) (Table I, run 6)

5 (172.0 mg, 0.50 mmol), 1,5-dibromo-2,5-bis(methylthio)benzene (**6**) (164.0 mg, 0.50 mmol), tetrakis(triphenylphosphine)palladium(0) (11.6 mg, 0.010 mmol) and THF (5.0 mL) were placed in a 10 mL ampoule in a glove box under argon. After the addition of a 2.0 M aqueous sodium carbonate solution (1.0 mL), the ampoule was evacuated, sealed, and heated at 80 °C for 72 h. The reaction mixture was dropwise poured into 200 mL of methanol, and the precipitate was filtered and then washed with methanol and hot water. The precipitate was dissolved in chloroform then reprecipitated in 200 mL of hexane. The precipitate was dried under vacuum to give a white powder: yield 97%; $^1\text{H NMR}$ (CD_2Cl_2 , 500 MHz): δ 7.31–6.92 (m, 5H), 2.45 (s, 6H), 1.91 (s, 3H). $^{13}\text{C NMR}$ (CD_2Cl_2 , 125 MHz): δ 154.9, 138.3, 133.1, 132.1, 126.2, 122.0, 117.7, 114.5, 15.7, 12.6; IR (KBr, cm^{-1}): 2949 ($\nu_{\text{C-H}}$); GPC (CHCl_3 , PSt calibration): $M_n = 7500$, $M_w = 10500$ ($M_w/M_n = 1.4$); Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{S}_2$: C, 69.7; H, 5.5. Found: C, 69.5; H, 5.3.

Poly[4,6-bis(methylsulfinyl)-1,3-phenylene-alt-2-methyl-1,3-phenylene] (8)

A dichloromethane (4 mL) solution of **7** (51.7 mg, 0.20 unit mmol), a 30% aqueous hydrogen peroxide solution (0.8 mL), and acetic acid (0.4 mL) were stirred at 30 °C for 10 h. The organic phase was extracted

with chloroform, and washed with water. After drying and evaporation, the residue was dissolved in 0.5 mL of chloroform and precipitated in hexane. The precipitate was dried under vacuum to give a white powder: yield 92%; ^1H NMR (CD_2Cl_2 , 500 MHz): δ 8.78 (s, 1H), 7.56–7.15 (m, 4H), 2.59 (s, 6H), 1.98 (s, 3H); IR (KBr, cm^{-1}): 2960 ($\nu_{\text{C-H}}$), 1050 ($\nu_{\text{S=O}}$); Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{O}_2\text{S}_2$: C, 62.0; H, 4.9. Found: C, 61.6; H, 5.3.

Poly[phenylene-4,6-bis(methylsulfonio)-1,3-diyl triflate] (1)

8 (100 mg, 0.34 unit mmol) was dissolved in triflic acid (6.8 mL). The solution stirred at room temperature for 7 d and poured into diethyl ether (100 mL). The precipitate was washed with diethyl ether and water, then dried under vacuum to give a light brown powder: yield: 98%; ^1H NMR ($\text{CF}_3\text{SO}_3\text{D}$, 500 MHz): δ 8.48 (s, 1H), 7.22 (s, 1H), 7.05 (s, 1H), 2.99 (s, 6H), 1.72 (s, 3H); IR (KBr, cm^{-1}): 2917 ($\nu_{\text{C-H}}$), 1256 ($\nu_{\text{C-F}}$), 1165 (δ_{SO_2}); Anal. Calcd for $\text{C}_{17}\text{H}_{12}\text{F}_6\text{O}_6\text{S}_4$: C, 36.8; H, 2.2. Found: C, 37.0; H, 2.5.

Materials

All reagents were obtained from the Kanto Chemical Co., Tokyo Kasei Co. and Aldrich Chemical Co., and used without further purification. 2-Methyl-1,3-phenylenebis(pinacol borate) (**5**) and 1,5-dibromo-2,4-bis(methylthio)benzene (**6**) were prepared according to a previous paper.³¹

Measurements

The ^1H and ^{13}C NMR, mass, and infrared spectra were recorded on a JEOL Lambda 500, a Shimadzu GCMS-QP5050, and a JASCO FT/IR-410 spectrometer, respectively. The elemental analysis was performed on a Perkin-Elmer PE-2400 and a Metrohm 645 Multi DOSIMAT. The UV–vis MCD were measured on a JASCO V-550 and J-820/MCD-414.

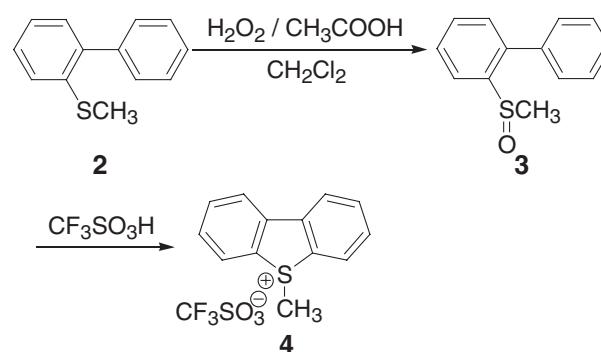
For the ^1H NMR Study of the Intramolecular Ring-closing

An inner NMR tube (ϕ 2 mm) was filled with acetone-*d*6 containing 0.1% TMS as the standard, and placed in the center of an outer standard NMR tube (ϕ 5 mm) which was filled with the $\text{CF}_3\text{SO}_3\text{D}$ (0.5 mL) solution of **3** (5.4 mg, 0.025 mmol).

RESULTS AND DISCUSSION

Synthesis and Characterization of Model Dimers

The model dimers were synthesized to study the coupling reaction that forms polymer **1** (Chart 1). 2-(Methylthio)biphenyl (**2**) was prepared by the palladium-catalyzed coupling reaction of 2-bromothioanisole



Scheme 1.

and phenylboronic acid. The coupling of an equivalent amount of the couplers almost quantitatively gave **2** (see Experimental Part) to support that the palladium-catalyzed coupling is effective for the precursor polymer formation. The pendant methyl sulfide of **2** was quantitatively oxidized with peracetic acid at 30 °C to yield **3**. The following intramolecular ring-closing of **3** afforded 5-methyldibenzothiophenium triflate (**4**). The ^{13}C NMR spectrum of **4** showed six signals in the aromatic region which were ascribed to the fused-ring molecular structure of **4** (see Experimental Part). The strong IR absorption bands attributed to the C–F and SO_2 stretching vibrations of the counter triflate anion at 1256 ($\nu_{\text{C-F}}$) and 1165 (ν_{SO_2}) cm^{-1} supported the sulfonio/triflate salt formation.

The ring closing reaction, *i.e.*, the fused-ring formation was monitored by ^1H NMR on the $\text{CF}_3\text{SO}_3\text{D}$ solution of **3** (Figure 1). During the initial period, the signals of **3** (δ 7.18, 6.98, 6.91, 6.70, and 6.45 ppm) disappeared and those of **4** (δ 7.33, 7.15, 7.01, and 6.85 ppm)^{34,39} appeared. After 3 d, the reaction was completed and no other peaks ascribed to a by-product (except for water) and side-reaction were detected during the reaction. These results indicated that the analogous reaction forms the corresponding fused-ring polymer without any structural defects.

Synthesis of the Precursor Polymer, Poly[4,6-bis(methylthio)-1,3-phenylene-alt-2-methyl-1,3-phenylene]

The precursor polymer, poly[4,6-bis(methylthio)-1,3-phenylene-alt-2-methyl-1,3-phenylene] (**7**), was prepared as shown in Scheme 2, by the following molecular design: Polycondensation of 2-methyl-1,3-phenylenebis(pinacol borate) (**5**) and 1,5-dibromo-2,4-bis(methylthio)benzene (**6**) leads to both a high molecular weight precursor polymer and the introduction of two alkylthio groups at the favorable positions of the precursor for the following ring formation reaction.

2-Methyl-1,3-phenylenebis(pinacol borate) (**5**) was prepared by the Grignard reaction of 2,6-dibromotoluene with pinacol borate.³¹ On the basis of the reaction conditions obtained through the model dimer

Table I. Conditions and results of polymerization of **5** and **6**^a

No.	Monomer concn	[Pd]/[M ₀]	Base aq. ^c /THF	Reaction time	Yield	M _n ^d	M _w /M _n	Degree of polymn
	M ^b		v/v	h	%	10 ³		Ph rings
1	0.1	1/20	1/2	72	96	2.9	1.6	22
2	0.1	1/50	1/2	72	91	4.6	1.6	36
3	0.1	1/100	1/2	72	95	2.6	1.4	20
4	0.1	1/50	1/5	24	95	3.4	1.5	26
5	0.1	1/50	1/5	48	98	4.4	1.8	34
6	0.1	1/50	1/5	72	97	7.5	1.4	58
7	0.2	1/50	1/5	72	73	2.2	1.2	17
8	0.2	1/50	1/5	72	95	2.9	1.2	22
9	0.2	1/50	1/5	72	98	3.6	1.6	28

^aReaction Temp. = 80 °C. Pd cat. = Pd(PPh₃)₄. ^bThe THF solution. ^c2 M aqueous Na₂CO₃ solution. ^dNumber- and weight-average molecular weight measured by GPC.

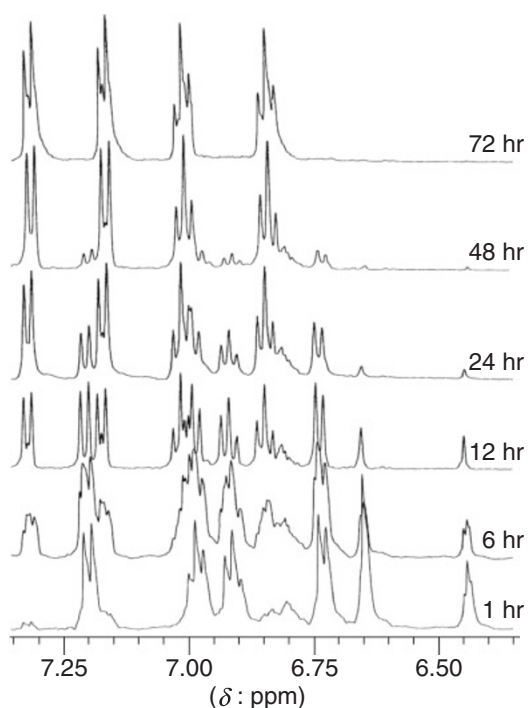
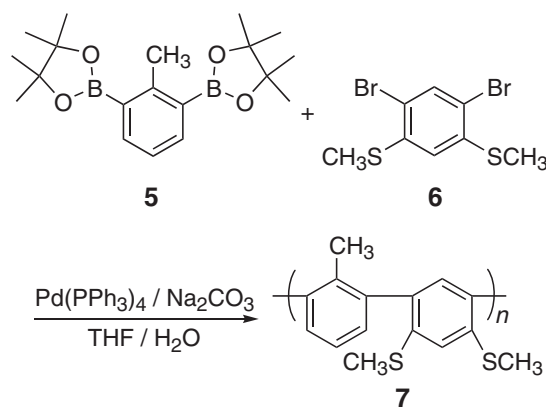


Figure 1. ¹H NMR spectra (monitoring the aromatic region) of the ring-closing reaction of **3** in CF₃SO₃D at 30 °C.

synthesis, **5** and 1,5-dibromo-4,6-bis(methylthio)benzene (**6**)³¹ were polymerized with tetrakis(triphenylphosphine)palladium(0) as a catalyst and sodium carbonate as a base in a THF and water mixture at 80 °C (Scheme 2). The polymerization conditions and results are shown in Table I.

The polymerization conditions were optimized for the monomer and catalyst concentration, the feed amount of the aqueous base solution and the reaction time. The obtained white-yellow polymer was soluble in the common solvents such as dichloromethane, toluene, and THF. The ¹³C NMR spectrum gave eight signals in aromatic region that are consistent with the precise 1,3-linking phenylene unit structure of **7** (see



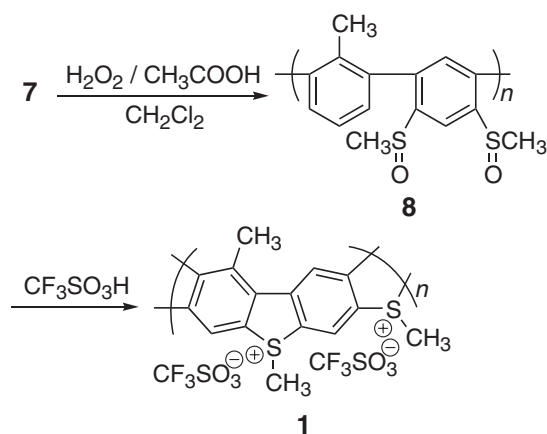
Scheme 2.

Experimental Part). The highest number averaged molecular weight was 7500 (degree of polymerization = 58 based on the phenylene ring, Table I, run 6) which satisfies a helical ladder structure with 8–9 pitches. (ca. 1 helical pitch = 7 phenylene units in **1**²¹).

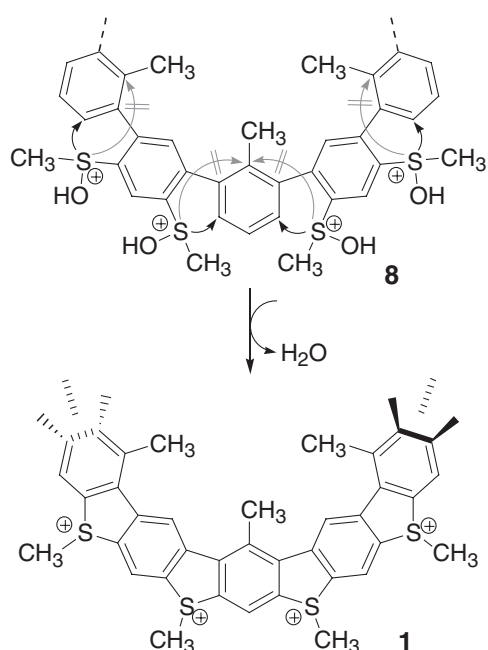
Ring Closing Reaction to Form the Helical Ladder Polymer Comprised of Fused-benzothiophene Ring

The pendant sulfide of **7** was oxidized with hydroxy peroxide and acetic acid at 30 °C using the optimized reaction temperature and time (see Experimental Part). The sulfoxide-substituted polymer, poly[4,6-bis(methylsulfinyl)-1,3-phenylene-*alt*-2-methyl-1,3-phenylene] (**8**), gave the ¹H NMR signal at 2.59 ppm as a symmetrical singlet which was shifted from that of **7** (2.45 ppm) due to the electron withdrawing nature of the sulfoxide. All signals ascribed to the methylsulfide and methyl-sulfone group disappeared, which indicated that all the pendant sulfide groups were converted to the sulfoxide. The IR spectrum showed the peak of the strong S=O stretch band at 1050 cm⁻¹.

The precursor polymer (**8**) was reacted with triflic acid for 1 week (Scheme 3). To avoid the intermole-



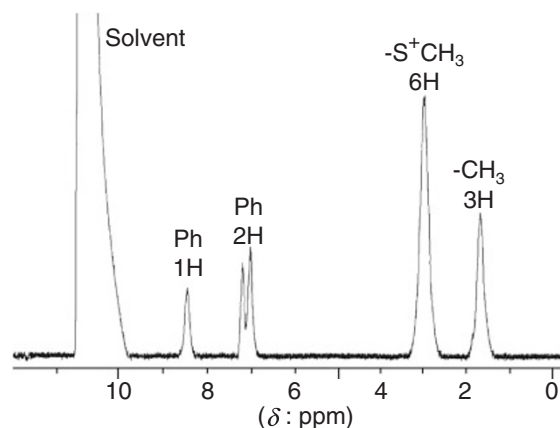
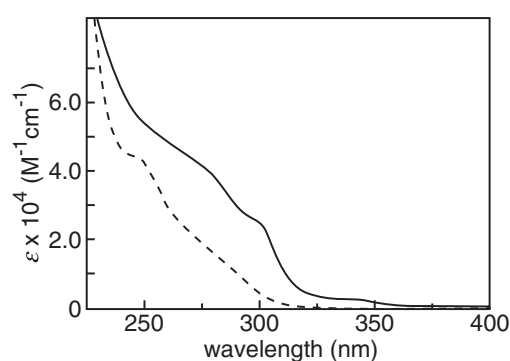
Scheme 3.



Scheme 4.

cular electrophilic reaction of sulfonium cation, the ring-closing reaction was carried out in highly diluted solution. The obtained polymer was soluble in DMF, DMSO, and a protonic acid, such as trifluoroacetic acid and triflic acid. The 2-methyl group of the phenylene ring in **8** resulted in the selective intramolecular and electrophilic attack of the pendant sulfoxides on the favored 4 and 6 positions of their neighboring phenylene ring (Scheme 4).

The ^1H NMR spectrum of the polymer in $\text{CF}_3\text{SO}_3\text{D}$ is shown in Figure 2.⁴⁰ The fused-ring structure of **1** was proved by the signal of the methyl group adjacent to the sulfur atoms which shifted to the lower magnetic field (δ 2.99 ppm) from that of the precursor sulfoxide (δ 2.59 ppm). The integral values of the protons derived from the phenyl ring (3H), the aryl methyl group (3H), and the methyl group on the sulfonio

Figure 2. ^1H NMR spectrum of **1** in $\text{CF}_3\text{SO}_3\text{D}$.Figure 3. UV-vis spectra of **1** (solid line) and **8** (dotted line) in 0.1 mM DMF solution.

bridges (4H) also supported the repeating unit structure of **1**.³¹ The results indicated that the ring-closing reaction of the alkylsulfinyl-substituted poly(1,3-phenylene) could form the helical structure without the helical conformation of precursor.³¹

UV-vis and MCD Spectra

The UV-vis absorption spectra of **8** and **1** are shown in Figure 3.⁴¹ The absorption maxima (λ_{max}) of **1** at 278, 307, and 342 nm and the shoulder at 375 nm shifted from those of **8** ($\lambda_{\text{max}} = 251$ nm, shoulder = 320 nm), suggesting an extension of the π -conjugation in the ladder structure of **1**. **1** was not circular dichroism (CD) active because its helical conformation was racemic.³¹ The racemic structure was favorable for the following magnetic circular dichroism (MCD) measurement.

MCD was used to analyze the electron transition in the fused-ring structure. The MCD was measured for the model dimers (**3** and **4**) in 0.1 mM acetonitrile solution and the polymers (**8** and **1**) in DMF solution under a magnetic field of 1.5 T. All the compounds showed symmetrical profiles in the MCD spectra during the measurements under positive and negative magnetic fields,⁴² and the following discussion was

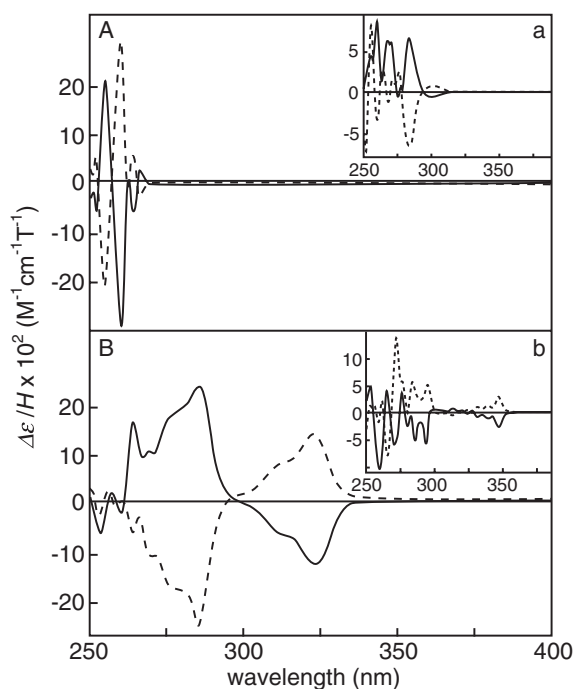


Figure 4. MCD spectra of **3** (A), **4** (B), *m*-terphenyl (a), and phenanthrene (b) under positive (solid line) and negative (dotted line) magnetic fields.

carried out using the spectra under the positive magnetic field.

The MCD of **3** showed a peak at 259 nm on the negative side which was ascribed to the π - π^* transition of the biphenyl moiety (Figure 4). **4** had peaks in not only the π - π^* transition range⁴¹ (261–298 nm, positive) but also at 310 and 325 nm in the negative side. We measured the MCD of *m*-terphenyl ([1,1';3',1'']terphenyl) and phenanthrene, which are unfused and fused cyclic compounds, respectively, as the control experiments (Figure 4, inset).^{38,43} The peaks of *m*-terphenyl at 270 and 280 nm on the positive side and those of phenanthrene at 285 and 294 nm on the negative side had been ascribed to a singlet electron (S_0 - S_1) transition of the fused-ring.³⁸ Other peaks were observed on the negative side at 328, 337 and 349 nm for phenanthrene, but not *m*-terphenyl; they had been attributed to a S_0 - S_2 transition based on the fused-ring.^{38,43} That is, the peaks observed for **4** at 310 and 325 nm could be assigned to the S_0 - S_2 transition which was based on the fused-ring of **4**.

Based on these results, the MCD of the polymers **8** and **1** was studied (Figure 5). The precursor polymer **8** showed positive peaks at 264, 270, and 275 nm in the π - π^* transition region. The negative peaks appeared in the range of 276–328 nm. On the other hand, the ring-closed polymer **1** exhibited broad peaks at 286, 317, and 343 nm (positive, negative, and positive, respectively), and the peaks corresponded to the absorption maxima of **1** in Figure 3. These results

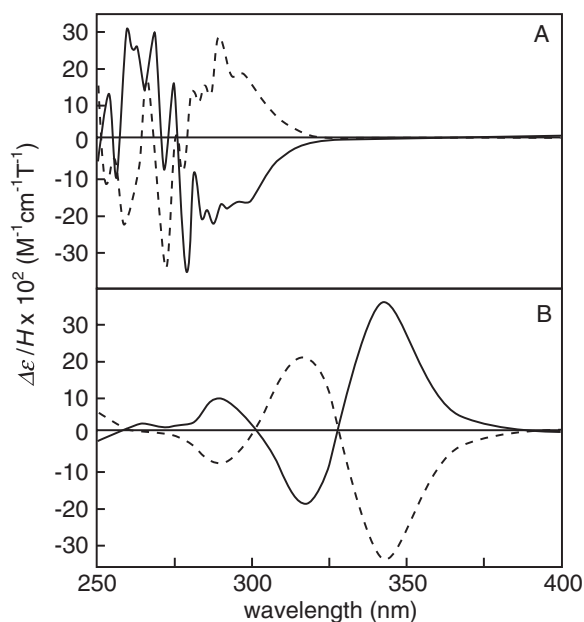


Figure 5. MCD spectra of **8** (A), **1** (B) under positive (solid line) and negative (dotted line) magnetic fields.

indicated that the MCD peaks of **1** at 286 and 317 nm were ascribed to the π - π^* transition and that at 343 nm is to the intrinsic electron transition of the fused-ring structure.⁴⁴

In summary, a novel helical ladder polymer comprised of fused-benzothiophenium rings, poly(thiaheterohelicene), was synthesized *via* the intramolecular ring-closing reaction of the methyl-sulfoxide-substituted poly(1,3-phenylene). The MCD spectroscopy indicated that the peaks based on the fused-ring appeared in the range of the intrinsic electron transition generated by the formation of the ladder structure. We have already simulated the electronic conduction of poly(thiaheterohelicene) from the view point of a molecular-based electronic device.⁴⁵ This simulation suggested not only an electron transmittance along the helical π -conjugation under a lower bias voltage (around the Fermi level of Au), but also a solenoid-like induced magnetism; such a poly(thiaheterohelicene) is a potential candidate for studying the one-dimensional wire of an organic molecular-based electromagnet.

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REFERENCES

1. T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Sugauma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, and H. Matsuda, *J. Am. Chem. Soc.*, **120**, 2047

- (1998).
2. J. Roncali, *Chem. Rev.*, **92**, 711 (1992).
 3. T. Yamamoto, M. Arai, H. Kokubo, and S. Sasaki, *Macromolecules*, **36**, 7986 (2003).
 4. K. Oyaizu, T. Iwasaki, Y. Tsukahara, and E. Tsuchida, *Macromolecules*, **37**, 1257 (2004).
 5. T. Nakano and Y. Okamoto, *Chem. Rev.*, **101**, 4013 (2001).
 6. C. Yamamoto, E. Yashima, and Y. Okamoto, *J. Am. Chem. Soc.*, **124**, 12583 (2002).
 7. E. Yashima, K. Maeda, and Y. Okamoto, *Nature* **399**, 449 (1999).
 8. E. Yashima, K. Maeda, and T. Nishimura, *Chem.—Eur. J.*, **10**, 42 (2004).
 9. K. Maeda, K. Morino, Y. Okamoto, T. Sato, and E. Yashima, *J. Am. Chem. Soc.*, **126**, 4329 (2004).
 10. M. M. Green, J.-W. Park, T. Sato, A. Teramoto, S. Lifson, R. L. B. Selinger, and J. V. Selinger, *Angew. Chem. Int. Ed.*, **38**, 3138 (1999).
 11. M. M. Green, K.-S. Cheon, S.-Y. Yang, J.-W. Park, S. Swansburg, and W. Liu, *Acc. Chem. Res.*, **34**, 672 (2001).
 12. M. Fujiki, J. R. Koe, M. Motonaga, H. Nakashima, K. Terao, and A. Teramoto, *J. Am. Chem. Soc.*, **123**, 6253 (2001).
 13. H. Nakashima, M. Fujiki, J. R. Koe, and M. Motonaga, *J. Am. Chem. Soc.*, **123**, 1963 (2001).
 14. K. Akagi, G. Piao, S. Kaneko, K. Sakamaki, H. Shirakawa, and M. Kyotani, *Science*, **282**, 1683 (1998).
 15. D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes, and J. S. Moore, *Chem. Rev.*, **101**, 3893 (2001).
 16. T. Verbiest, S. V. Elshocht, M. Kaouranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz, and A. Persoons, *Science*, **282**, 913 (1998).
 17. J. M. Fox, N. R. Goldberg, and T. J. Katz, *J. Org. Chem.*, **63**, 7456 (1998).
 18. S. Sioncke, S. V. Elshocht, T. Verbiest, M. Kauranen, K. E. S. Phillips, T. J. Katz, and A. Persoons, *Synth. Met.*, **124**, 191 (2001).
 19. T. Verbiest, S. Sioncke, A. Persoons, L. Vyklický, and T. J. Katz, *Angew. Chem. Int. Ed.*, **41**, 3882 (2002).
 20. K. Paruch, T. J. Katz, C. Incarvito, K.-C. Lam, B. Rhatigan, and A. L. Rheingold, *J. Org. Chem.*, **65**, 7602 (2000).
 21. K. Tanaka, H. Suzuki, and H. Osuga, *J. Org. Chem.*, **62**, 4465 (1997).
 22. T. Caronna, T. Sinisi, M. Catellani, L. Malpezzi, S. V. Meille, and A. Mele, *Chem. Commun.*, **13**, 1139 (2000).
 23. T. Caronna, M. Catellani, S. Luzzati, L. Malpezzi, S. V. Meille, C. Ritchter, and R. Sinisi, *Chem. Mater.*, **13**, 3906 (2001).
 24. A. Rajca, H. Wang, M. Pink, and S. Rajca, *Angew. Chem. Int. Ed.*, **39**, 4481 (2002).
 25. A. Rajca, M. Miyasaka, M. Pink, H. Wang, and S. Rajca, *J. Am. Chem. Soc.*, **126**, 15211 (2004).
 26. M. Miyasaka, A. Rajca, M. Pink, and S. Rajca, *Chem.—Eur. J.*, **10**, 6531 (2004).
 27. H. Wynberg, *Acc. Chem. Res.*, **4**, 65 (1971).
 28. K. Yamada, H. Nakagawa, and H. Kawazura, *Bull. Chem. Soc. Jpn.*, **59**, 2429 (1971).
 29. F. B. Malloy and C. W. Malloy, “Organic Reactions,” Vol. 30, Wiley Interscience, New York, N.Y., 1984, p 1.
 30. T. Iwasaki, Y. Tsukahara, and H. Nishide, *Chem. Lett.*, **34**, 164 (2005).
 31. T. Iwasaki, Y. Kohinata, and H. Nishide, *Org. Lett.*, **7**, 755 (2005).
 32. K. Yamamoto, E. Shouji, H. Nishide, and E. Tsuchida, *J. Am. Chem. Soc.*, **115**, 5819 (1993).
 33. A. Haryono, K. Miyatake, J. Natori, and E. Tsuchida, *Macromolecules*, **32**, 3146 (1999).
 34. K. Oyaizu, T. Mikami, F. Mitsuhashi, and E. Tsuchida, *Macromolecules*, **35**, 67 (2002).
 35. E. Tsuchida and K. Oyaizu, *Bull. Chem. Soc. Jpn.*, **76**, 15 (2003).
 36. A. D. Buckingham and P. J. Stephens, *Annu. Rev. Phys. Chem.*, **17**, 399 (1966).
 37. P. N. Schatz and A. J. McCafery, *Q. Rev. Chem. Soc.*, **23**, 552 (1969).
 38. M. Vasak, M. Whipple, and J. Michl, *J. Am. Chem. Soc.*, **100**, 6867 (1978).
 39. The chemical shift of **4** in CF₃SO₃D was different from the one in CD₃CN due to the deuteration on the phenylene rings in CF₃SO₃D (protonation in CF₃SO₃H). The details had been reported in ref 34.
 40. CF₃SO₃D was selected as the solvent for the ¹H NMR study since the signals of the methyl groups adjacent to the sulfur atoms and a solvent, such as DMF-*d*₇ (2.74, 2.91, and 8.01 ppm) and DMSO-*d*₆ (2.50 ppm), overlapped.
 41. The absorption spectra of **3** and **4** had been reported in ref 33.
 42. Slight unsymmetrical profiles measured at the positive and negative magnetic fields in Figures 4 and 5 was caused by the apparatus setup. When the direction of the magnetic field (from N to S pole) is parallel to one of the circular polarized irradiation, the magnetic field is called “positive”.
 43. T. Dahlgren, J. Glans, S. Gronowitz, A. Davidsson, B. Norden, P. B. Pedersen, and E. W. Thulstrup, *Chem. Phys.*, **40**, 397 (1979).
 44. The actual method to analyze the MCD spectrum for polymers is very complicated due to the molecular weight distribution and the variety of conformations, and has not yet been established.
 45. K. Tagami, M. Tsukada, Y. Wada, T. Iwasaki, and H. Nishide, *J. Chem. Phys.*, **119**, 7491 (2003).