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COMMUNICATION

Chirality induction in metal-induced achiral polythiophene aggregates assisted by optically active amines and polythiophene†‡

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A regioregular achiral polythiophene bearing oxazoline pendant groups formed a unique optically active metal-induced supramolecular aggregate upon complexation with chiral amines or in the presence of a chiral polythiophene in a good solvent for the polymers, thus showing an induced circular dichroism.

Polythiophenes (PTs) are a class of popular π -conjugated polymers that have been extensively studied with much interest because of their possible applications in electric and optoelectric devices¹ and actuators.² On the other hand, chiral PTs have also attracted significant interest in recent years due to their unique chiroptical properties showing an optical activity when they are aggregated to form supramolecular π -stacked assemblies in poor solvents or in a film,³ whereas they exhibit no optical activity in good solvents, except for water-soluble chiral PTs that show an optical activity solely due to a singlehanded helical conformation in the non-aggregate state.⁴

In general, chiral PTs have been prepared by the homopolymerization of chiral thiophenes or the copolymerization with achiral ones.³ Recently, Shinkai and coworkers reported that the chirality, probably a helical chirality with an excess of one-handedness, could be induced in an achiral cationic PT when complexed with DNA^{5a} or adenosine triphosphate^{5b} or included in a helical cavity of polysaccharides^{5c,d} in an aqueous solution, thus showing an induced circular dichroism (ICD) in the π -conjugated chromophore regions of the achiral PT. Inganäs et al. also found a preferred-handed helicity induction on achiral PTs in the presence of polypeptides in water.⁶ Meijer et al.⁷ and Koeckelberghs et al.⁸ also reported an interesting supramolecular chirality induction in achiral PTs derived from the chiral information transfer from chiral PT chains to achiral ones in poor solvents via intermolecular π -stacking when both homopolymers were mixed in poor solvents or both segments covalently linked via block-copolymerization.



Chart 1 Structures of polythiophenes and chiral amines.

We previously found that a chiral, regioregular (head-totail) PT (poly[3-{4-((R)-4-ethyl-2-oxazolin-2-yl)phenyl}thiophenel) (PEOPT. Chart 1) bearing an optically active oxazoline residue self-assembled into supramolecular chiral aggregates in poor solvents⁹ or in the presence of metal salts capable of coordinating to the oxazoline residues even in $CHCl_3$, a good solvent, ¹⁰ which showed a characteristic ICD in the π - π * transition region. Such a supramolecular chirality of the PEOPT aggregates could be reversibly controlled (ON and OFF) by the addition or removal of an electron from the polymer main chain.¹¹ Here we report that an analogous regioregular, achiral PT bearing an achiral oxazoline residue, poly[3-{4-(4,4dimethyl-2-oxazolin-2-yl)phenyl}thiophene] (P1, Chart 1), aggregated in the presence of metal salts in a good solvent, and a unique supramolecular chirality was induced upon complexation with chiral amines or in the presence of PEOPT, thus showing an ICD in the achiral P1 chromophore region.

The **P1** was prepared according to Scheme S1 (ESI[‡]) in a way similar to that previously reported for the synthesis of **PEOPT**.⁹ The number-average molecular weight (M_n) was estimated to be 5.8×10^3 as determined by size exclusion chromatography with polystyrene standards using CHCl₃ as the eluent. The ¹H NMR spectrum of **P1** in CDCl₃ showed a sharp singlet centered at 6.85 ppm due to the thiophene ring proton at the 4-position, indicating that the polymer possesses a head-to-tail structure.^{9,10}

Metal-induced aggregations of **P1** were first investigated using silver trifluoromethanesulfonate (AgOTf) because it lacks absorption in the polythiophene absorption region above 250 nm. The UV/vis titrations indicated a 2:1 stoichiometry between the oxazoline residues of **P1** and Ag(t) ions as previously observed for the **PEOPT**-metal complexations (Fig. S1, ESI‡).¹⁰ With the aim of inducing chirality in the achiral **P1**-metal salt aggregates, commercially available chiral amino alcohols (**2–6**) and amine (**7**)

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Fig. 1 CD and absorption spectra of **P1** in the presence of AgOTf-(1*S*,2*R*)- and -(1*R*,2*S*)-**2** complexes (a) and AgOTf-chiral amine complexes (b) in CHCl₃/CH₃CN (97.5/2.5 vol/vol) at 25 °C; [**P1**] = 1 mM unit⁻¹, [**P1**]: [AgOTf]: [chiral amine] = 1:1:1. These spectra were measured after the mixtures had been allowed to stand for 30 min at rt.

(Chart 1), which can also coordinate to the metal ions, were added to the **P1**-metal salt aggregates and then their CD spectra were measured.

Fig. 1a and b shows the typical CD and absorption spectra of P1 in the presence of AgOTf and (1S,2R)- or (1R,2S)-2 in CHCl₃/ CH₃CN (97.5/2.5 vol/vol). The ternary mixtures exhibited splittype ICDs of the mirror images of each other in the π - π * transition region of P1 and the ICD intensity gradually increased with time, showing a constant value after 30 min (Fig. S2, ESI[‡]).¹² Similar time-dependent ICD changes were observed for the PEOPT-metal complexes.¹⁰ The appearance of the ICDs was accompanied by a blue-shift in λ_{max} (18 nm) in the absorption, and the ICDs are completely different from the previously reported ICDs based on the chiral PT aggregates due to the intermolecular π -stacked interactions in poor solvents.9 As we previously reported, the chiral PEOPT exhibited an ICD upon complexation with various metal ions in the absence of the chiral amines, and we proposed a predominantly one-handed helical conformation of PEOPT induced by the intermolecular coordination of the oxazoline group to metal ions, resulting in the formation of supramolecular chiral aggregates without any π -stacking.¹⁰

For the present achiral P1, the metal coordination most likely produces an equal mixture of right- and left-handed helical aggregates of P1 and the chiral amines may contribute to inducing either a right- or left-handed helical aggregate via coordination to the metal ions (Fig. 2). The CD and UV/vis titration experiments of P1 with a 1:1 complex of AgOTf and (1S,2R)-2 were then performed (Fig. S3, ESI^{\ddagger}). The ICD intensity gradually increased in a sigmoidal fashion by the addition of an increasing amount of the AgOTf-(1S,2R)-2 complex and reached an almost constant value at around [AgOTf-(1S,2R)-2]/[P1] = 1.0. These ICD changes were accompanied by clear-cut isosbestic points in the absorption spectra, suggesting that the polymer forms a slight excess of a one-handed helical aggregate at [AgOTf-(1S,2R)-2]/[P1] =0-0.5 upon binding of **P1** to Ag(1) ions as supported by the ¹H NMR spectroscopy (Fig. S4, ESI[‡]); the proton resonances derived from the oxazoline residues significantly broadened in the presence of Ag(I) ions. Further change in the population of the right- and left-handed helical aggregates into a onehandedness may cooperatively take place by the further addition of the AgOTf-(1S, 2R)-2 complex because the UV-visible spectra negligibly changed at [AgOTf-(1S,2R)-2]/[P1] = 0.5-2.0.



Fig. 2 Possible models for chiral supramolecular aggregates (a–d) of **P1** in the presence of Ag(t) and chiral amines. **P1** takes a random-coil conformation in a good solvent (a), but can possess a helically twisted *s-cis* or *s-trans* conformation (b) with dihedral angles of 20° and 120° between the adjacent thiophene rings, respectively. Upon complexation with Ag(t) ions, an equal mixture of right- and left-handed helical aggregates is formed. Further addition of chiral amines produces either a right- or left-handed helical aggregate.

The diffusion-ordered ¹H NMR spectroscopy (DOSY) measurements showed that the diffusion constant (*D*) of **P1** significantly decreased from 5.25×10^{-10} to 2.09×10^{-10} m² s⁻¹ upon complexation with AgOTf, but increased to 2.50×10^{-10} m² s⁻¹ in the presence of the chiral amine **2**, while the *D* value of **2** decreased from 13.8×10^{-10} to 7.43×10^{-10} m² s⁻¹ in the presence of Ag(1) and **P1** (Table S1, ESI‡). These data support the fact that the chiral amine **2** coordinates to the Ag(1) ions to dissociate the metal-induced **P1** aggregates, resulting in a decrease in the size of the aggregates.

P1 also formed chiral aggregates with Ag(1) ions in the presence of other chiral primary amines, thus showing ICDs with similar spectral patterns, but different intensities (Fig. 2b and Table S2, ESI‡); mono-substituted chiral amino alcohols (5 and 6) and amine (7) tended to exhibit weaker ICDs. In addition, structurally similar chiral amino alcohols of the same configurations at the stereogenic center with an amino group (2–4) afforded the same Cotton effect signs, suggesting that the **P1**–Ag aggregation system may be utilized as a novel chirality sensor for determining the absolute configuration of chiral amino alcohols.

On the other hand, the types of metals were also anticipated to affect the **P1**-aggregate formation as observed for chiral **PEOPT**-aggregate formation.¹⁰ Among the metal salts tested (Cu(I), Cu(II), Fe(II), Fe(III), Co(II), Ni(II), and Zn(II)), Cu(OTf)₂ and Cu(ClO₄)₂ as well as AgOTf induced a chiral aggregate formation of **P1** with chiral amines (Fig. S6 and Table S3, ESI‡), although the CD spectral patterns were different from each other, while the other metal salts with chiral amines showed no ICD at all.

Finally, we investigated the chiral information transfer from the chiral **PEOPT** to the achiral **P1** in a good solvent through metalinduced aggregate formation derived from the intermolecular coordination of metals to the oxazoline residues between **PEOPT** and **P1**. Such a chiral information transfer ("*sergeant and soldiers effect*")¹³ was achieved when the chiral and achiral PTs were



Fig. 3 (a) Plots of the molar circular dichroism (2nd Cotton effect) $(\Delta \epsilon_{2nd})$ of P1–PEOPT mixtures with Cu(OTf)₂ (red) and AgOTf (blue) in CHCl₃/CH₃CN (99/1 vol/vol) *versus* PEOPT content; [P1] + [PEOPT] = 0.2 mM unit⁻¹, ([P1] + [PEOPT]): [Cu(OTf)₂ or AgOTf] = 1:1. These spectra were measured after the mixtures had been allowed to stand for 3 h at rt. (b) CD and absorption spectra of P1 (black), P1/PEOPT (1/1) mixture (red), and PEOPT (blue) with Cu(OTf)₂ in CHCl₃/CH₃CN (99/1 vol/vol) at 25 °C; [P1] + [PEOPT] = 0.2 mM unit⁻¹, ([P1] + [PEOPT]): [Cu(OTf)₂] = 1:1. These spectra were measured after the mixtures had been allowed to stand for 3 h at rt.

mixed in poor solvents, thereby the intermolecular supramolecular π - π stacking took place,^{7,8} thus showing an ICD in the achiral PT chromophore region. Fig. S7 (ESI[‡]) shows the CD and absorption spectra of mixtures of PEOPT and P1 with different molar ratios in the presence of Cu(II) (a) and Ag(I) ions (d). The ICD intensities of the mixed chiral and achiral PT-metal complexes gradually increased with time, but they did not reach constant values even after 3 h. The plots of the second Cotton effect intensity ($\Delta \varepsilon_{2nd}$) of the PT mixtures with Ag(I) ions versus the amounts of PEOPT in the mixtures showed an almost linear relationship between them, indicating that almost no chiral information transfer took place for the mixtures in the presence of Ag(I) (Fig. 3a). In sharp contrast, the same plots with Cu(II) ions displayed a remarkable nonlinear relationship between the content of PEOPT and the $\Delta \varepsilon_{2nd}$ values. Most importantly, the Cotton effect signs of the PEOPT and P1 mixtures were reversed from those of the PEOPT-Cu(II) complex, and their ICD patterns were significantly different from that of the PEOPT-Cu(II) complex¹⁰ (Fig. 3b and Fig. S7a, ESI[‡]). These dramatic changes in the ICD patterns and signs clearly suggest that the chirality of **PEOPT** is definitely transferred to the achiral P1 chains, which are incorporated into the metal-induced supramolecular chiral aggregates.

In conclusion, we found a unique chirality induction in a metal-induced achiral PT aggregate bearing an achiral oxazoline residue by chiral amines. In addition, the supramolecular chirality is also transferred from the chiral PT to achiral PT chains when specific metal salts are used as an intermolecular cross-linking agent *via* coordination to the functional pendant residues. The present metal-induced chiral aggregates derived from the **PEOPT** and **P1** mixtures assisted by chiral PT in a good solvent were completely different from their chiral aggregates induced in poor solvents *via* well-accepted π -stacked, interchain interactions (Fig. S8, ESI‡). We expect that the metal-induced chiral supra-molecular aggregates of the achiral

PT with chiral amines may be used as supramolecular chiral catalysts for asymmetric synthesis and also as chiral materials for chiral recognition.¹⁴

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