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Electron-Induced Switching of the Supramolecular Chirality of Optically Active Polythiophene Aggregates

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Abstract: A chiral regioregular polythiophene (PT), poly[3-{4-((*R*)-4-ethyl-2-oxazolin-2-yl)phenyl}thiophene] (poly-**1**), forms chiral aggregates which exhibit a unique induced circular dichroism (ICD) in the $\pi-\pi^*$ transition region derived from the supramolecular chirality in the presence of various poor solvents or metal salts in chloroform. We report here that the chirality of such supramolecular aggregates can be switched ("on" and "off") through electron transfer. We have found that upon the addition of copper(II) trifluoromethanesulfonate [$Cu(OTf)_2$] to the chiral aggregates of poly-**1** in a chloroform−acetonitrile mixture, the ICD disappears because of the oxidative doping of the poly-**1** main chain, while a further addition of amines such as triethylenetetramine (TETA) induces undoping of the poly-**1** which results in the reappearance of the ICDs. Therefore, the supramolecular chirality of the poly-**1** assemblies was reversibly controlled by the addition or removal of an electron from the poly-**1** main chain. This may be the first example of a reversible supramolecular chirality switch on chiral PT aggregates. We investigated the mechanism of the chirality switch through the doping and undoping process on the polymer main chain by means of absorption and CD spectroscopies, ESR, cyclic voltammetry, X-ray diffraction, and AFM measurements.

Introduction

Polythiophenes (PTs) are among the most interesting and useful π-conjugated polymers.[1] Hence, a number of PTs have been prepared in view of their potential applications to electrically conductive materials such as electrolytic condensers, semiconductor devices, field effect transistors (FETs), polymeric light-emitting diodes (LEDs), and chemical sensors.[2] In addition, chiral PTs[3−5] have attracted much interest in recent years, because they may be used as circular polarized electroluminescence (CPEL) devices[5a,6] and enantioselective sensors,[7] electrodes,[3a,8] catalysts,[9] and adsorbents.[10] Chiral PTs are well

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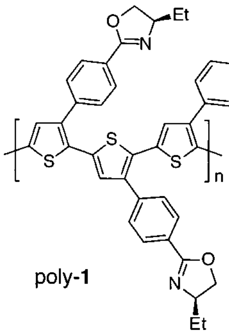
Chart 1


poly-**1**

known to exhibit optical activity in the $\pi-\pi^*$ transition derived from the main chain chirality when they are aggregated to form a supramolecular π-stacked, self-assembly with intermolecular interactions in poor solvents, at low temperature, or in film, whereas they show no optical activity in the region in a good solvent or at high temperatures.[4] This unusual chiroptical behavior is sharply contrasted with other optically active nonconjugated polymers.[11]

We previously found that a chiral, regioregular (head-to-tail) PT, poly[3-{4-((*R*)-4-ethyl-2-oxazolin-2-yl)phenyl}thiophene] (poly-**1** in Chart 1), bearing an optically active oxazoline residue self-assembled into supramolecular chiral aggregates in a poor solvent or in the presence of metal salts capable of coordinating to the oxazoline residues which showed a characteristic induced circular dichroism (ICD) in the $\pi-\pi^*$ transition region.[12] Here we report that the chirality of such supramolecular aggregates of poly-**1** can be reversibly switched ("on" and "off") through a doping−undoping process using a suitable metal salt, an amine, and a poor solvent. Switching of molecular chirality by electrical means[13] or by light irradiation[14] has been extensively studied. However, to the best of our knowledge, electron-induced chirality switching of supramolecular aggregates has not yet been achieved. The development of a molecular chirality switching process may lead to possible applications in molecular devices and memory and data storage systems.[13−15]

Results and Discussion

CD and Absorption Titrations of Poly-1 with Cu(OTf)$_2$ and Amines in a Chloroform−Acetonitrile Mixture (1/1, v/v). Regioregular (head-to-tail) poly-**1** prepared by McCullough's method was used throughout the course of this study. The molecular weight (M_n) was 5.3×10^3 ($M_w/M_n = 1.25$, DP = 21).[12] Upon the addition of a poor solvent, acetonitrile, into a chloroform solution of poly-**1** (1/1, v/v), the polymer self-assembled to form a chiral π-stacked, supramolecular aggregate, thus exhibiting an intense, split-type ICD in the $\pi-\pi^*$ transition region derived from the main chain chirality [Figure 1A (solid line)] (the molar ellipticity ($[\theta]_{1st}$) and a chiral anisotropy factor, *g*-value ($\Delta\epsilon/\epsilon$), of the first Cotton of poly-**1** in a chloroform−acetonitrile mixture (50 vol %) = -7.85×10^4 (deg cm^2 dmol^{-1}) and 3.7×10^{-3}, respectively).[12b,16] The solution color spontaneously changed from yellow-orange to purple, accompanied by a large red shift in the absorption up to ca. 200 nm.[12] Interestingly, the addition of a small amount of Cu(OTf)$_2$ ([Cu(II)]/[oxazoline residues of poly-**1**] = 0.1) to the solution caused a dramatic decrease in the ICD intensity by a factor of ca. 1/20. A further addition of Cu(OTf)$_2$ (0.2−0.5 equiv) brought about the complete disappearance of the ICD (Figure 1A), and the solution color immediately changed from purple to gray. These significant changes in the ICDs were accompanied by a gradual red shift to near-infrared (NIR) region beyond 1100 nm in the absorption spectra; also, the absorptivity in the NIR region increased with an increase in the amounts of Cu(OTf)$_2$ (Figure 1B).

Similar changes in the absorption spectra were observed for regioregular poly(3-hexylthiophene) (PHT) with Cu(OTf)$_2$ in chloroform or in a chloroform−acetonitrile mixture (1/1, v/v) (see Supporting Information). These changes in the CD and absorption spectra indicated that the polymer was oxidatively doped by Cu(OTf)$_2$ to form a planar, more conjugated quinoidal structure, which might π-stack considerably.[17,18] The formation of cation radicals on the polymer main chain was evidenced by the appearance of a characteristic ESR signal. Figure 2 shows ESR spectra of the poly-**1** solution in the presence (b, c, e, f)

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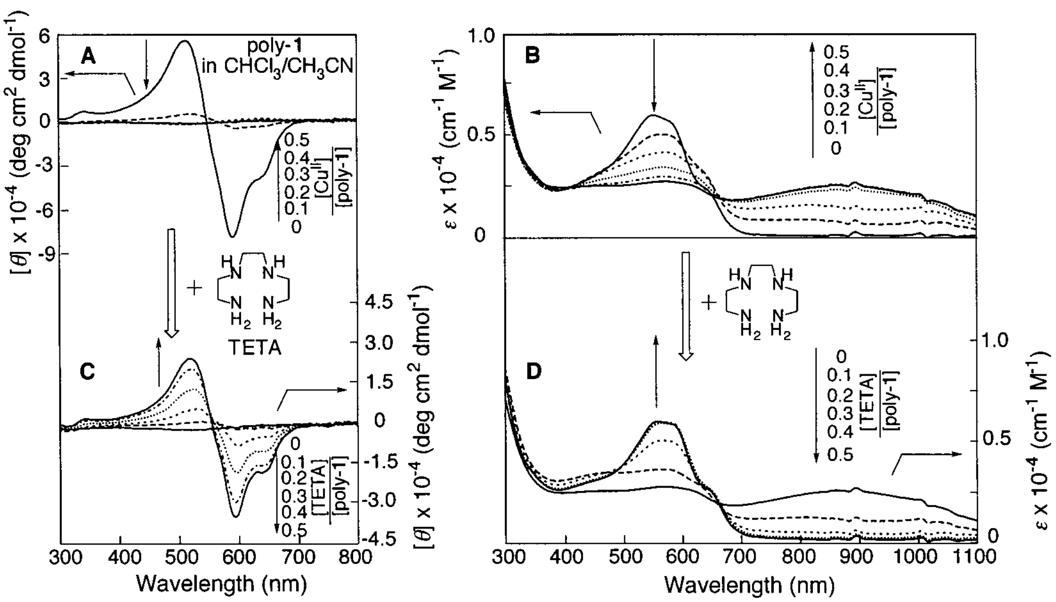

Figure 1. CD and absorption spectral changes of poly-**1** upon the addition of Cu(OTf)$_2$ to the original polymer solution in a chloroform−acetonitrile mixture (1/1, v/v) (A, B) and a further addition of TETA to the polymer solution with Cu(OTf)$_2$ (C, D) in a 0.50 cm quartz cell at ambient temperature (ca. 22−24 °C). Poly-**1** concentration is 0.05 mg/mL (0.2 mM monomer units).

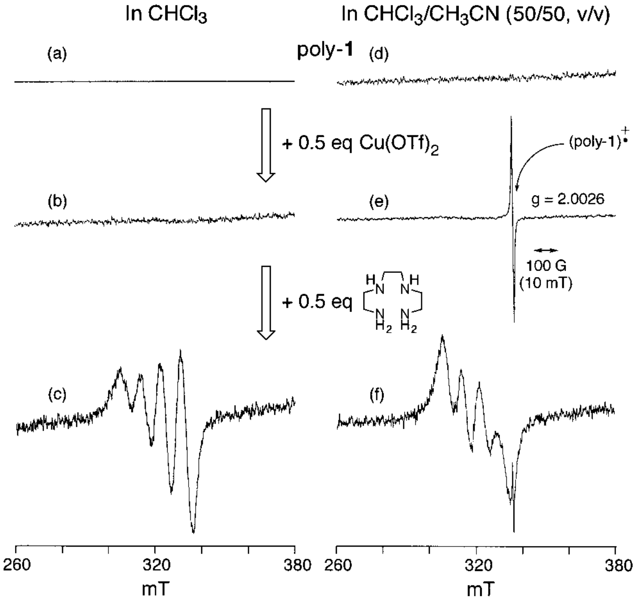

Figure 2. ESR spectra of poly-**1** in chloroform (a, b, c) and chloroform−acetonitrile (1/1, v/v) (d, e, f) at ambient temperature (ca. 22−24 °C) with a poly-**1** concentration of 0.25 mg/mL (1.0 mM monomer units). All spectra were measured before (a, d) and after the addition of Cu(OTf)$_2$ (b, e) to the original poly-**1** solution (a, d) and further addition of TETA (c, f) to (b, e), respectively; the molar ratio of Cu(OTf)$_2$ and TETA to poly-**1** is 0.5.

and absence (a, d) of Cu(OTf)$_2$ ([Cu(II)]/[poly-**1**] = 0.5) in a chloroform−acetonitrile mixture (1/1, v/v). Although poly-**1** showed no ESR signal in chloroform even in the presence of Cu(II), the polymer exhibited a Gaussian-type ESR signal in the solution centered at $g = 2.0026$ with the peak-to-peak width (ΔH_{pp}) = 4.8 G because of the cation radicals (bipolarons) generated on the doped polymer (Figure 2e). The spin concentration (N_s) of the doped poly-**1** was estimated using 2,2-diphenyl-1-picrylhydrazyl (DPPH) as a standard and was 3.3×10^{19} spins per 1 g of poly-**1** which corresponds to ca. 1.4 spins per 100 monomer units of poly-**1**. The observed *g*-value and the spin concentration of the doped poly-**1** were comparable to those of other doped PTs reported in the literature (for ESR data of the doped poly-**1** and PHT together with the reported data for PTs, see Supporting Information),[17a,b,18] which indicates that π-radicals in the doped poly-**1** delocalize on the polymer main chain, mainly on the carbon skeleton.[19]

Further treatment of the doped poly-**1** with amines such as triethylenetetramine (TETA) resulted in reduction (undoping) as evidenced by the reappearance of the ICD spectra as well as regeneration of the purple color; the absorptivity in the NIR region gradually decreased, and the absorption spectra recovered almost to the original ones after the addition of an equivalent amount of TETA to Cu(OTf)$_2$ (Figure 1C and D). Other aliphatic amines (triethylamine and diethylamine) and an aromatic amine [2,2′-bipyridyl (bpy)] can be used to assist in this redox switch process, whereas other metal salts such as Fe(II), Fe(III), and Cu(I) in chloroform-poor solvents (acetone and methanol) systems hardly doped the poly-**1** oxidatively, indicating that the appropriate combination of metal salts and poor solvents such as the Cu(II) and acetonitrile system may be required for the doping of the poly-**1** main chain. Undoping of the doped poly-**1** using TETA was confirmed by ESR spectroscopy (Figure 2). When TETA was added to the doped polymer, the radical concentration of the polymer decreased with an increase in the amount of TETA, and the well-resolved hyperfine ESR signals derived from the Cu(II)−TETA complex appeared (Figure 2f). A regioregular PHT having no oxazoline residues showed similar changes in ESR signals in the presence of Cu(OTf)$_2$ followed by TETA regardless of the solvents used (see Supporting Information). These results suggest that the oxazoline residues of poly-**1** can trap Cu(II) ions by coordination in chloroform to prevent the doping, but in the presence of acetonitrile the poly-**1** self-assembled to form a π-stacked, structured aggregate which frees a portion of the Cu(II) ions so that they can act as an oxidizing agent to dope the poly-**1** main chain.

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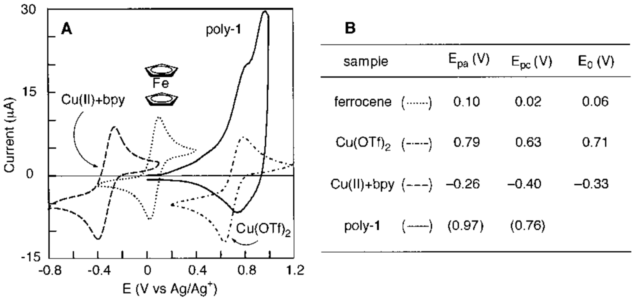

sample	E_{pa} (V)	E_{pc} (V)	E_0 (V)
ferrocene (……)	0.10	0.02	0.06
Cu(OTf)$_2$ (----)	0.79	0.63	0.71
Cu(II)+bpy (– – –)	−0.26	−0.40	−0.33
poly-**1** (——)	(0.97)	(0.76)	

Figure 3. Cyclic voltammograms of poly-**1** film, Cu(OTf)$_2$ (2 mM), Cu(OTf)$_2$ (2 mM) with 2,2′-bipyridyl (bpy) (40 mM), and ferrocene (2 mM) in 0.1 M Bu$_4$NPF$_6$/acetonitrile solution (A). Oxidation (E_{pa}) and reduction (E_{pc}) peaks and standard redox potential (E_0) are shown in (B); $E_0 = (E_{pa} + E_{pc})/2$. The numbers in parentheses for poly-**1** represent peak potentials in an irreversible cyclic voltammogram.

The above-mentioned doping and undoping process must be governed by the reduction potential of the oxidants in relation to the oxidation potential of the polymer. Cyclic voltammetric (CV) measurements[18,20] of poly-**1**, Cu(OTf)$_2$, and the Cu(II)-bpy complex were then performed in acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$) (0.1 M) as the supporting electrolyte (Figure 3), because the Cu(II)−TETA complex decomposed under the same conditions. The CV profiles of Cu(OTf)$_2$ and the Cu(II)−bpy complex were reversible, similar to ferrocene used as a standard, and their redox potentials (E_0) were estimated to be +0.71 [Cu(I) = Cu(II) + e$^-$] and −0.33 V ([Cu(I)−bpy] = [Cu(II)−bpy] + e$^-$) versus the Ag/Ag$^+$ reference electrode, respectively (see Figure 3B). On the contrary, the precise redox potential of poly-**1** could not be determined because of the irreversible CV profile of the polymer; the onset of oxidation ([poly-**1**] → [poly-**1**]$^+$ + e$^-$) under the same conditions seemed to occur at ca. +0.2 V (Figure 3A). The overlap of the two voltammograms between poly-**1** and Cu(OTf)$_2$ indicated that an electron can transfer from the polymer to Cu(II). However, the redox potential of the Cu(II) shifted considerably to the negative value (−0.33 V) upon coordinating to amines such as bpy, which means that an electron can transfer from Cu(I) to the doped polymer ([poly-**1**]$^+$) to generate a neutral poly-**1** once bpy coordinates to the copper ions. Accordingly, the Cu(II)−bpy complex cannot dope the poly-**1** in the chloroform−acetonitrile mixture. These CV results also supported the redox-switch process observed in the CD, UV−visible, and ESR spectra as shown above.

Structural Changes of the Poly-1 Aggregates before and after Doping. X-ray diffraction (XRD) analysis was carried out to investigate the changes in structures and packing modes for the poly-**1** aggregates before and after doping with Cu(OTf)$_2$ (Figure 4).[5d,18,21] The poly-**1** formed supramolecular chiral self-assemblies in the presence of a poor solvent, and the aggregates showed typical reflections which correspond to a well-ordered, π−π stacked lamellar structure with an interlayer spacing of 22.9 Å (*1,0,0*) and a stacking distance of the two polymer chains of 3.7 Å together with parallel spacing of the main chains of 7.4 Å (*3,0,0*).[22] Here we assume that supramolecular chirality may be induced on the laminated poly-**1**; each poly-**1** layer may be loosely twisted clockwise or counterclockwise so that the poly-**1** aggregates exhibit optical activity (Figure 5B). After being doped with Cu(OTf)$_2$, the first-order (*1,0,0*) and third-order (*3,0,0*) parallel spacings of the main chain reflection increased from 22.9 to 23.9 Å and from 7.4 to 7.7 Å, respectively. Such a small, but significant, increase in the lattice spacing may be regarded as being because of incorporation of the counteranions (TfO$^-$ = CF$_3$SO$_3^-$) into the interlayers of the poly-**1** aggregates. A similar increase in the lattice spacing upon chemically doping has been reported for other PTs.[18]

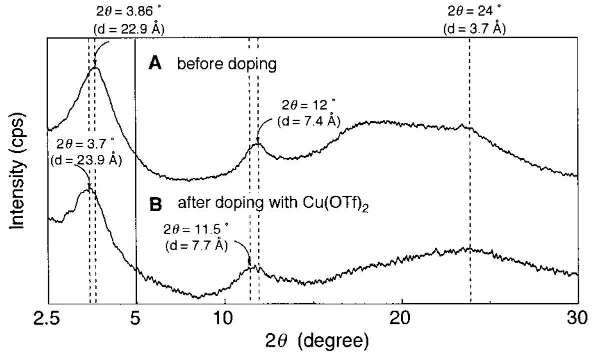

Figure 4. X-ray diffractograms for the powder poly-**1** samples precipitated from a chloroform−acetonitrile mixture (1/1, v/v) before (A) and after (B) doping with Cu(OTf)$_2$.

It has been reported that radical cations of oligothiophenes have a tendency to form an almost complete face-to-face π-stacked complex either in solution or in the solid state and that these intermolecular stacks lead to their conductivity.[23] In comparison, neutral oligothiophenes could not form such extensive intermolecular contacts. The same structural features may be the case for PTs including poly-**1**, so that the doped poly-**1** chains could stack more efficiently than the neutral poly-**1** chains did. These structural changes might be closely related to the disappearance of the ICD of the poly-**1** aggregates after doping; the supramolecular aggregates probably changed from the one-directionally twisted (clockwise or counterclockwise) packing to the nontwisted, parallel interchain π-stacks (Figure 5B and D).

Chirality Switching. The reversible ICD changes ("on" and "off") of the supramolecular chirality of the poly-**1** aggregates were clearly observed by alternate addition of Cu(OTf)$_2$ and TETA as shown in Figure 6. The reversible color change of

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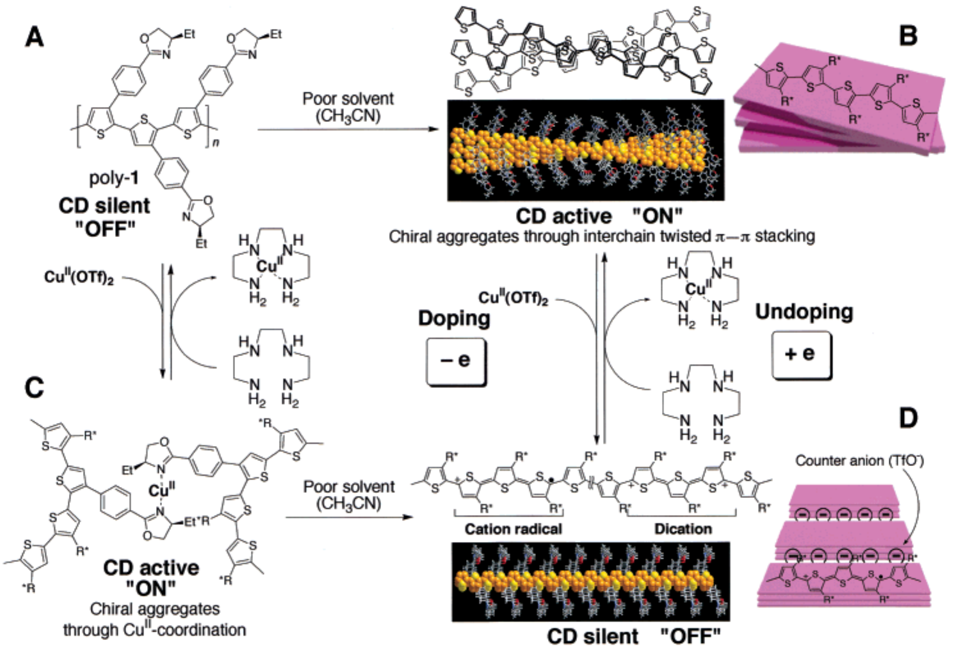

Figure 5. Schematic illustrations of chiral supramolecular aggregate formation of poly-**1** (A) in the presence of acetonitrile (B) and Cu(II) (C). A possible structure of the doped poly-**1** aggregates (D) and two different switching processes of supramolecular chirality of poly-**1** aggregates are also shown.

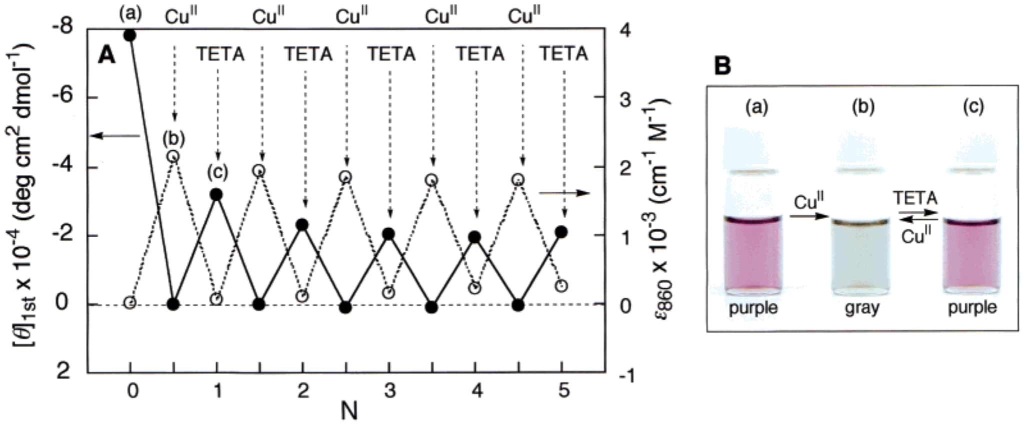

Figure 6. Plots of molar ellipticity of the first Cotton effect ($[\theta]_{1st}$) and molar absorptivity of poly-**1** at 860 nm in a chloroform−acetonitrile mixture (1/1, v/v) (a) upon the addition of Cu(OTf)$_2$ (b) and TETA (c) versus the number of cycles *N* (A). All spectra were measured in a 0.50 cm quartz cell at ambient temperature (ca. 22−24 °C) with a poly-**1** concentration of 0.05 mg/mL (0.2 mM monomer units). The molar ratio of Cu(OTf)$_2$ and TETA to poly-**1** is 0.5. The color changes in the poly-**1** solutions are also shown in (B).

the poly-**1** solution from purple to slightly gray was accompanied by the changes in the ICDs and the absorptivities. These redox-induced changes of ICD and absorption spectra probably resulted from the change in the packing mode of the poly-**1** stacks from the one-directionally twisted to nontwisted parallel packing (Figure 5B and D).

Even in a good solvent, chloroform, another reversible switching of supramolecular chirality of poly-**1** aggregates can be accomplished by alternate addition of Cu(OTf)$_2$ and TETA as expected (Figure 7). Poly-**1** formed chiral aggregates which exhibited a split-type ICD in the π−π* transition region in the presence of Cu(OTf)$_2$ in chloroform (Figure 7b),[12a] while a further addition of TETA induced the disappearance of the ICD (Figure 7c). The supramolecular chirality of poly-**1** aggregates was reversibly controlled by alternate addition of Cu(OTf)$_2$ and TETA (Figure 7A).

Figure 5 summarizes the different behavior of these two chiral switches on the basis of the changes in supramolecular chiral aggregates of poly-**1**. An optically active poly-**1** (Figure 5A), which showed no optical activity in chloroform in the main chain region, was transformed into different supramolecular chiral aggregates and showed unique ICDs in the π−π* transition region in the presence of poor solvents (Figure 5B) or metal salts (Figure 5C). The addition of Cu(OTf)$_2$ to the solvent-induced chiral poly-**1** aggregates brought about the disappearance of the ICDs, because the main chain was doped, and the thiophene rings were isomerized to form a planar quinoidal structure which resulted in achiral parallel interchain π−π stacking of the PT main chain (Figure 5D).[24] A further addition of amines such as TETA facilitated undoping of the poly-**1** because of electron transfer from the Cu−amine complex to the polymer; therefore, the chirality of the poly-**1** aggregates could be reversibly controlled through the doping−

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(24) The addition of acetonitrile to the Cu(II)-induced chiral poly-**1** aggregates (C) caused doping of the poly-**1** main chain and exhibited dramatic changes in CD and absorption spectra (see Supporting Information), which were different from those shown in Figure 1. However, the subsequent alternative addition of TETA and Cu(OTf)$_2$ resulted in exactly the same reversible chirality switching events.

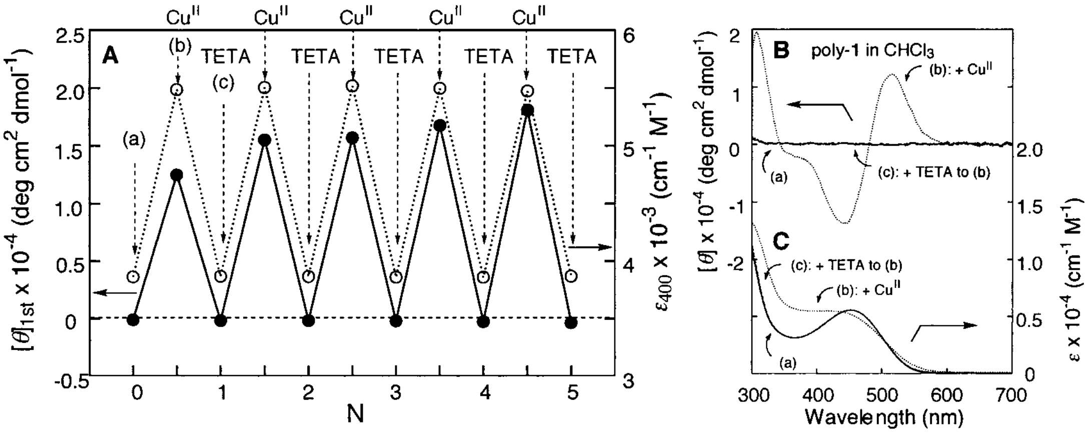

Figure 7. Plots of molar ellipticity of the first Cotton effect and molar absorptivity at 400 nm of poly-**1** in chloroform upon the addition of Cu(OTf)$_2$ (b) and TETA (c) versus the number of cycles *N* (A). All spectra were measured in a 0.50 cm quartz cell at ambient temperature (ca. 22−24 °C) with a poly-**1** concentration of 0.05 mg/mL (0.2 mM monomer units). The molar ratio of Cu(OTf)$_2$ and TETA to poly-**1** is 0.5. The CD (B) and absorption (C) spectral changes of the poly-**1** solution are also shown (right); the full lines (a), dotted lines (b), and broken lines (c) represent the spectra of the poly-**1** solution before (a) and after the addition of Cu(OTf)$_2$ (b) and further addition of TETA (c) to (b), respectively.

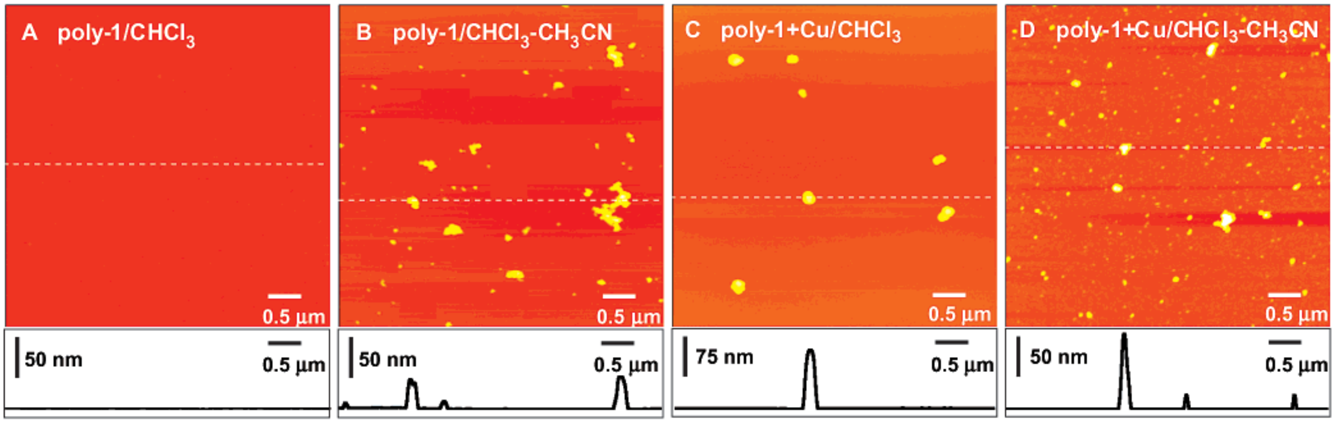

Figure 8. AFM images of poly-**1** on mica substrates prepared from chloroform (A, C) and a chloroform−acetonitrile mixture (1/1, v/v) (B, D) in the absence (A, B) and presence (C, D) of Cu(OTf)$_2$. The molar ratio of Cu(OTf)$_2$ to the monomer units of poly-**1** is 0.5.

undoping process upon the alternative addition of Cu(OTf)$_2$ and TETA.

AFM measurements were carried out to investigate the change in morphology (size and form) of the chiral poly-**1** aggregates under various conditions (Figure 8) in the tapping mode.[25] Although poly-**1** could not self-assemble in chloroform (Figure 8A), poly-**1** formed a number of small round particles with diameters of less than 0.1 μm together with a few large particles (0.2−0.3 μm) in the presence of acetonitrile (Figure 8B). Upon the addition of Cu(OTf)$_2$ to the polymer solution in a chloroform−acetonitrile mixture, the change of morphology was not very significant (Figure 8D). Using AFM, it is difficult to see a difference in the conformation or packing mode of the chiral supramolecular aggregates of poly-**1** before and after doping. On the other hand, the AFM image of the poly-**1** complex with Cu(OTf)$_2$ in chloroform showed regular round particles (0.2−0.3 μm) (Figure 8C), and a further addition of TETA to the complex brought about generation of rather small particles. This result indicated that the conformation and size of the complex can be controlled using appropriate metal salts and ligands.

Conclusions

We have found that the supramolecular chirality of the poly-**1** aggregates was reversibly controlled by the addition or removal of an electron from the poly-**1** main chain. The chirality switching through such a doping and undoping process of the main chain may be applicable to other chiral PTs prepared so far.[4] Such a redox-induced supramolecular chirality switch will provide novel molecular devices and can be applicable to data storage systems and enantioselective electrodes.[15] We believe that the redox-based chirality switch can also be possible electronically in the solid state. Further investigation along this line is now in progress.

Experimental Section

Measurements. CD and absorption spectra were measured using a Jasco J-725 spectropolarimeter and a Jasco V-570 spectrophotometer, respectively. LD spectra were measured on a Jasco J-725 spectropolarimeter with an LD attachment. The concentration of poly-**1** was calculated on the basis of monomer units. ESR spectra were recorded on an X-band (9.4 GHz) on a JES-TE2000 spectrometer (JEOL Ltd.) with a 100 kHz modulation frequency using the transverse-magnetic (TM) mode cavity at room temperature. DPPH was used as the reference for the *g*-value and spin concentration calibration. X-ray diffraction measurements were carried out with a RIGAKU RINT-1200, and the Cu Kα radiation was taken for the incident X-ray beam. Laser Raman

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spectra were measured on a Jasco RMS-200 spectrophotometer with an excitation line of 532 nm. Cyclic voltammograms were measured in acetonitrile with Bu_4NPF_6 (0.1 M) at a sweep rate of 100 mV/s using a CV-50W (BAS Inc.) with a conventional three-electrode cell employing a Pt working electrode (0.07 cm^2), a Pt counter electrode, and a Ag/Ag^+ reference electrode. The thin layer of poly-**1** was deposited on the Pt working electrode by casting the poly-**1** solution in chloroform containing 50 vol % acetonitrile. AFM measurements were performed on a Nanoscope IIIa microscope (Digital Instruments) using standard silicon tips in the tapping mode. Height and phase images were simultaneously measured at the resonance frequency of the tips with 125 μm long cantilevers (255−265 kHz).

Materials. Poly-**1** and PHT were prepared according to the previously reported method.[12,26] The molecular weights (M_n) of poly-**1** and PHT were determined to be 5.3×10^3 and 8.2×10^3, respectively, by size exclusion chromatography (SEC) (polystyrene standards) using chloroform as the eluent. Chloroform, acetonitrile, and acetone were dried over CaH_2 and distilled under nitrogen. Methanol was dried over turning magnesium and iodine, and distilled under nitrogen. $Cu(OTf)_2$ and Bu_4NPF_6 were purchased from Tokyo Kasei (Tokyo, Japan). TETA and $Fe(ClO_4)_2$ were obtained from Nacalai Tesque (Kyoto, Japan). DPPH, bpy, and $Fe(ClO_4)_3$ were from Wako (Osaka, Japan), Kanto Chemical (Tokyo, Japan), and Kishida Chemical (Osaka, Japan), respectively. Copper(I) trifluoromethanesulfonate toluene complex ($(CuOTf)_2 \cdot C_7H_8$) was purchased from Aldrich. These metal salts were used as received.

CD and Absorption Titrations of Poly-1 with $Cu(OTf)_2$ and TETA in Chloroform with Acetonitrile (50 vol %). A typical experimental procedure is described below. A stock solution of poly-**1** (5 mg/100 mL, 0.2 mM monomer units) in a chloroform−acetonitrile mixture (1/1, v/v) was prepared under nitrogen. A 2 mL portion of the poly-**1** solution was transferred to a 0.5 cm quartz cell using a pipet under nitrogen, and the initial CD and absorption spectra were measured at ambient temperature (ca. 22−24 °C). Stock solutions of $Cu(OTf)_2$ (14.5 mg/5 mL, 8 mM) and TETA (11.7 mg/10 mL, 8 mM) in acetonitrile were also prepared in a drybox (NX1-M00320, Vacuum Atmospheres, Hawthorne, USA) under an argon atmosphere. To the polymer solution were added increasing volumes of the $Cu(OTf)_2$ solution (0−25 μL, 0−0.5 equiv), and the CD and absorption spectra were taken for each addition of the $Cu(OTf)_2$ (see Figure 1A and B). To the polymer solution in the presence of 0.5 equiv of $Cu(OTf)_2$ were then added increasing volumes of the TETA solution (0−25 μL, 0−0.5 equiv), and the CD and absorption spectra were taken for each addition of TETA (see Figure 1C and D).

X-ray Diffraction of Poly-1 before and after Doping. A stock solution of poly-**1** (50 mg/10 mL) in chloroform was prepared and filtered through a 0.50 μm membrane filter. After the stock solution was transferred to a 30 mL flask equipped with a stopcock, 10 mL of acetonitrile was added to the flask, and the solution was cooled slowly in a refrigerator to obtain the polymer powders. The precipitated polymer (10 mg) was collected and spread on a sample holder with a square hole [20 (l) × 16 (w) × 0.2 (h) mm] in the center, then smoothed flat. After measuring the XRD of the poly-**1** aggregates before doping, the sample holder was immersed in an acetonitrile solution of $Cu(OTf)_2$ (5 mM) for 10 min in a drybox under an argon atmosphere, and the solvent was removed by decantation. The doped polymer, thus obtained, was dried in a drybox under an argon atmosphere and covered with a well-greased microscope slide to prevent oxidation in air to measure XRD of the doped poly-**1** aggregates. The doping was confirmed by measuring a Raman spectrum of a doped poly-**1** film as a control experiment; a vibrational peak at 1439 cm^{-1} assigned to the symmetric $C_\alpha{-}C_\beta$ stretching deformation in the thiophene ring almost completely disappeared after immersing the film into the $Cu(OTf)_2$ solution for ca. 15 min.[20]

Chirality Switching of Supramolecular Aggregates of Poly-1 with $Cu(OTf)_2$ and TETA in a Chloroform−Acetonitrile Mixture (1/1, v/v). A stock solution of poly-**1** (5 mg/100 mL, 0.2 mM monomer units) in a chloroform−acetonitrile mixture (1/1, v/v) was prepared, and a 2 mL portion of the poly-**1** solution was transferred to a 0.5 cm quartz cell equipped with a screw cap using a 2 mL pipet. The initial CD and UV−visible−NIR spectra were recorded at ambient temperature (ca. 22−24 °C). Stock solutions of $Cu(OTf)_2$ (29 mg/2 mL, 40 mM) and TETA (11.7 mg/2 mL, 40 mM) in acetonitrile were also prepared in a drybox under argon atmosphere. A 5 μL portion of the $Cu(OTf)_2$ solution was added to the polymer solution, and then the CD and UV−visible−NIR spectra were recorded. One cycle was accomplished by further addition of 5 μL of the TETA solution to the mixture and by measuring the CD and UV−visible−NIR spectra. This cycle was repeated several times (see Figure 6).

AFM Measurements of Supramolecular Aggregates of Poly-1. A stock solution of poly-**1** (50 mL, 0.4 mM) in chloroform was prepared. A 1 mL portion of the poly-**1** solution was transferred to a 2 mL flask equipped with a stopcock. After 1 mL of acetonitrile was added to this flask, 5 μL of the $Cu(OTf)_2$ solution (20 mM) was added, and then the solution was cast on freshly cleaved mica substrates. The solvents were evaporated simultaneously in a stream of nitrogen to measure AFM images immediately. In a similar way, AFM images of poly-**1**s in chloroform in the presence and absence of $Cu(OTf)_2$ and in a chloroform−acetonitrile mixture were measured.

Molecular Modeling and Calculations. Molecular modeling and molecular mechanics calculations were performed with the Dreiding force field (version 2.21)[27] as implemented in CERIUS^2 software (version 3.8; Molecular Simulations Inc., Burlington, MA) running on an Indigo^2-Impact graphics workstation (Silicon Graphics). The polymer model (20 repeating units of monomer units) of poly-**1** was constructed using a Polymer Builder module in CERIUS^2. Charges on atoms of poly-**1** were calculated with use of QEq in CERIUS^2; total charge of the molecule was zero. The starting main chain conformation of a polymer model was defined as a conformation of a rotational single bond between neighboring thiophene rings. The initial dihedral angles of a single bond from planarity were set to 180° (all anti form). The constructed models were accomplished by conjugate gradient method. The energy minimization was continued until the root-mean-square (rms) value became less than 0.1 kcal mol^{-1} Å^{-1}.

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Supporting Information Available: Figures of absorption and ESR spectral changes of PHT in solution upon addition of $Cu(OTf)_2$ and TETA, absorption and CD spectral changes of Cu(II)-induced chiral poly-**1** aggregates in chloroform upon addition of acetonitrile and further addition of TETA, and a table of ESR data of the doped poly-**1** and PHT (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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