Metal-Induced Supramolecular Chirality in an Optically Active Polythiophene Aggregate

Hidetoshi Goto,[a] Yoshio Okamoto,[b] and Eiji Yashima*[a]

Abstract: Chiral polythiophenes (PTs), in sharp contrast to other optically active polymers, exhibit optical activity in the π–π* transition region which is derived from the chirality of the main chain when they self-assemble to form a supramolecular π-stacked aggregate with intermolecular interactions in a poor solvent or in a film. We now report that the regioregular, optically active PT poly[(*R*)-3-{4-(4-ethyl-2-oxazolin-2-yl)-phenyl}thiophene] (poly-**1**) exhibits unique split-type induced circular dichroism (ICD) in the π–π* transition region of the main chain upon complexation with various metal salts such as trifluoromethanesulfonates of copper(I), copper(II), silver(I), and zinc(II), and iron(II) perchlorate in chloroform, which is a good solvent for poly-**1**. The appearance of ICD and slight changes in the UV/Vis spectra (no color change), except for the zinc salts, indicated that the chirality may not be induced by chiral π-stacked aggregates of poly-**1**, but by the chirality of the main chain, for example, a predominantly one-handed helical structure induced by intermolecular coordination of the oxazoline groups to metal ions. The sign of the Cotton effect depends on the metal salt; most metal salts induced ICDs with similar Cotton-effect patterns, while zinc salts caused an inversion of the signs of the Cotton effect of poly-**1** accompanied by a gradual red shift in the absorption of up to 125 nm. The changes in the conformation and the size of the poly-**1** aggregates induced by different metal salts were also investigated by ^{1}H NMR titrations, static light scattering (SLS), atomic force microscopy (AFM), and membrane filtration. On the basis of these results, we propose a possible model for the chiral supramolecular aggregates of poly-**1** with metal salts.

Keywords: aggregation · circular dichroism · oxazolines · polythiophenes

Introduction

Polythiophenes (PTs) are typical π-conjugated polymers[1] and have been extensively studied with regard to applications in macromolecular sensor systems[2] and electronic and optical devices such as polymer light-emitting diodes (LEDs) and organic transistors,[3] because their chemical and physical properties can be easily tuned by modifying the structure of the monomer unit, by controlling the regioregularity of 3-substituted PTs,[1f, 4] or by just blending PTs with different substituents.[3d] In addition, chiral PTs bearing an optically active substituent in the side group have attracted great interest, due to their unusual chiroptical properties and potential applications, for example, in circular polarized electroluminescence (CPEL) devices,[5] enantioselective electrodes.[6a] Chiral PTs, like other π-conjugated chiral polymers, exhibit optical activity in the π–π* transition region in a poor solvent, at low temperatures, and in films, in which they form a chiral supramolecular self-assembly through intermolecular π-stacking interactions. However, in sharp contrast with other optically active polymers, chiral PTs usually show no optical activity in this region in a good solvent or at high temperature.[6–10] Although a number of chiral PTs have been prepared so far, most previous studies focused on their unusual chiroptical behavior in dependence on the solvent (solvatochromism) and temperature (thermochromism), and only a few reports are related to their chiral-recognition abilities. The first chiral recognition by a chiral PT was demonstrated by Lemaire et al.[6a] They investigated the chiral-recognition ability of regiorandom chiral PTs with an achiral detector (cyclic voltammetry) on the basis of changes in the shape of the voltammograms of the chiral PTs in the presence of chiral doping agents such as camphor sulfonic acid. We recently reported the first clear example of chiral recognition with a regioregular (head-to-tail: HT) chiral PT derived from poly[(*R*)-3-{4-(4-ethyl-2-oxazolin-2-yl)phenyl}thiophene] (poly-**1**) bearing an optically active oxazoline

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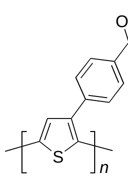
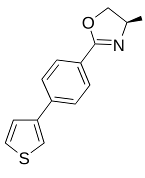


poly-**1** (regioregular)
poly-**2** (regiorandom)



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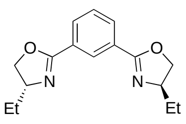

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Metal salts (MX_n)

M = Mg^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Cu^{+}, Cu^{2+}, Ag^{+}, Zn^{2+}
X = Cl^-, Br^-, ClO_4^-, $CF_3SO_3^-$, $CH_3CO_2^-$

residue.[11a] The polymer exhibited a completely inverted circular dichroism (CD) by responding to the chirality of chiral amino alcohols.

Poly-**1** was designed and synthesized on the assumption that its chiral oxazoline residues could coordinate to various metal ions to form a chiral supramolecular aggregate which could be used as a polymeric catalyst for asymmetric synthesis, since some metal complexes with chiral bis-oxazolines have been used as highly enantioselective catalysts.[12] Moreover, chiral oxazoline residues can be easily converted to the corresponding chiral amino esters by acid hydrolysis and further to achiral carboxyl groups by saponification of the amino esters. We found that a partially hydrolyzed PT containing a chiral amino ester group (33 mol%) was soluble in DMSO and responded to the chirality of amines: the induced CD (ICD) in the π–π* transition region depended on the absolute configuration of the chiral amine.[11a] Furthermore, poly-**1** showed a unique ICD in a relatively low wavelength UV/Vis region upon complexation with metal ions such as Cu^{II} and Fe^{III} in chloroform, which is a good solvent for poly-**1**, as well as in poor solvents.[11] The ICDs are completely different from the previously reported ICDs, which were due to chiral PT aggregation through intermolecular π-stacking interactions. We consider that the induced chirality of poly-**1** may be derived from the chirality of the main chain, such as a predominantly one-handed helical conformation generated by intermolecular coordination of the oxazoline group to metal ions. We now report on detailed studies on such unusual and interesting metal-induced ICDs by UV/Vis and CD spectroscopy, ^1H NMR titration, static light scattering (SLS), atomic force microscopy (AFM), and filtration experiments.

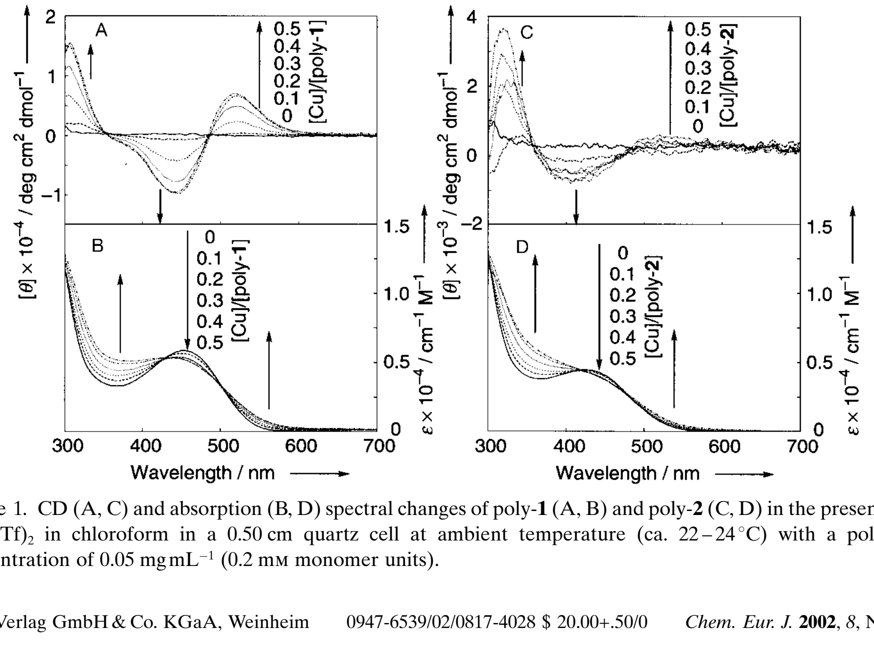

Figure 1. CD (A, C) and absorption (B, D) spectral changes of poly-**1** (A, B) and poly-**2** (C, D) in the presence of $Cu(OTf)_2$ in chloroform in a 0.50 cm quartz cell at ambient temperature (ca. 22–24 °C) with a polymer concentration of 0.05 mg mL^{-1} (0.2 mM monomer units).

Results and Discussion

CD and UV/Vis studies on the complexation of PTs with metal salts

salts: The complexation of chiral regioregular (poly-**1**) and regiorandom (poly-**2**) PTs with various metal salts was investigated by CD and absorption spectroscopy. As previously reported for other chiral PTs,[7] poly-**1** and poly-**2** also showed no ICD in the π–π* transition region in a good solvent (chloroform), while poly-**1** exhibited a unique split-type ICD with a positive first Cotton effect and a negative second Cotton effect in the absorption region in the presence of metal salts.[11a] Figure 1 shows typical CD and absorption spectral changes of poly-**1** in the presence of increasing amounts of $Cu(OTf)_2$ ($[Cu^{II}]$/[monomer units of poly-**1**] = 0–0.5) in chloroform.[13] These changes in the ICDs were accompanied by a gradual blue shift of λ_{max} (448 nm) of up to about 30 nm and the appearance of an absorption at a longer wavelength with clear-cut isosbestic points at 430 and 505 nm, and the color of the solution changed slightly, from yellow-orange to yellow. The complex showed almost the same ICD over a temperature range of −10 to 60 °C and hardly exhibited linear dichroism (LD).[14] These results clearly indicate that chirality on the poly-**1** main chain is not induced by the chiral, intermolecularly π-stacked aggregates of poly-**1**, as observed in a poor solvent, but by a main-chain chiral conformation, such as a predominantly one-handed helical structure induced by intermolecular complexation between the oxazoline residues and Cu^{II} ions.

Other explanations for the ICD of the poly-**1**/Cu^{II} complex include chiral induction by metal-to-ligand charge transfer (MLCT) between the chiral oxazoline residues and $Cu(OTf)_2$. However, this can be excluded, because the complex of $Cu(OTf)_2$ with the optically active bis-oxazoline **3**, a model compound for poly-**1**, exhibited no ICD in the range 350–600 nm under the same conditions as the poly-**1**/Cu^{II} complex. Another possibility is derived from oxidation of the main chain, since $Cu(OTf)_2$ can act as a dopant. However, the doping of the HT poly(3-hexylthiophene) with $Cu(OTf)_2$ caused a significant red shift (>300 nm) in the π–π* transition, and this possibility can therefore also be excluded. In contrast, poly-**2** showed a very weak ICD with Cu^{II} ions, accompanied by only minor changes in the UV/Vis spectra

(C and D in Figure 1), and this indicates that regioregularity is an important factor for controlling the chiral structures.

We then measured the CD spectra of poly-**1** in the presence of various metal salts to investigate the effect of the metals on the supramolecular chirality induction in the poly-**1** main chain ([metal salt]/[monomer units of poly-**1**] = 0.5; Table 1). These metal salts were selected since their complexes with chiral bis-oxazolines have been used as efficient catalysts for asymmetric synthesis.[12] Because the metal salts used are insoluble in chloroform, stock solutions in appropriate solvents such as acetonitrile, THF, acetone, or ethanol were prepared and added to a solution of poly-**1** in chloroform before the CD measurements. Most transition metal ions (Cu^{II}, Cu^{I}, Fe^{II}, Fe^{III}, Co^{II}, Ni^{II}, Pd^{II}, and Ag^{I}) also induced chirality in poly-**1** in chloroform, and their complexes thus showed similar ICDs. However, alkaline earth metal salts ($Mg(OTf)_2$ and $MgBr_2$) caused no ICD, and Zn^{II} salts caused significantly different ICDs in poly-**1**. The CD intensities of the poly-**1** complexes strongly depend on the metal, the electric charge, and the coordination structures. Ag^{I} and Cu^{I} tended to induce more intense ICDs, but for M^{II} and M^{III} ions, there is no clear trend. The poly-**1**/$Cu(OTf)_2$ complex showed similar ICDs regardless of the solvent used to dissolve $Cu(OTf)_2$, except for ethanol, which caused a slight decrease in the ICD intensity, probably due to its solvation of Cu^{II} ions, which may disturb the coordination of Cu^{II} ions to the oxazoline residues.[15]

Table 1. CD and absorption spectral data of poly-**1** in the presence of various metal salts in chloroform at about 22–24 °C.[a]

Metal complex[b]			CD spectrum[c] $[\theta] \times 10^{-4}$ [deg cm^2 dmol^{-1}]/λ_{max} [nm]		Absorption spectrum[c]
Metal salt	Oxidation state	Solvent[d]	First Cotton	Second Cotton	λ_{max} [nm]
$MgBr_2$	+2	THF	–[e]	–[e]	452
$Mg(OTf)_2$[f]	+2	acetonitrile	–[e]	–[e]	450
$Fe(ClO_4)_2$	+2	acetonitrile	1.52/514	– 1.94/448	441
$Fe(ClO_4)_3$	+3	acetonitrile	1.24/514	– 1.84/445	446
$Co(ClO_4)_2$	+2	acetonitrile	0.54/514	– 0.80/448	447
$Ni(ClO_4)_2$	+2	acetonitrile	1.08/508	– 1.35/445	446
$Pd(OAc)_2$	+2	THF	–[e]	– 0.17/430	447
$Cu(OTf)_2$	+2	acetonitrile	0.92/511	– 1.24/435	432
		THF	1.10/517	– 1.42/443	414
		acetone	0.86/520	– 1.20/443	422
		ethanol	0.62/520	– 1.00/443	431
$Cu(OTf)_2$[g]	+2	acetonitrile	0.03/520	– 0.10/410	410sh
$Cu(ClO_4)_2$	+2	acetonitrile	0.26/520	– 0.52/443	431
$CuCl_2$	+2	THF	0.12/503	– 0.36/431	443
$CuBr_2$	+2	THF	0.22/524	– 0.88/425	438
CuOTf	+1	acetonitrile	2.15/529	– 3.32/447	442
AgOTf	+1	acetonitrile	1.89/563	– 2.90/457	458
$Zn(OTf)_2$	+2	acetonitrile	– 0.75/570	0.72/396	530sh, 575sh
$Zn(ClO_4)_2$	+2	acetonitrile	0.30/516	– 0.87/453	437
$ZnCl_2$	+2	THF	– 0.25/513	0.25/390sh	450
$ZnBr_2$	+2	THF	– 0.23/517	0.25/390sh	450

[a] Poly-**1** concentration 0.05 mg mL^{-1}, cell length 0.5 cm. The molar ratio of metal salts to poly-**1** was 0.5. [b] OTf = trifluoromethanesulfonate. [c] sh = shoulder. [d] Solvent used for dissolving the metal salt (0.5 vol %). [e] No distinct CD. [f] On addition of $Mg(OTf)_2$, the poly-**1** solution became slightly turbid. [g] Poly-**2** was used instead of poly-**1**.

$Zn(OTf)_2$ brought about dramatic changes in the UV/Vis and ICD patterns of poly-**1** compared with those of the other metal complexes (Figure 2). On addition of $Zn(OTf)_2$ to a solution of poly-**1** in chloroform, split-type reversed ICD was observed. These changes in the ICDs were accompanied by a significant change in the absorption spectra; λ_{max} was red-shifted by up to about 125 nm, with a series of vibronic transitions at 530 and 575 nm and clear-cut isosbestic points at 406 and 491 nm. Poly-**2** also showed a similar ICD, but the CD intensity decreased by a factor of eight. More interestingly, the ICD patterns of poly-**1** were significantly influenced by the counteranions; $ZnCl_2$ and $ZnBr_2$ induced similar ICDs to $Zn(OTf)_2$, whereas $Zn(ClO_4)_2$ caused an inversion of the ICD with signs similar to those induced by $Cu(OTf)_2$. The counteranions of Cu^{II} also influenced the ICD intensities of poly-**1**, but their patterns were not inverted. We can thus control the supramolecular chirality of the poly-**1** aggregates with metal salts, although the reason is not clear at this moment. Similar counteranion effects were observed in catalytic asymmetric Diels–Alder reactions with chiral metal complexes of bis-oxazolines and were considered to be due to a difference in the coordinating affinity of anionic ligands to metals.[12c]

Complexation dynamics and size of supramolecular aggregates: The stoichiometry of the complex formation between poly-**1** and metal salts ($Cu(OTf)_2$ and $Zn(OTf)_2$) was determined by means of continuous-variation plots (Job

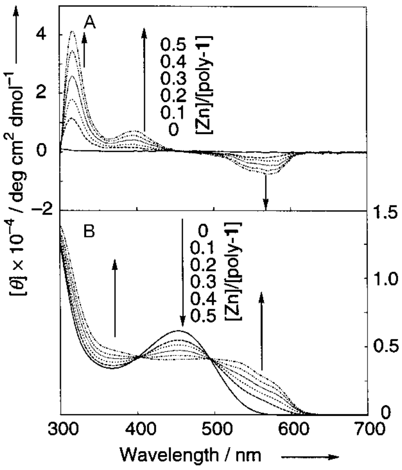

Figure 2. CD (A) and absorption (B) spectral changes of poly-**1** in the presence of $Zn(OTf)_2$ in chloroform at ambient temperature (ca. 22–24 °C). For other conditions, see Figure 1.

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plots) from CD spectroscopic studies in which the total concentration of poly-**1** and metal salt was kept constant at 0.4 mM (Figure 3).[16] Maximum complex formation occurred at a molar fraction of $Cu(OTf)_2$ and $Zn(OTf)_2$ of about 0.33 relative to monomer units of poly-**1** (i.e., 1:2 complexation), and the metal ions appear to undergo interchain coordination to two oxazoline groups on average, since an intrachain coordination of metal ions to adjacent oxazoline residues is difficult, as shown by molecular modeling.

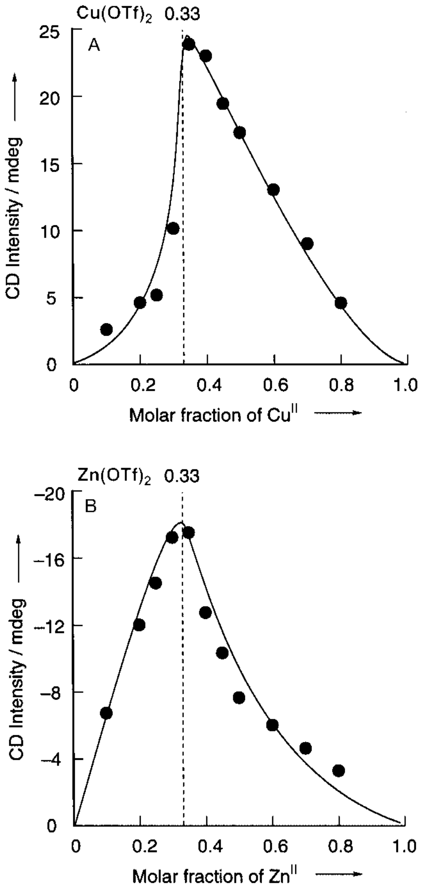

Figure 3. Job plots of poly-**1** with $Cu(OTf)_2$ (A) and $Zn(OTf)_2$ (B) in chloroform at 25 °C. The total concentration was 0.4 mM, and the CD intensity of the complex was analyzed.

The ICD intensity of the poly-**1**/metal complexes gradually increased with time, and the changes in the ICD intensities of the poly-**1**/$Cu(OTf)_2$ with time were monitored under the conditions of 2:1 complexation at 25 °C in chloroform to estimate the rate constant k and the stoichiometric number of complex formation (Figure 4). If the equation and rate law for 2:1 complexation are represented by Equations (1) and (2), respectively, the relation between the ICD intensity and time can be analyzed by using Equations (3) and (4).

$$2\,\text{oxazoline} + \text{Cu}^{\text{II}} \xrightarrow{k} \text{complex} \tag{1}$$

$$\frac{d[\text{complex}]}{dt} = k[\text{oxazoline}]^2[\text{Cu}^{\text{II}}] \tag{2}$$

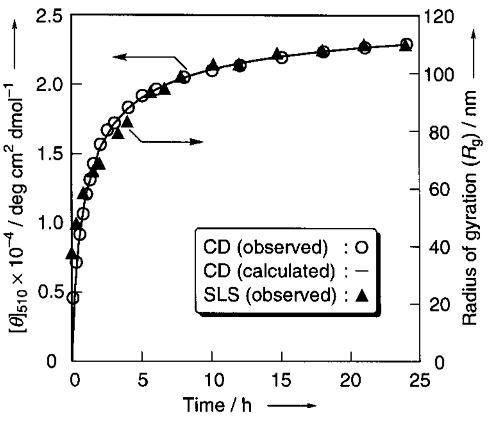

Figure 4. Changes in CD intensity at 510 nm and the radius of gyration R_g of poly-**1** in the presence of $Cu(OTf)_2$ in chloroform at 25 °C with time; the initial poly-**1** concentration and the molar ratio of $Cu(OTf)_2$ to poly-**1** were 0.05 mg mL^{-1} (0.2 mM monomer units) and 0.5, respectively. The curve for the CD intensity changes was calculated with the parameters $[\theta]_{\max} = 2.64 \times 10^4$ deg cm^2 dmol^{-1} and $k = 8.31 \times 10^3$ M^{-2} s^{-1}.

$$\frac{2k[\text{oxazoline}]_0^2 t}{[\theta]_2^{\max}} = \frac{1}{([\theta]_{\max} - [\theta])^2} - \frac{1}{[\theta]^2_{\max}} \tag{3}$$

$$t_{1/2} = \frac{3}{2k[\text{oxazoline}]_0^2} \tag{4}$$

In Equations (1)–(4), [oxazoline], [Cu^{II}], and [complex] are the concentrations [M] of the oxazoline residues of poly-**1**, $Cu(OTf)_2$, and the oxazoline/Cu^{II} complex; [oxazoline]$_0$ is the initial concentration [M] of the monomer units of poly-**1**; t and $t_{1/2}$ [s] are the measured time and half-life; and $[\theta]$ and $[\theta]_{\max}$ [deg cm^2 dmol^{-1}] are the observed and calculated maximum ICD intensities. All data were used for calculating $[\theta]_{\max}$ and k in Equation (3), and plots of t versus $1/([\theta]_{\max} - [\theta])^2$ led to a linear relation with a correlation coefficient $r > 0.999$, and the standard deviations of the calculated values from the experimental ones in curve fitting with Equation (3) were less than 3%. The obtained k, $t_{1/2}$, and $[\theta]_{\max}$ values were 8.31×10^3 M^{-2} s^{-1}, 1.28 h, and 2.64×10^4 deg cm^2 dmol^{-1} ($\Delta\varepsilon = 8.0$ cm^{-1} M^{-1}), respectively. These results also support 2:1 complexation between the oxazoline residues of poly-**1** and Cu^{II} ions and agree with the results of the Job plots.

Induction of time-dependent intermolecular chiral aggregation of poly-**1** by metal ions was also indicated by SLS measurements on poly-**1**/$Cu(OTf)_2$ complex in chloroform ([Cu^{II}]/[monomer units of poly-**1**] = 0.5). Although the original poly-**1** in chloroform did not show any scattering from polymer molecules because of its low molecular weight, the complex exhibited scattering whose intensity increased with time. The SLS data were analyzed by Zimm–Berry plots to estimate the radius of gyration R_g, and the changes in the R_g value were plotted versus time (Figure 4). The R_g value gradually increased with time and it reached an almost constant value after 24 h ($R_g = 110$ nm, corresponding to a particle size of 220 nm). As seen in Figure 4, the changes in the R_g values of the poly-**1**/$Cu(OTf)_2$ were almost proportional to those in the ICDs of the complex with time, and therefore the maximum R_g value could be calculated to be about 132 nm by using the equations analogous to Equations (2) and (3), in which $[\theta]_{\max}$ and $[\theta]$ are replaced with $R_{g,\max}$ and R_g, respectively.

Atomic force microscopy (AFM) provided direct evidence for the growth in particle size of the poly-**1**/Cu(OTf)$_2$ complex.[17] Figure 5 shows the changes in the particle size of the complex with time, investigated by AFM in the tapping mode. The AFM measurements were performed by casting the poly-**1**/Cu(OTf)$_2$ complex in chloroform on mica substrates, followed by evaporation in a stream of nitrogen to avoid a further aggregation on the mica. The AFM image in Figure 5 A shows a number of small, round particles with an average diameter and height of 100 ± 30 and 35 ± 15 nm, respectively, in the initial stage. The particle size gradually increased with time, and the average diameter and height after 4 h were 239 ± 39 and 119 ± 27 nm, respectively. These results roughly agree with the SLS results, although it is still difficult to observe the chiral supramolecular structures at a single-molecule level by AFM.

We also estimated the particle size of the poly-**1** aggregates in the presence of metal salts by filtration experiments. A solution of poly-**1** in chloroform containing an appropriate amount of Cu(OTf)$_2$ was filtered through membrane filters with pore sizes of 0.50, 0.20, 0.10, and 0.02 µm, and the intensity changes of the filtrates in the CD and absorption spectra were measured (Figure 6).[18] Although the solution of poly-**1** could pass through the membrane filter with a pore size of 0.02 µm, the poly-**1**/Cu(OTf)$_2$ complex could not pass through the membranse with smaller pores because of the increase in the particle size of the aggregates with increasing amount of Cu(OTf)$_2$. On addition of 0.2 equiv Cu(OTf)$_2$ to the monomer units of poly-**1**, about half of the complex was retained by the 0.20 µm membrane filter, and the filtrate permeated through the membrane with a pore size of 0.02 µm. However, the solution had almost completely lost its optical activity. This result, together with those from SLS and AFM, clearly indicates that the optical activity of poly-**1** is induced by intermolecular supramolecular aggregation. When more than 0.5 equiv of Cu(OTf)$_2$ were added to the poly-**1** solution, most of the aggregates could not pass through the membrane with a pore size of 0.20 µm. These results indicate that the particle size of the poly-**1**/Cu(OTf)$_2$ aggregates showing optical activity is greater than about 0.20 µm. Similar particle-size-dependent optical activity of chiral polymer aggregates was reported for optically active polysilanes in poor solvents.[18b]

Structure of the poly-1/metal salt complex: To obtain information on the structure of the chiral supramolecular assemblies of poly-**1** complexed with different metal salts, we monitored the changes in the ^{1}H NMR chemical shifts during the titration of a solution of poly-**1** in CDCl$_3$ with CuOTf and Zn(OTf)$_2$ (Figure 7). Because Fe^{II}, Fe^{III}, Ni^{II}, Co^{II}, and Cu^{II} ions are paramagnetic, such NMR titration experiments were difficult. The ^{1}H NMR titrations were also done for **1**, a model compound of poly-**1**, for comparison. Peaks were assigned on the basis of 2D COSY experiments. On addition of CuOTf and Zn(OTf)$_2$ to the poly-**1** solution ([Cu^I or Zn^{II}]/[poly-**1**] = 0–0.5; Figure 7 A and B), the signals of the oxazoline residues gradually shifted downfield, followed by broadening of the peaks, although Zn(OTf)$_2$ induced completely different ICDs on poly-**1** than CuOTf. Further addition of the metal salts caused precipitation of the poly-**1** complexes. The thiophene and aromatic ring signals hardly changed in the presence of the metal salts, that is, the poly-**1** main chains do not form a π-stacked lamellar aggregate, which is frequently observed for PTs in poor solvents. Similar changes in the proton signals occurred during the complexation of **1** with the metal salts (Figure 7 C and D). Although most signals shifted downfield, a significant difference could not be detected between poly-**1** and **1** with the same metal salts. These results suggest that metal ions coordinate to the oxazoline residues, and this may induce the subsequent conformational change of poly-**1** to form a chiral supramolecular aggregate in dependence on the nature of the metal ion.

To gain further information on the structures of the chiral supramolecular aggregates of

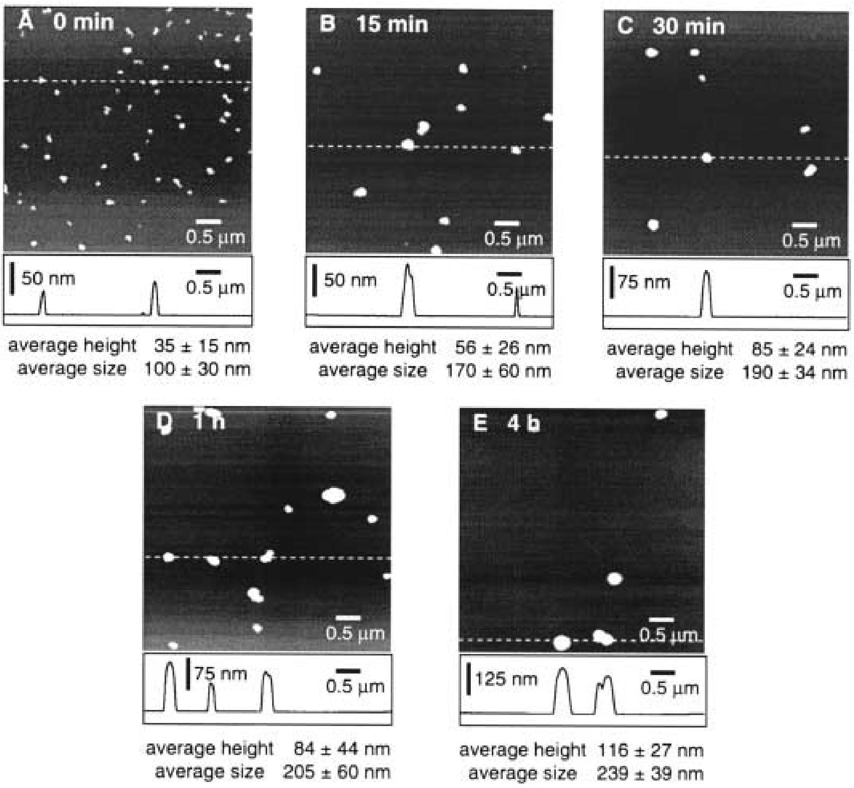

Figure 5. Changes in AFM images of the complexes of poly-**1** with Cu(OTf)$_2$, prepared from a chloroform solution of poly-**1** in the presence of Cu(OTf)$_2$; the initial poly-**1** concentration and the molar ratio of Cu(OTf)$_2$ to poly-**1** were 0.05 mg mL^{-1} (0.2 mM monomer units) and 0.5, respectively. The AFM images were taken after 0 (A), 0.25 (B), 0.5 (C), 1 (D), and 4 h (E). The heights along the trace drawn through the micrograghs are also shown.

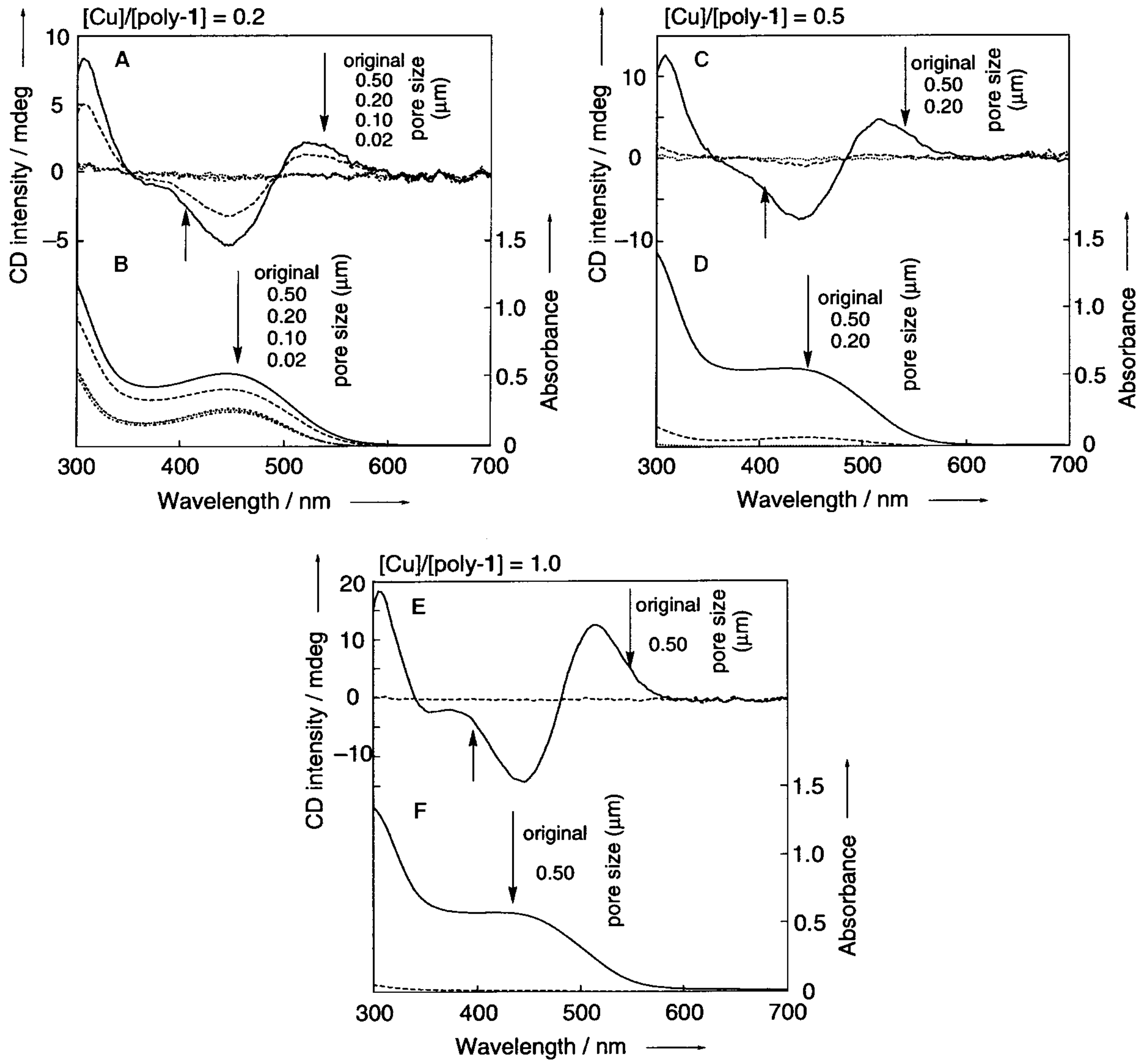

Figure 6. CD (A, C, E) and absorption (B, D, F) spectral changes of poly-**1** with Cu^{II} in chloroform after filtration through membrane filters with pore sizes of 0.50, 0.20, 0.10, and 0.02 µm at ambient temperature (ca. 22–24 °C) with a poly-**1** concentration of 0.05 mg mL^{-1} (0.2 mM monomer units) before filtration. The molar ratio of Cu(OTf)$_2$ to poly-**1** was 0.2 (A, B), 0.5 (C, D), and 1.0 (E, F).

poly-**1** with metal salts, we performed X-ray diffraction measurements on the aggregates formed with Cu(OTf)$_2$ and Zn(OTf)$_2$, but the X-ray diffractograms showed that the poly-**1**/metal complexes had an amorphous structure, so that a precise model for the chiral supramolecular structures of the poly-**1**-metal complexes cannot be determined. However, possible models can be proposed by using the spectroscopic data of the aggregates together with computer modeling and molecular mechanics calculations (Figure 8). The NMR, Job plot, and UV/Vis data demonstrated that a metal atom is coordinated on average to two nitrogen atoms of oxazoline residues of non-π-stacked main chains in an interchain fashion, because intrachain coordination to two adjacent oxazoline groups is sterically difficult. Figure 8 illustrates two possible structures of the complexes. The polythiophene backbones are assumed to have a helically twisted *s-trans* (**B**) or *s-cis* (**C**) conformation, so that the polymer chains can not form a π-stacked lamellar structure. The metal ions are bound intermolecularly on two oxazoline residues to give a coordination polymer (**D**) or a loose double-stranded helical polymer complex (**E**). The former complex may be more favorable than the latter from a structural point of view. Here, the helical conformation of the poly-**1** molecule is optically active. However, further intermolecular assemblies may be necessary for clustering into large colloidal particles (**F**) that retain the helical conformation and thus show ICD. However, we do not have unambiguous spectroscopic data for these models, and further experiments are needed.

Conclusion

We have found novel metal-induced chirality in a chiral PT aggregate bearing optically active oxazoline residues. The ICD intensity and pattern depended on the nature of the metal ion and counteranion. The stoichiometric number, the size, and structure of the supramolecular aggregate of the poly-**1** complexes with metal salts were investigated by means

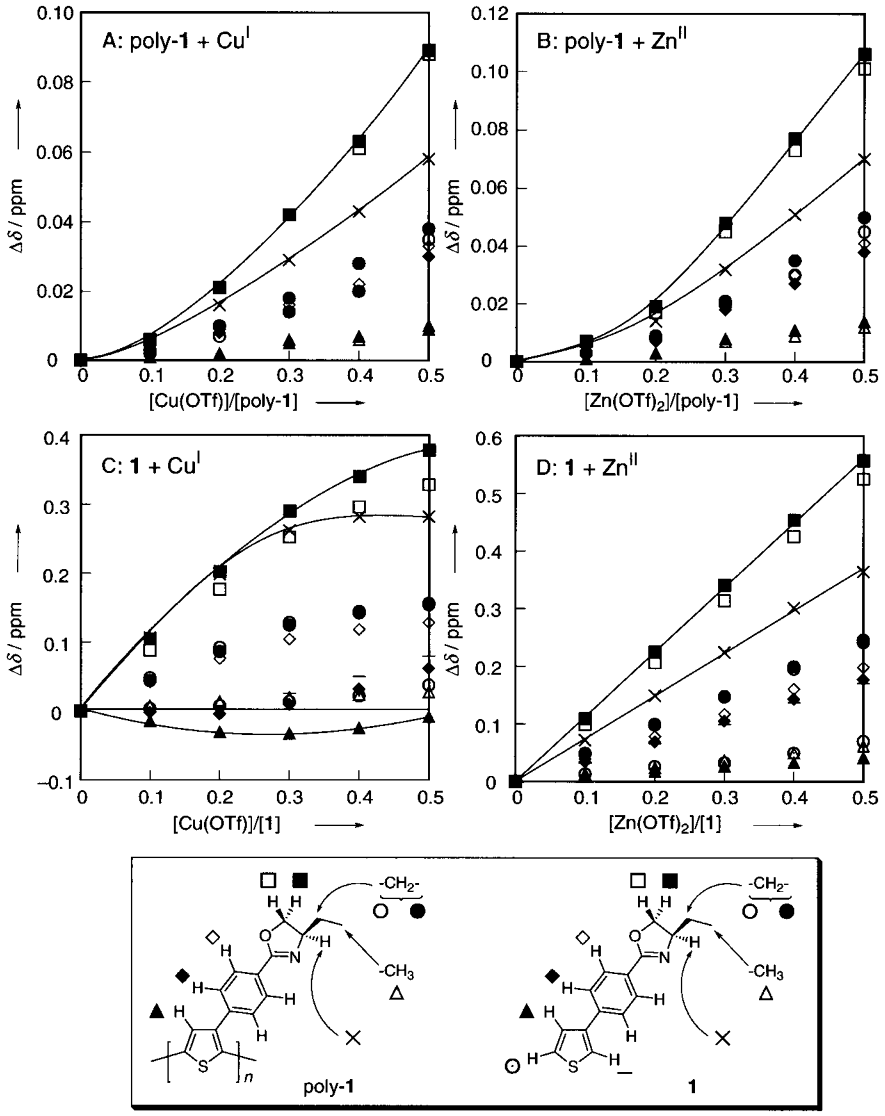

Figure 7. Changes in ^1H NMR chemical shifts of poly-**1** (A, B) and **1** (C, D) in $CDCl_3$ in the presence of CuOTf (A, C) and $Zn(OTf)_2$ (B, D) at 25 °C. The initial poly-**1** concentration was 2 mg mL^{-1} (8 mM monomer units). Positive values indicate a downfield shift.

of Job plots, SLS analysis, filtration experiments, AFM measurements, and ^1H NMR titrations, so that a possible model for the metal-induced chiral aggregation could be proposed. To elucidate the detailed chiral supramolecular structures of poly-**1** with metal salts, further investigations on a series of oligothiophenes with a well-defined structure are necessary.[19] We expect that the chiral supramolecular aggregates of poly-**1** with metal ions may be used as macromolecular chiral catalysts for asymmetric synthesis and as sensors for chiral recognition. These studies are now in progress.

Experimental Section

Materials: The regioregular (HT content > 90 %) and regiorandom (HT content ≈ 40 %) PTs poly-**1** and poly-**2** were prepared according to previously reported methods.[11] The molecular weights M_n of poly-**1** and poly-**2** were determined to be 5.3×10^3 and 3.4×10^3, respectively, by size-exclusion chromatography (polystyrene standards) with chloroform as eluent. The relatively low molecular weights of these polymers may be due to precipitation from the solvent during polymerization, which may prevent further propagation reactions. $CDCl_3$ (99.8 % D) and CD_3CN (99.8 % D), obtained from Nippon Sanso (Tokyo, Japan), were dried over CaH_2, distilled under nitrogen, and stored under nitrogen over 4A molecular sieves (Nacalai Tesque, Kyoto, Japan). Chloroform, acetonitrile, and acetone were dried over CaH_2, distilled under nitrogen, and stored under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen. Methanol was dried over magnesium turnings and iodine and distilled under nitrogen. $Cu(OTf)_2$ was purchased from Tokyo Kasei (Tokyo, Japan), and CuOTf, $Zn(OTf)_2$, AgOTf, $MgBr_2$, and $Mg(OTf)_2$ from Aldrich. $Pd(OAc)_2$ was obtained from Wako Pure Chemical (Osaka, Japan). Other metal salts listed in Table 1 were purchased from Kishida Chemical (Osaka, Japan). All metal salts were used as received.

Measurements: ^1H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a Varian VXR-500S spectrometer with TMS as internal standard. Absorption and CD spectra were measured on a Jasco V-570 spectrophotometer and a Jasco J-725 spectropolarimeter, respectively, in a 0.5 cm quartz cell unless otherwise noted. LD spectra were measured on a Jasco J-725 spectropolarimeter with an LD attachment. Temperature was controlled with a Jasco PTC-348WI apparatus for CD measurements. The concentrations of poly-**1** and poly-**2** were calculated on the basis of monomer units. SLS experiments were performed on a DLS-700 (Otsuka Electronics Co.) equipped with a 5 mW HeNe laser (632.8 nm) at 25 °C. AFM measurements were carried out on a Nanoscope IIIa microscope (Digital Instruments) in the tapping mode. Height and phase images were simultaneously measured at the resonance frequency of the silicon tips with cantilevers 125 μm in length. X-ray diffraction measurements were made on a RIGAKU RINT-1200 and with $Cu_{K\alpha}$ radiation.

UV/Vis and CD titrations of poly-1 and poly-2 with various metal salts: Typical experimental procedure: Stock solutions of poly-**1** (5 mg/100 mL, 0.2 mM monomer units) in chloroform and $Cu(OTf)_2$ (35.4 mg/5 mL, 20 mM) in acetonitrile were prepared in a dry box (NX1-M00320, Vacuum Atmospheres Company, Hawthorne, USA) under an argon atmosphere. The poly-**1** solution (2 mL) was transferred to a 0.5 cm quartz cell with a stopcock by using a 2 mL pipette, and the initial UV/Vis and CD spectra were measured. Increasing volumes of the $Cu(OTf)_2$ solution (0–10 μL, 0–0.5 equiv) were added to the poly-**1** solution, and then absorption and CD spectra were recorded for each addition of the $Cu(OTf)_2$. The solution of the poly-**1**/Cu^{II} complex was allowed to stand for 15 min before the measurements. In a similar manner, the UV/Vis and CD titrations of poly-**1** with other metal salts were performed.

Job plots of poly-1 with metal salts: The stoichiometries of complexation between poly-**1** and $Cu(OTf)_2$ and $Zn(OTf)_2$ were determined by using continuous-variation plots (Job plots).[16] Stock solutions of poly-**1** and

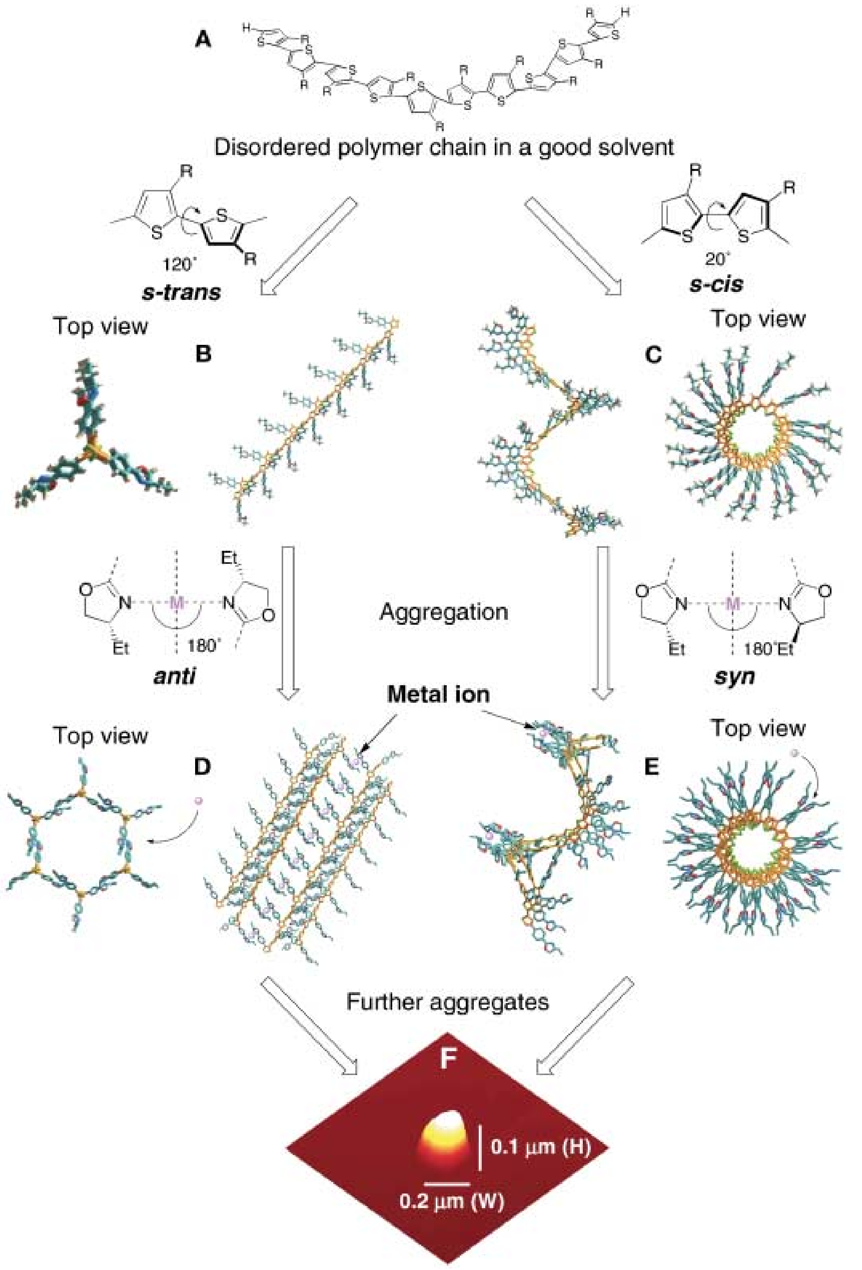

Figure 8. Possible models for supramolecular aggregates (**A** – **E**) and 3D AFM image (**F**) of poly-**1** with metal salts.

$Cu(OTf)_2$ in chloroform containing a very small amount of acetonitrile (0.5 vol %) were prepared in a dry box under an argon atmosphere (50 mL, 0.4 mM). Portions of the two solutions were transferred to eight 2 mL flasks equipped with a stopcock in such a way that their ratio changed from 0 to 1, while the total volume was kept at 2 mL. The sample solutions were allowed to stand for 24 h, the CD spectrum for each flask was recorded at 25 °C, and the CD intensities were plotted against the molar fraction of $Cu(OTf)_2$ to give the Job plot shown in Figure 3. The same procedure was used for $Zn(OTf)_2$.

Filtration experiments on poly-1/Cu(OTf)$_2$: Advantec membrane filters with pore sizes of 0.50, 0.20, and 0.10 µm (Toyo Roshi Co. Ltd., Japan) and a Whatman biofilter (pore size 0.02 µm) were used. Stock solutions of poly-**1** (100 mL, 0.2 mM) in chloroform and $Cu(OTf)_2$ (5 mL, 20 mM) in acetonitrile were prepared in a dry box under an argon atmosphere. The poly-**1** solution (10 mL) was transferred to a flask equipped with a stopcock by using a 10 mL pipette. To this was added an appropriate volume (20, 50, 100, and 200 µL) of the $Cu(OTf)_2$ solution ($[Cu^{II}]$/[monomer units of poly-**1**] = 0.2, 0.5, 1.0, 2.0), and then the UV/Vis and CD spectra were recorded (the CD intensity of the poly-**1**/$Cu(OTf)_2$ complex was hardly influenced by acetonitrile up to a volume ratio of ca. 5 %). Each solution was filtered with the membrane filters, and the absorption and CD spectra of the filtrates were recorded.

AFM measurements on supramolecular aggregates of poly-1 with Cu(OTf)$_2$: A stock solution of poly-**1** (50 mL, 0.2 mM) in chloroform was prepared. 2 mL aliquots of the poly-**1** solution were transferred to five 2 mL flasks equipped with a stopcock, and then the $Cu(OTf)_2$ solution (10 µL, 20 mM) was added to each flask. The solutions were allowed to stand for 0, 0.25, 0.5, 1, and 4 h, and then cast on freshly cleaved mica substrates. The solvents were evaporated in a stream of nitrogen, and AFM images were recorded.

^{1}H NMR titrations of poly-1 and 1 with metal salts: Typical experiment: Stock solutions of poly-**1** or **1** (4 mg/2 mL, 8 mM) in $CDCl_3$ and CuOTf (20.7 mg mL^{-1}, 80 mM) or $Zn(OTf)_2$ (29.1 mg mL^{-1}, 80 mM) in CD_3CN were prepared in a dry box under an argon atmosphere. The poly-**1** solution (500 µL) was transferred to a 5 mm NMR tube with a Hamilton microsyringe, and the initial ^{1}H NMR spectrum was recorded at 25 °C . To this were added increasing volumes of the CuOTf solution (0 – 25 µL, 0 – 0.5 equiv) under nitrogen and the ^{1}H NMR spectra were measured for each addition of CuOTf. The same procedure was used in the titration of poly-**1** with $Zn(OTf)_2$, and of **1** with the CuOTf and $Zn(OTf)_2$.

Molecular modeling and calculations: Molecular modeling and molecular mechanics calculation were performed with the Dreiding force field (version 2.21)[20] as implemented in CERIUS^2 software (version 3.8; Molecular Simulations Inc., Burlington, MA, USA) running on an Indigo^2-Impact graphics workstation (Silicon Graphics). The polymer model (20 repeating monomer units) of poly-**1** was constructed with a Polymer Builder module in CERIUS^2. Charges on atoms of poly-**1** were calculated by using QEq in CERIUS^2; total charge of the molecule was zero. The starting main-chain conformation of a polymer model was defined as a rotational conformation of a single bond between neighboring thiophene rings. The initial dihedral angle of a single bond from planarity was set to 120 (*s-trans*) and 20° (*s-cis*) to give polymer models with a twisted helical conformations. The models were constructed by the 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}. Cu^{II} ions were then manually placed in the coordination sites of poly-**1** (the oxazoline nitrogen atoms) to give a possible model for the supramolecular aggregates (see Figure 8).

Acknowledgements

We thank Professor Y. Matsushita and Professor Y. Takahashi (Nagoya University) and Professor T. Hattori and Y. Inaki (Nagoya University) for their help in the SLS and the X-ray diffraction measurements, respectively. This work was partially supported by Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science and the Ministry of Education, Culture, Sports, Science, and Technology, Japan. H.G. thanks JSPS Research Fellowships (No. 00857) for Young Scientists.

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[14] As described above, poly-**1** forms aggregates in the presence of Cu^{II}, so we measured LD spectra and found that the contributions of LD arising from macroscopic anisotropy are negligible because the optical densities from LD are less than 1×10^{-3}, which are much smaller than those from CD. For macroscopic anisotropy effects, see a) Y. Shindo, Y. Ohmi, *J. Am. Chem. Soc.* **1985**, *107*, 91–97; b) E. Yashima, H. Fukaya, P. Sahavattanapong, Y. Okamoto, *Enantiomer* **1996**, *1*, 193–199.

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Received: March 28, 2002 [F3984]

0947-6539/02/0817-4036 $ 20.00+.50/0