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Unexpected Chiroptical Inversion Observed for Supramolecular Complexes Formed between an Achiral Polythiophene and ATP

Chun Li,[a, c] Munenori Numata,[a] Masayuki Takeuchi,[a] and Seiji Shinkai*[a, b]

Abstract: A series of supramolecular complexes between a water-soluble achiral polythiophene derivative (PT-**1**) and various nucleotides has been prepared. It was found that upon the introduction of adenosine diphosphate (ADP), adenosine triphosphate (ATP), and uridine triphosphate (UTP) into aqueous solutions of achiral PT-**1**, which has a random-coiled conformation, chiral supramolecular π-stacked aggregates of PT-**1** can be constructed. These complexes exhibit an unique split-type induced circular dichroism (ICD) in the π–π* transition region of the main chain. In particular, it was found that the Cotton effect of the chiral supramolecular PT-**1**/ATP aggregates reveals a dramatic inversion of chirality with a change in the concentration of ATP, which has not been previously observed in chiral macromolecular complexes. On the basis of extensive investigations performed with UV/Vis spectroscopy, CD spectroscopy, TEM, AFM, and dynamic light scattering (DLS), a possible mechanism for the formation of chiral superstructures of PT-**1** and chiroptical inversion induced by changes in ATP concentration is proposed.

Keywords: aggregation · chirality · nucleotides · polythiophene · supramolecular complexes

Introduction

Chirality induction, amplification, and inversion in supra- and macromolecular π-conjugated systems have attracted widespread interest in view of their importance for the better understanding and mimicking of stereochemical aspects in biological systems and for potential applications to molecular electronics, sensing, and asymmetric catalysis.[1,2] Oligo- and polythiophenes (PTs) that bear covalently linked chiral α or β substituents have been widely studied for these purposes, in which highly ordered, optically active superstructures were constructed by intermolecular π-stacking in poor solvents at low temperature or in thin films.[3–11] Although the chirality of these supramolecular aggregates is generally determined by the intrinsic structure of the components, the inversion of optical rotation of the chiral PT aggregates can be achieved by changing solvent and temperature, or by controlling the cooling rate of the films from a disordered phase at high temperature.[3,4,6]

Recently, we and others succeeded in the construction of supramolecular optically active PTs upon noncovalent complexation of achiral PTs and biopolymers with helical conformations such as DNA,[12] peptides,[13] and polysaccharides,[14] and detected an induced chirality in the backbone of PTs owing to the interpolymer complex formation through electrostatic or hydrophobic interactions. Herein, our attention is focused on extending this concept to the creation of supramolecular optically active PTs by noncovalent complexation with small chiral bioanions. We report a new approach to chirality induction in an optically inactive water soluble PT derivative, PT-**1**, upon noncovalent complexation with a small bioanion, adenosine triphosphate (ATP), in water and the subsequent chiroptical inversion through adjustment of the ATP concentration. To the best of our knowledge, this is the first observation of chirality induction and inversion in an intermolecularly π-stacked com-

[a] Dr. C. Li, Dr. M. Numata, Dr. M. Takeuchi, Prof. Dr. S. Shinkai
Department of Chemistry and Biochemistry
Graduated School of Engineering, Kyushu University
Fukuoka 819-0395 (Japan)
Fax: (+81) 92-802-2820
E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

[b] Prof. Dr. S. Shinkai
Center for Future Chemistry, Kyushu University
Fukuoka 819-0395 (Japan)
Fax: (+81) 92-802-2820
E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

[c] Dr. C. Li
New address:
Department of Chemistry, Tsinghua University
Beijing 100084 (China)

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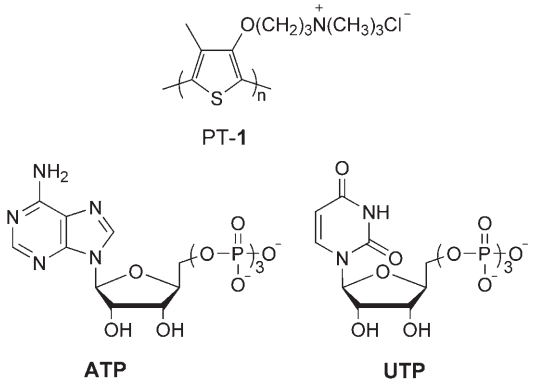

plex that consists of an achiral conjugated polymer and small chiral bioanions.[15]

Results and Discussion

UV/Vis and CD Spectroscopic Studies on Complexation of PT-1 with ATP

The complexation of an achiral polythiophene derivative PT-**1** with ATP was monitored by absorption and CD spectroscopy. As reported previously,[14] PT-**1** shows high solubility in water and exhibits an absorption maximum at 400 nm as expected for a random-coiled conformation of the PT backbones (Figure 1a). In the mixtures of PT-**1** with ATP, the absorption maximum is red-shifted to 538 nm, along with a change in the solution from yellow to purple, which can be used for colorimetric ATP sensing.[16] The red shift of the absorption maximum and the appearance of characteristic vibronic bands are associated with changes in the conformation and the aggregation mode of PT backbones,[3c] in which a more planar conformation and a stronger intermolecular π-stacking interaction are induced upon noncovalent binding with ATP.

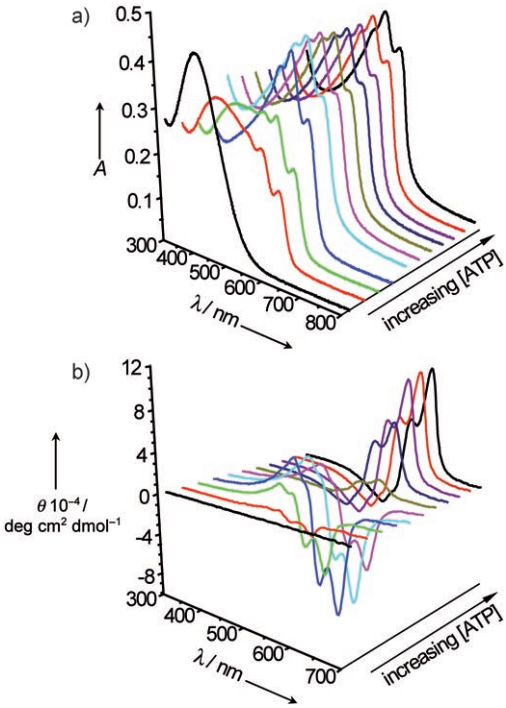

Figure 1. a) UV/Vis and b) CD spectra of PT-**1** (0.10 mM) in the absence and the presence of various amounts of ATP in water at 20 °C. ATP concentrations (from front to back): 0, 0.001, 0.0125, 0.025, 0.10, 0.15, 0.175, 0.20, 0.25, 0.375, and 0.50 mM.

PT-**1** itself is optically inactive, and no CD pattern in the π–π* transition region was detected, which indicates that PT-**1** adopts an achiral random-coiled conformation in water. Interestingly, upon the introduction of ATP, an intense split-type induced CD (ICD) in the π–π* transition region was observed (Figure 1b). The zero-crossing point close to the absorption maximum indicates the presence of strong exciton coupling between PT backbones in the chirally π-stacked PT-**1**/ATP complex.[3c] Although chirality induction in an optically inactive conjugated polymer through noncovalent bonding interaction with small chiral molecules is well known for polyacetylene derivatives,[15,17] polyaniline,[18] and polypyrrole,[19] there is no precedent in which chiral supramolecular polythiophene complexes are constructed by this strategy; that is, this is the first observation of the chirality induction of an optically inactive polythiophene derivative through noncovalent binding with small bioanions attained in aqueous solution. Moreover, the results obtained here are in stark contrast to those of chiral supramolecular complexes formed by complexation of achiral PTs with biomacromolecules such as DNA,[12] polypeptides,[13] and polysaccharides,[14] in which chiral structural factors are induced intramolecularly within each individual polymer chain. Most interestingly, the Cotton effect of the chiral supramolecular PT-**1**/ATP aggregates reveals a dramatic inversion of chirality with a change in the concentration of ATP (Figure 1b), which has never been observed in chiral macromolecular complexes. The most striking feature

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Seiji Shinkai *was born in 1944 in Fukuoka, Japan and received his PhD in 1972 from Kyushu Univ. After postdoctoral work at the Univ. of California, Santa Barbara, he joined Kyushu Univ. in 1975 and became a full Prof. there in 1988. Since then, he has been director of various projects, both local and international. His research interests focus on host–guest chemistry, molecular recognition, sugar sensing, allosteric functions, organogels, sol–gel transcription, polysaccharide–polynucleotide interactions, and so on. He has published over 700 scientific papers as well as 130 book chapters and reviews.*

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of this behavior is that the absorption spectra are similar to each other, whereas the CD spectra are very different, and the unexpected inversion of the CD pattern is induced at higher ATP concentrations.

Effect of Nucleotides on Formation of Chiral Complex

To shed light on the mechanism of chiral supramolecular complex formation, the effects of nucleotides that bear different numbers of phosphate groups and different structures of nucleobases on the aggregation structure and chirality induction in achiral PT-**1** were examined. Figure 2 compares

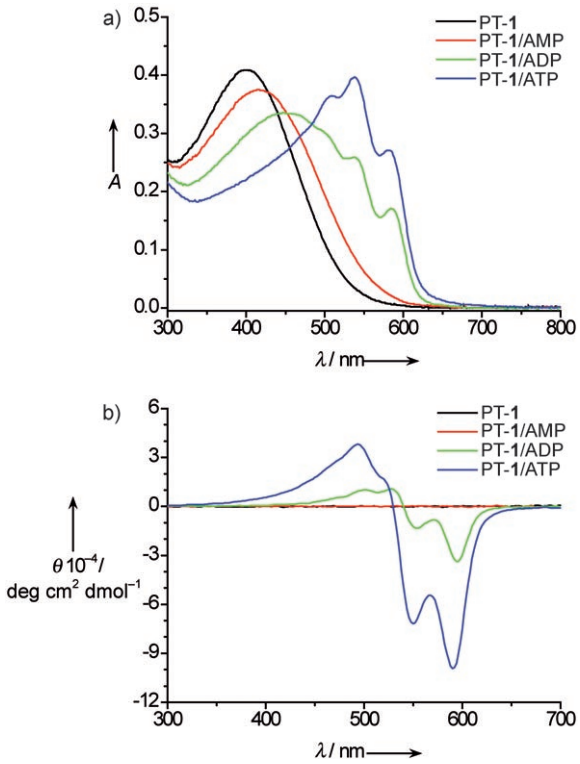

Figure 2. a) UV/Vis and b) CD spectra of PT-**1** (0.10 mM) in the absence and the presence of AMP (0.10 mM), ADP (0.035 mM), and ATP (0.025 mM) in water at 20 °C.

the absorption and CD spectra of PT-**1** in the presence of adenosine monophosphate (AMP), adenosine diphosphate (ADP), and ATP. Upon the introduction of adenosine nucleotides, the absorption maxima are red-shifted from 400 (PT-**1** only in water) to 416 (AMP), 448 (ADP), and 538 nm (ATP), thus indicating that a more-planar conformation and a strong intermolecular interaction are induced upon noncovalent binding with these bioanions. CD spectroscopic results indicate that chiral aggregates of PT-**1** can also be induced by noncovalent complexation with ADP, whereas no chiral superstructure is formed from AMP even at its high concentrations. The strongest ICD intensity observed for the complex with ATP suggests that the multiple electrostatic interactions between oligoanionic triphosphate and quaternary ammonium groups of PT-**1** play a crucial role in promoting the formation of chiral superstructures from PT-**1**.[20] Moreover, the effect of nucleotide triphosphates that bear different nucleobases on the aggregation structure and chirality induction in achiral PT-**1** was also examined (Figure 3).

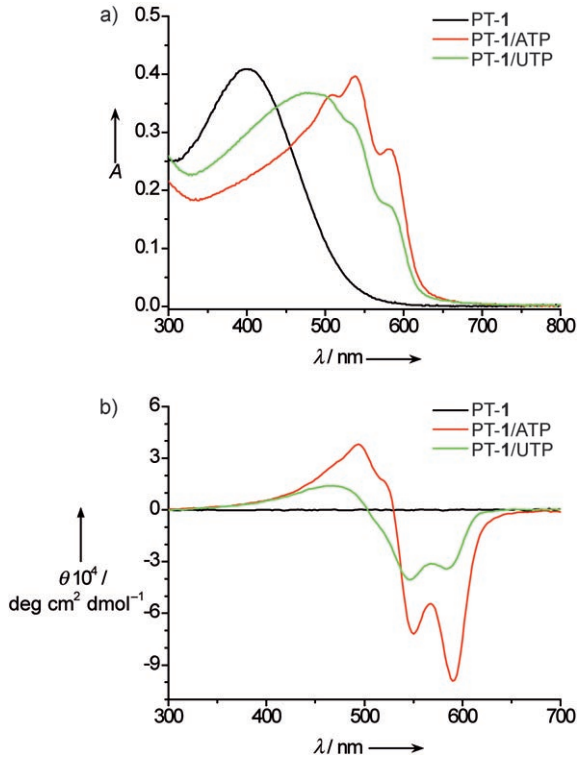

Figure 3. a) UV/Vis and b) CD spectra of PT-**1** (0.10 mM) in the absence and the presence of ATP (0.025 mM) and UTP (0.025 mM) in water at 20 °C.

It was found that ATP can induce a more-ordered superstructure and give a stronger optical activity in the π–π* transition of the PT-**1** backbone than uridine triphosphate (UTP). These results indicate that the π-stacking interaction between nucleobases is another dominant factor for the induction of a helical packing mode of PT-**1** main chains into the chiral superstructure.

Temperature-Dependent Absorption and CD Spectra of Chiral Supramolecular Complexes

To obtain more insight into the formation mechanism of the optically active supramolecular PT-**1**/ATP complex, temperature-dependent absorption and CD spectra of the PT-**1**/ATP and PT-**1**/UTP complexes were collected (Figure 4). It is clear that with increasing temperature, the magnitudes of the absorption and ICD bands, which originate from the chiral superstructures, with the fine vibronic structures are decreased gradually. At 60 °C, the ICD signal of the PT-**1**/UTP complex totally disappears, and the vibronic bands from the aggregated phase are displaced by a broad peak at

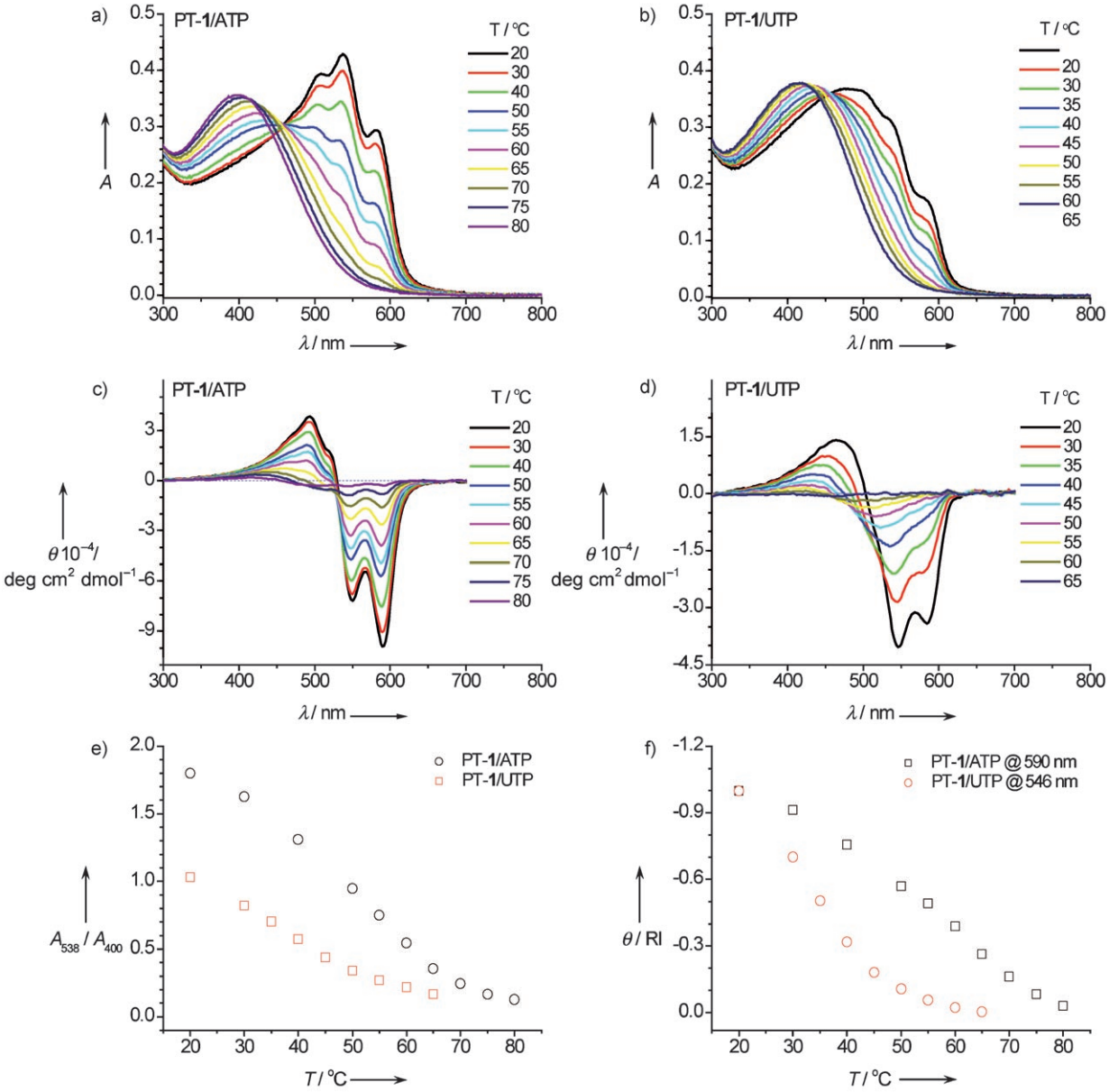

Figure 4. Temperature-dependent a,b) absorption and c,d) CD spectra of the a,c) PT-**1**/ATP and b,d) PT-**1**/UTP complexes. [PT-**1**] = 0.10 mM, [ATP] = [UTP] = 0.025 mM. Plots of e) the relative absorbance of PT-**1** at 538 nm (π-stacking aggregates) and 400 nm (random coil) (A_{538}/A_{400}) and f) ICD intensities of the chiral complexes against temperature.

410 nm, which signifies that the chiral superstructures formed at room temperature are dissociated into nonaggregated PT-**1** with the achiral random-coiled conformation. In contrast, the PT-**1**/ATP complex exhibits only a 60% decrease in the ICD intensity at 60 °C with respect to that at 20 °C. Moreover, the presence of a clear isosbestic point in the temperature-dependent CD spectra of the PT-**1**/ATP complex also confirms that the more-ordered chiral superstructure with the preferred handedness is induced upon noncovalent complexation of PT-**1** and ATP compared to that of PT-**1** and UTP. These results further indicate that the hydrophobic interaction between the nucleobases is a key factor for promoting the formation of stable chiral superstructures of PT-**1**.

Stoichiometry of Chiral Supramolecular Complex Formation

The stoichiometry of the complex formation was evaluated by means of continuous-variation plots from CD spectroscopic studies (Figure 5). The ICD intensity increases gradually with the increase in the molar fraction of PT-**1** (repeating unit) and attains the maximal values of around 0.75 (for PT-**1**/ADP) and 0.85 (for PT-**1**/ATP), which correspond to the molar ratios of 3:1 (PT-**1**/ADP) and 6:1 (PT-**1**/ATP). The stoichiometric ratios obtained here deviate from those simply expected from the complementary electrostatic interaction and give the net positive charge of the supramolecular complexes. This finding allows us to conclude that

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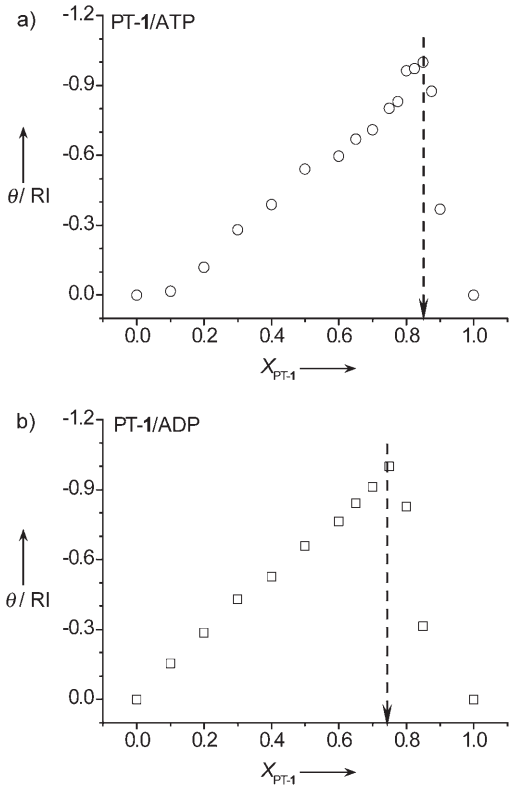

Figure 5. Job plots for the formation of the chiral a) PT-**1**/ATP and b) PT-**1**/ADP complexes in water at 20 °C. [PT-**1**] + [ATP or ADP] = 0.20 mM; $X_{PT\text{-}1}$ = [PT-**1**]/([PT-**1**] + [ATP or ADP]).

stable homogeneous dispersion in water is maintained by these excess cationic charges. The high cooperativity of electrostatic, hydrophobic, and aromatic stacking interactions would be responsible for these ratios, as reported for those of supramolecular complexes formed between thiacarbocyanine dye and nucleotides.[2d]

Microscopic and DLS Studies of Supramolecular Complexes with Opposite Optical Rotation and Possible Mechanism for Chiroptical Inversion

In contrast to the chirality inversion observed for the PT-**1**/ATP complex, the CD patterns of the PT-**1**/ADP and PT-**1**/UTP complexes in the aggregated phase are identical for all the conditions examined here ([PT-**1**] = 0.10 mM, [ADP] (or [UTP]) = 0.025–0.50 mM). These results indicate that ATP is a specific building block for the concentration-induced chirality inversion in this two-component molecular assembly, which consists of an achiral PT-**1** host and a nucleotide guest, and suggest that the high cooperativity of electrostatic and hydrophobic interactions, that is, the balance between these two interactions, are responsible for this novel chiroptical inversion.[21] The solvent-induced chirality inversion in PT[6c] and poly(*p*-phenylenevinylene)[22] aggregates is tentatively attributed to the formation of two types of π-stacked chiral superstructures: a cholesteric liquid-crystalline-type assembly of coplanar chains and a stack of twisted backbone chains. In these systems, however, it is not clear what type of architecture is responsible for each observed handedness. As shown in Figure 1a, at the higher ATP concentration, the chiral PT-**1**/ATP complexes with positive first Cotton effect exhibit red-tailing in the absorption spectra, thus suggesting the presence of larger light-scattering aggregates. To get a full picture of the chiroptical inversion of the complexes, TEM and AFM images of the chiral PT-**1**/ATP complexes with opposite optical rotation were recorded (Figure 6). The microscopic observation gives direct evi-

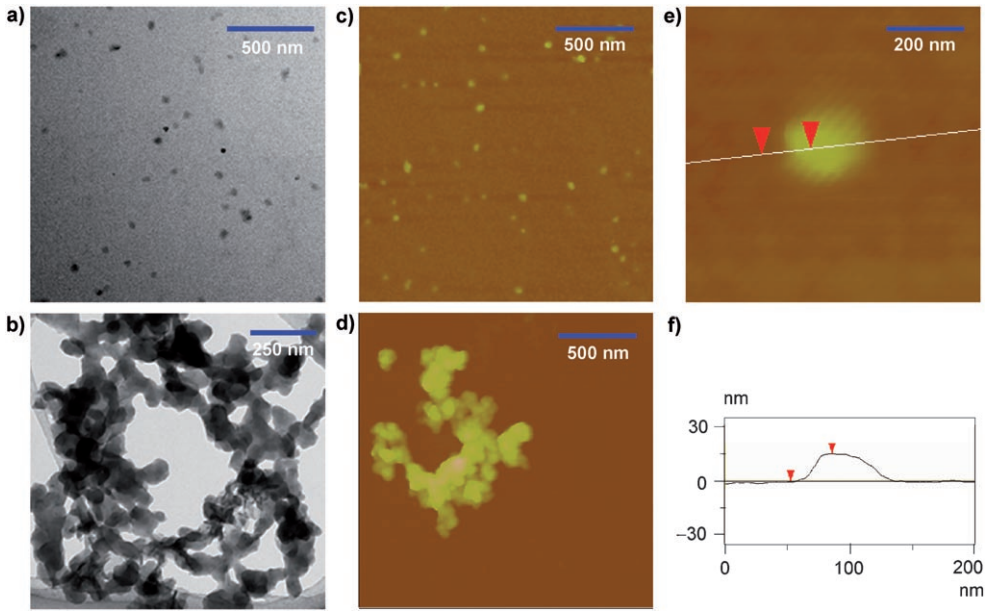

Figure 6. a,b) TEM and c,d) AFM images of the PT-**1**/ATP complexes with opposite Cotton effects. a,c) The PT-**1**/ATP complex with negative first Cotton effect; [PT-**1**] = 0.10 mM, [ATP] = 0.025 mM. b,d) The PT-**1**/ATP complex with positive Cotton effect; [PT-**1**] = 0.10 mM, [ATP] = 0.25 mM. e) Magnified image of one composite observed in c). f) Section analysis of image e).

dence that the complexes with opposite Cotton effects have different aggregation structures: at the lower ATP concentration, the complex with negative first Cotton effect forms disk-like aggregates with diameters of around 50 nm, whereas entangled fibrous structures are observed for the complex with positive first Cotton effect formed at the higher ATP concentration. Dynamic light scattering (DLS) analysis provides direct information about the size of the chiral supramolecular aggregates in solution (Figure 7). At the lower

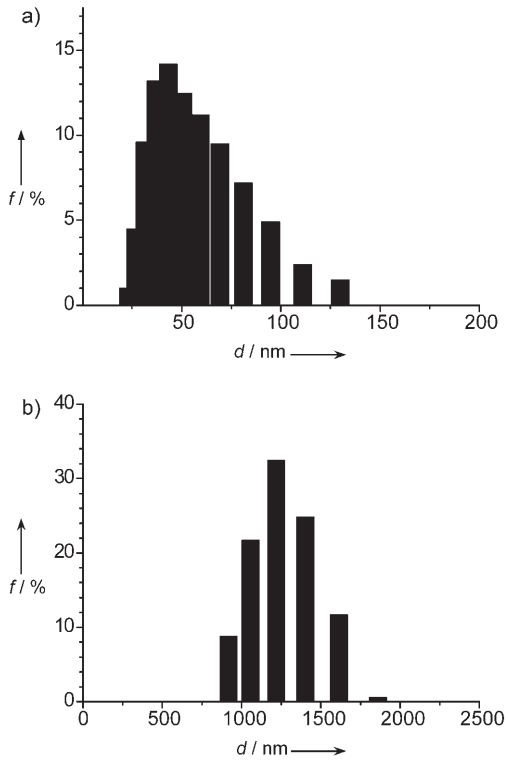

Figure 7. DLS profiles of the PT-**1**/ATP complexes with opposite Cotton effects. a) PT-**1**/ATP complex with negative first Cotton effect; [PT-**1**] = 0.10 mM, [ATP] = 0.025 mM. b) PT-**1**/ATP complex with positive first Cotton effect; [PT-**1**] = 0.10 mM, [ATP] = 0.25 mM.

ATP concentration (0.025 mM), the complexes with negative first Cotton effect have an average hydrodynamic diameter (d) of 52.5 nm measured at a PT-**1** concentration of 0.10 mM at 25 °C. On the other hand, the complexes with positive first Cotton effect prepared at the higher ATP concentration (0.25 mM) have an average d of 1300 nm. These results are consistent with those observed by microscopic methods (TEM and AFM), thus indicating that the complexes with opposite Cotton effects have different aggregation structures and that the superstructures observed by microscopic methods are already formed in solution, not during the sample-preparation processes. Combining the spectroscopic and microscopic results discussed above, we propose, therefore, that the electrostatic binding modes between the oligoanionic triphosphate of ATP and the cationic ammonium charge in PT-**1** may depend on the ATP concentration and subsequently influence the π–π stacking between nucleobase adenine groups. The synergistic effect between these two types of interactions could lead to a small energy difference between these two diastereomeric forms of the PT-**1**/ATP complexes formed at different ATP concentrations.

Conclusions

In conclusion, we have developed a novel, efficient approach to the construction of chiral supramolecular complexes from an achiral water-soluble PT host and a chiral ATP guest through noncovalent interactions in water. We expect that this noncovalent approach will not only open a new way for the construction of chiral superstructures of conjugated polymers through intermolecular π-stacking interactions, but also provide an important clue to the realization of chiral inversion which has so far been attained only by a change in solvent and temperature.

Experimental Section

General

All chemicals were obtained commercially from Aldrich and Tokyo Kasei Kogyo Co., Ltd. and were used as received. The water-soluble polythiophene derivative, PT-**1**, was synthesized and purified as reported previously.[14a] Aqueous stock solutions of ATP, ADP, AMP, and UTP were prepared in pure water (Millipore, 18.2 MΩ), and the concentrations of nucleotides were determined by using $\varepsilon_{259\ (ATP,\ ADP,\ AMP)} = 1.54 \times 10^4\,M^{-1}cm^{-1}$ and $\varepsilon_{262\ (UTP)} = 1.00 \times 10^4\,M^{-1}cm^{-1}$, respectively, in phosphate buffer (100 mM, pH 7.0).

Sample Preparation

As a typical procedure, the supramolecular complexes were prepared by adding PT-**1** aqueous stock solution (5 mM based on the repeating unit) into a dilute aqueous solution of nucleotides with the given concentrations. The pH values of ATP with concentrations of 0.025–0.50 mM are in the range of 5–6. To get reproducible results, all spectra of the complexes were recorded by mixing fresh solutions of PT-**1** and nucleotides, as the complex formation shows, to some extent, hysteresis upon the stepwise introduction of guest nucleotides.

Measurements

UV/Vis and CD spectra were acquired on a Hitachi U-3000 spectrophotometer and a Jasco J-720WI spectropolarimeter, respectively. AFM and TEM observations were carried out on a Topo METRIX SPM2100 and a JEOL JEM-2010 microscope (acceleration voltage 120 kV), respectively. DLS studies were conducted on an Otsuka Electronics Photal DLS-7000DL instrument equipped with a HeNe laser (632.8 nm) at 25 °C.

Acknowledgements

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[20] To further assess the effects of the electrostatic interaction on the chirality induction and chiroptical inversion observed for the supramolecular complex between achiral PT-**1** and ATP, CD spectra of PT-**1** (0.10 mM) in the presence of various amounts of ATP in HEPES buffer (10 mM, pH 7.4) were recorded (see Supporting Information). It was found that ATP in buffer solution can also induce the formation of the optically active supramolecular complex PT-**1**/ATP. However, no ATP concentration-induced chiroptical inversion was observed, thus indicating that the pH value itself (i.e. the charge of ATP) is not a dominant factor for this unexpected chiroptical inversion, which is a result of the high cooperativity of electrostatic, hydrophobic and aromatic stacking.

[21] Guanosine triphosphate (GTP), which bears a purine base, can also form optically active supramolecular complexes with PT-**1**, thus giving a positive first Cotton effect that is opposite to that of the PT-**1**/ATP complex. Moreover, no chiroptical inversion was observed by increasing the GTP concentration (see Supporting Information).

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