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Optically active fluoro-substituted polyaniline prepared in organic media: The synthesis, chiroptical properties, and comparison with optically active non-substituted polyaniline

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Abstract

Optically active polyaniline (PANI) bearing an electron-withdrawing fluorine substituent, poly(2-fluoroaniline) (F-PANI), was synthesized in organic solvents by using (+)- or (−)-camphorsulfonic acid (CSA) as a chiral dopant, in which 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) was used as an electron acceptor. Formations of the optically active (chiral) F-PANI/(+)- or (−)-CSA, the dedoped F-PANI, and the redoped F-PANI/CSA were confirmed by the FT-IR, UV/vis/near-IR, and/or circular dichroism (CD) spectroscopy. The CD spectra of the chiral F-PANIs/(+)- and (−)-CSA were investigated in various organic solvents and compared with those of non-substituted PANI/(+)- or (−)-CSA. The F-PANI/(+)-CSA and PANI/(+)-CSA interestingly indicated almost mirror-imaged CD spectra in the visible region, although CD absorptions of the F-PANI/CSA were slightly blue shifted compared with those of PANI/CSA. The chiral F-PANI/CSA was unexpectedly confirmed to remain the initial chiral conformation during reversible dedoping/redoping cycles in solution state. The chiroptical properties of F-PANI/(+)-CSA in organic solvents were found to be affected by the solvent, probably due to the solvent effect to the polymer backbone, and the helical conformation was drastically reversed by change of the solvent. Furthermore, the conformation of F-PANI/CSA in *m*-cresol can be significantly changed when the F-PANI/CSA was dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios, in which the sign inversions of CD absorption bands were caused when the ratio of DMSO in the *m*-cresol/DMSO cosolvent exceeded 10%. On the other hand, in the case with PANI/(+)-CSA, the similar sign inversions of CD absorption bands were not observed under the similar conditions, and then the helical conformation of chiral F-PANI/CSA was supposed to be rather flexible compared with that of chiral PANI/CSA, presumably due to relatively weak interaction among F-PANI backbone, CSA, and *m*-cresol.
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1. Introduction

Polyaniline (PANI), a low-cost inherently conductive polymer, has attracted considerable attention in the past several decades due to its unique electrochemical property, ease of preparation, environmental stability, and potential use in a wide range of applications including electrochromic devices, light-emitting diodes, electrostatic discharge protection, secondary batteries, and corrosion protecting paint [1–6]. Meanwhile, 'optically active (chiral)' conductive polymers recently have been attracting much attention due to their potential use in diverse areas such as electrochemical asymmetric synthesis, chiral chromatography, and membrane separation technology [7–12]. For the past two decades, chiral PANI has been also developed. Wallace et al. synthesized chiral PANI by electrochemically polymerization of aniline in the presence of a chiral acid dopant, (+)- or (−)-10-camphorsulfonic acid (CSA), and by postprotonation of dedoped PANIs (so-called emeraldine bases, PANI–EBs) with (+)- or (−)-CSA [13–19]. Kane-Maguire et al. prepared chiral PANI film using a modification of an in situ chemical polymerization procedure for preparation of HCl–doped PANI (PANI/HCl), in which the chiral PANI was synthesized with ammonium peroxydisulfate [$(NH_4)_2S_2O_8$, APS] in (+)- or (−)-CSA aqueous solution [20]. More recently, Thiyagarajan et al. reported template assisted enzymatically synthesized water-soluble chiral PANI nanocomposites in the absence of a chiral dopant, where horseradish peroxidase and poly(acrylic

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acid) were used as an enzyme catalyst and a molecular template, respectively, [21].

We also reported chemically synthesized chiral PANI and the alkyl and alkoxy substituted derivatives in organic media, where 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and CSA were used as an electron acceptor and a chiral dopant, respectively, [22–28]. In particular, the resulting PANIs/(+)- and (−)-CSA indicated distinct different chiroptical and electronic properties from the cases of PANIs/(+)- and (−)-CSA formed by other synthetic methods. Thus, the resulting PANIs remained the optically activity even when these were dissolved in *m*-cresol, and the results were quite different from the previous demonstrations by Havinga et al. and Wallace et al. [29,30]. For example, Wallace reported that the complete loss of optical activity over the visible spectral region was observed when *m*-cresol was added into the initially prepared PANI/(+)-CSA solution in chloroform. In addition, the $CHCl_3$ solution of PANI/(+)-CSA synthesized by a common synthetic procedure (postprotonation of PANI–EB with (+)-CSA) generally indicates three distinctive UV/vis/near-IR absorption peaks at 360, 440, and 780 nm, which are typical absorption peaks of doped PANI (so-called emeraldine salt, ES), whereas the *m*-cresol solution shows an absorption peak at ~440 nm and a steadily increasing 'free-carrier tail' starting from ~1000 nm to the IR region [31]. This interesting behavior is considered to be derived from rearrangement from a 'compact coil' to an 'extended coil' conformation, and it is named as secondary doping effect. On the other hand, chiral PANI/CSA prepared by our synthetic method almost kept the 'compact coil' conformation even when it was dissolved in *m*-cresol. Thus, no 'free-carrier tail' was observed although the slightly red-shifted bipolaron absorption band was detected according to slightly expanded polymer chains in the solution [23]. In other words, these distinct different behaviors in the CD and UV/vis measurements suggested that chiral PANI formed by our synthetic procedure using DDQ in organic solvents might have strong helical conformation, compared with chiral PANIs prepared by common synthetic methods.

Fluoro-substituted polymers possess unique physical properties, due to the very low polarizability of the fluorine atom, the abnormally strong nature of the C–F bonds, and the relatively small size of the fluorine atom [32–35]. In general, fluoro-substituted polymers exhibit higher thermal stability, enhanced chemical resistance, and low surface energy as compared with their non-fluorinated analogues. Therefore, a large number of studies about syntheses and properties of fluoro-substituted PANIs and the copolymers have been carried out [36–42], and an biosensor and an bacterial fuel cell using fluoro-substituted PANIs were recently investigated as one of the applications [43–44]. Furthermore, the nucleophilic aromatic substitution (S_NAr) reaction of a fluorinated aromatic compound is known to smoothly proceed, in which the aromatic fluorine group can be replaced with various groups, such as –OR, –NRR′, and –SR ones, and then (chiral) PANIs having various functional groups could be synthesized by the S_NAr reaction of fluoro-substituted (chiral) PANIs [45]. However, as far as we know, there are no examinations about syntheses of fluoro-substituted chiral PANIs and the physical properties including chiroptical ones, unexpectedly.

Hence, we studied herein the chemically synthesis of poly(2-fluoroaniline) doped with (+)- or (−)-CSA [F-PANI/(+)- or (−)-CSA, **4a** or **4b**] by using DDQ in organic media, and the electronic and chiroptical properties of the resulting chiral F-PANI/CSA, the dedoped F-PANI (F-PANI–EB, **5**), and the redoped F-PANI/CSA in various organic media were investigated and compared with those of non-substituted chiral PANI/(+)- or (−)-CSA prepared by the similar synthetic method.

2. Experimental section

2.1. Materials

2-Fluoroaniline and aniline (Kanto Chemical Co., Inc.) were distilled under reduced pressure and stored below −10 °C prior to use. Both of CSAs (Aldrich Chemical Company, Inc.) were dried under vacuum at 60 °C for 24 h before use. A DDQ (Aldrich Chemical Company, Inc.) was used as supplied. Tetrahydrofuran (THF, Kanto Chemical Co., Inc.) was predried using sodium and was distilled prior to use. A dry *N*-methyl-2-pyrrolidone (NMP) was purchased from Kanto Chemical Co., Inc. Chloroform was dried with molecular sieves 4 Å. Unless otherwise stated, other reagents and solvents were of analytical grade from Kanto Chemical Co., Inc. and were used without further purification. Chiral PANI/(+)-CSA or (−)-CSA was synthesized with DDQ in organic media according to our previous report [23].

2.2. Spectroscopic studies

The UV/vis/near-IR and circular dichroism (CD) measurements were carried out using a JASCO V-570 spectrophotometer and a JASCO J-720WI spectropolarimeter, respectively. Infrared spectra were recorded on a FT-IR spectrophotometer (Shimazu FT-IR 8400S).

2.3. Preparation of F-PANIs/(+)- or (−)-CSA (*4a* or *4b*)

Based on the synthetic procedure for chiral PANI/CSA [22–25], polymerization of 2-fluoroaniline was carried out in cosolvent of chloroform–THF using either (+)- or (−)-CSA as the chiral dopant. Typically, 1.162 g (5.0 mmol) of (+)-CSA and 0.278 g (2.5 mmol) of 2-fluoroaniline were well dissolved in 20 mL of chloroform at room temperature. A solution containing 0.568 g (2.5 mmol) of DDQ dissolved in 6.7 mL of fresh distilled THF was then added dropwise with constant stirring at room temperature for 6 h. The mixture was dropwisely poured into acetone in order to remove excess CSA, unreacted and/or reduced DDQ, and unreacted 2-fluoroaniline and its oligomers. The resulting precipitate was filtrated and washed with an adequate amount of acetone, and then dried under reduced pressure at room temperature to give the purified F-PANI/(+)-CSA, **4a** in 58% yield (0.33 g). The FT-IR and

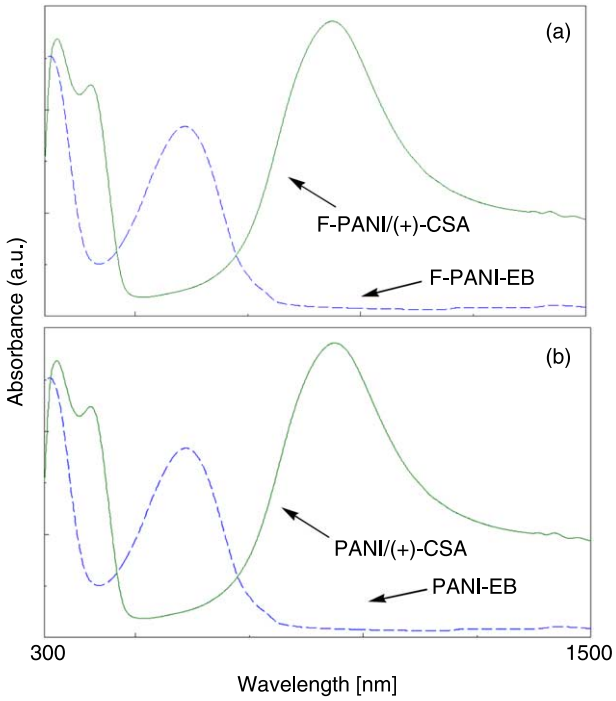


Fig. 1. (a) The UV/vis/near-IR spectra of F-PANI/(+)-CSA (F-PANI **4a**) in *m*-cresol and F-PANI–EB (F-PANI **5**) in NMP and (b) the spectra of PANI/(+)-CSA in *m*-cresol and PANI–EB in NMP.

UV/vis/near-IR spectra were shown in Figs. 1 and 2. Anal. Found: C, 59.28; H, 5.81; F, 8.41; N, 5.84; S, 6.64.

2.4. Chemical dedoping/redoping of the F-PANIs/(+)- and (−)-CSA

Chemical dedoping and redoping of F-PANIs/(+)- and (−)-CSA were carried out based on the common synthetic procedure for dedoping/redopong of PANI/CSA. The

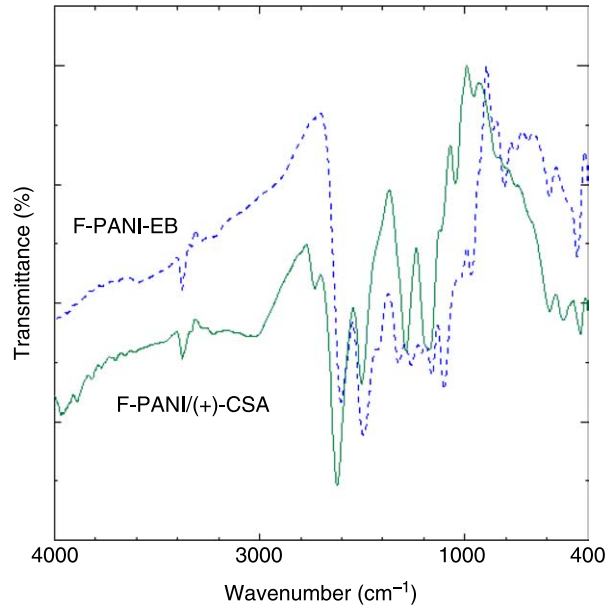


Fig. 2. The FT-IR spectra of F-PANI/(+)-CSA (F-PANI **4a**) and F-PANI–EB (F-PANI **5**).

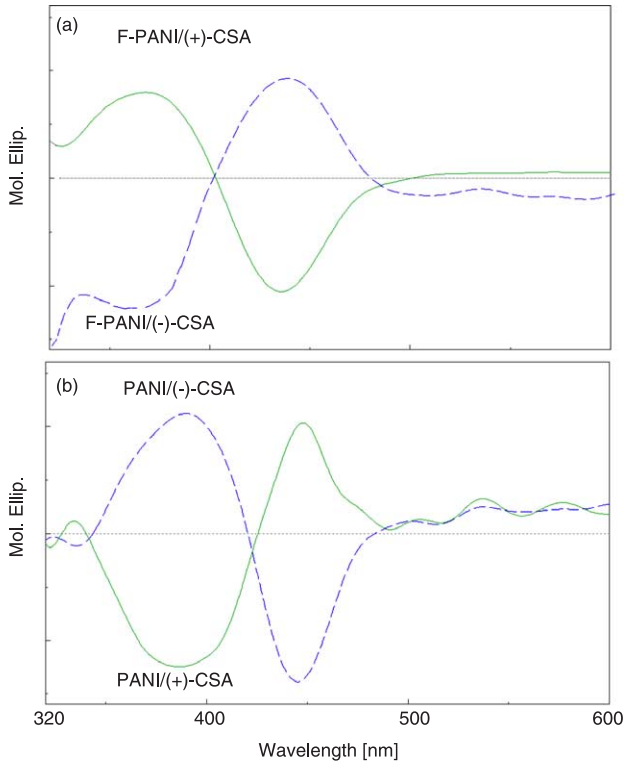


Fig. 3. (a) The CD spectra of F-PANI/(+)-CSA and F-PANI/(−)-CSA (F-PANI **4a** and **4b**) in the *m*-cresol and (b) the CD spectra of PANI/(+)-CSA and PANI/(−)-CSA in the *m*-cresol.

F-PANIs/(+)- and (−)-CSA (**4a** and **4b**) were dedoped by suspending them in 30 mL of aqueous NaOH solution (1.0 N) for 30 min to give the corresponding emeraldine base (F-PANI–EB, **5**). The redoping of F-PANI–EB was carried out by addition of (+)- or (−)-CSA to the solution of F-PANI–EB in *m*-cresol, dimethylsulfoxide (DMSO), dimethylformamide (DMF), or NMP, resulting in the formation of the corresponding F-PANIs/CSA. These FT-IR, UV/vis/near-IR, and/or CD spectra were shown in Figs. 1–5.

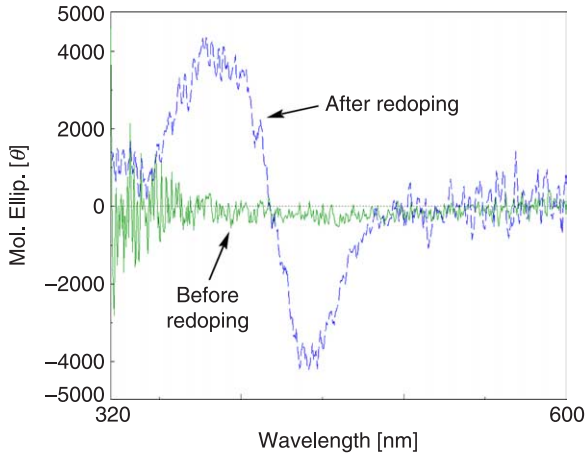


Fig. 4. The CD spectra of F-PANI–EB (F-PANI **5**) before and after the redoping by addition of (+)-CSA in *m*-cresol (0.10 g/L).

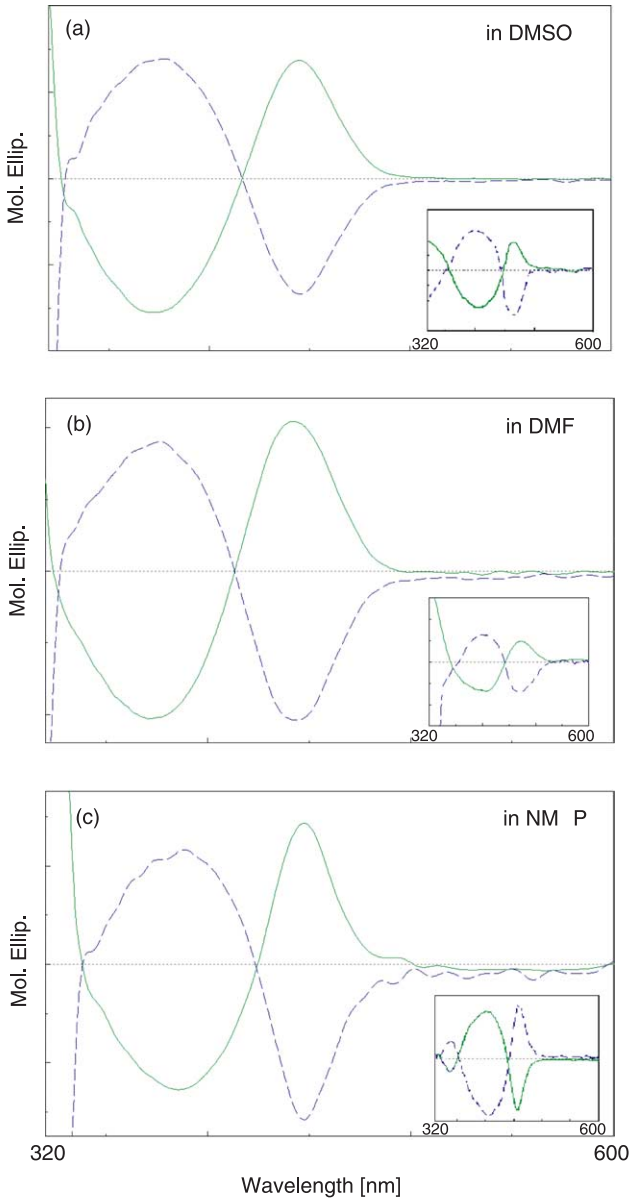
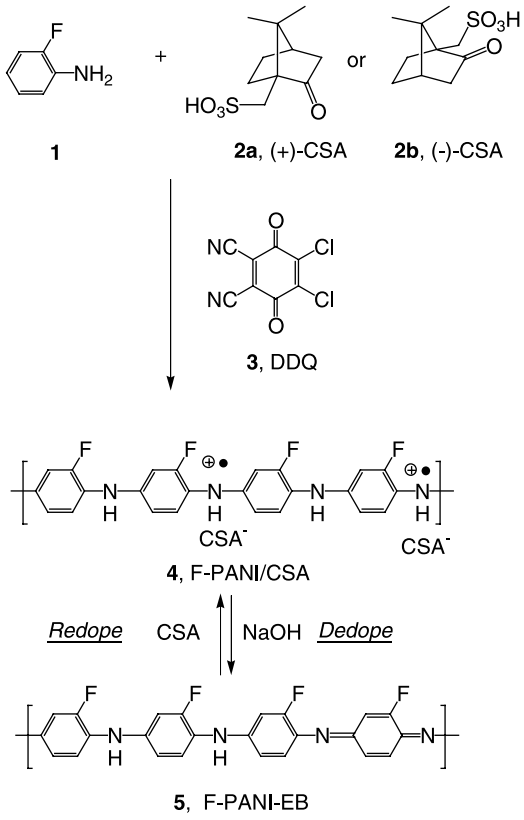


Fig. 5. The CD spectra of F-PANI/(+)-CSA (- - -) and F-PANI/(−)-CSA (···) in various solvents ((a) DMSO, (b) DMF, and (c) NMP). Inset: the CD spectra of PANI/(+)-CSA (- - -) and PANI/(−)-CSA (···) in the various solvents.

3. Results and discussion

Polymerization of 2-fluoroaniline (**1**) was carried out in a cosolvent of $CHCl_3$ and THF, in which DDQ (**3**) and (+)- or (−)-CSA (**2**) were employed as an electron acceptor and a chiral dopant, respectively, (Scheme 1). As a result, F-PANIs/(+)- and (−)-CSA were formed in good yields (**4a**: 58% and **4b**: 52%), and the dedoped F-PANI **5** was readily formed from F-PANIs/(+)- and (−)-CSA by treatment with 1 N NaOH aqueous, according to a common synthetic procedure for dedoped PANI. Incidentally, the polymerizations of monomer **1** with APS in 1 N HCl aqueous solution and in 1 N HCl solution including dodecylbenzene sulfonic acid (DBSA) hardly proceeded to yield the corresponding F-PANIs in 7 and 9% yields, respectively. This result indicated that the DDQ



Scheme 1.

mediated polymerization should be suitable for F-PANI synthesis. Additionally, the similar DDQ mediated polymerization of 2-trifluoromethylaniline in the presence of CSA in $CHCl_3$–THF did not propagate to give the corresponding oligomer at best.

The formations of the desired F-PANIs/(+)- and (−)-CSA (**4a** and **4b**) and F-PANI–EB (**5**) were confirmed by UV/vis/near-IR and FT-IR spectroscopes. Fig. 1(a) shows the UV/vis/near-IR spectra of F-PANI/(+)-CSA in *m*-cresol and F-PANI–EB in NMP. The spectrum of F-PANI/(+)-CSA exhibited the typical three absorption bands derived from ES form of PANI around 328, 404, and 940 nm, and no free-carrier tail was detected as the similar to that of PANI/(+)-CSA or (−)-CSA prepared by the DDQ mediated polymerization in organic solvent [23]. In addition, the absorption band around 328 nm should arise from π–π* electron transition within benzenoid segment, and the absorption bands, which have local maximum around 404 and 940 nm should be related to doping level (the protonation of the polymer backbone) and formation of polaron, respectively. Incidentally, the spectrum of F-PANI/(–)-CSA was inevitably similar to that of F-PANI/(+)-CSA. The spectrum of F-PANI–EB, which was prepared via dedoping of F-PANI/CSA, was measured in NMP and it indicated typical two absorption bands derived from EB form of PANI around 315 and 613 nm, which should be assigned to the π–π* transition of the phenyl ring and to the 'exciton' transition (n–π* transition), respectively. Each spectrum of F-PANI–EB formed from F-PANI/(+)-CSA or F-PANI/(−)-CSA was predictably same.

The spectra of PANI/(+)-CSA in *m*-cresol and PANI–EB in NMP, which were synthesized under the same reaction conditions to the cases of the present F-PANIs (**4** and **5**), were shown in Fig. 1(b). As previously reported [23], these spectra of PANI/(+)-CSA and PANI–EB showed the typical absorption bands for the corresponding ES and EB, around 350, 429, and 842 nm and around 330 and 642 nm, respectively. In addition, comparison between these spectra of F-PANI and PANI exhibited that these absorption bands assigned to the bands of F-PANI/(+)-CSA derived from the benzenoid π–π* transition and the bipolaron were slightly blue shifted, presumably due to the presence of the electron withdrawing group (fluorine group) in the polymer backbone. In addition, the red-shift of the absorption band based on the polaron band of F-PANI/(+)-CSA in comparison with that of PANI/(+)-CSA might be due to slightly rearrangement from the 'compact coil' to the corresponding 'extended coil'.

The FT-IR spectra of F-PANI/(+)-CSA and F-PANI–EB were shown in Fig. 2. The spectrum of PANI/(+)-CSA exhibited peaks at 1623, 1501, and 1287 cm^{-1}, probably due to stretching vibrations of the quinoid and benzenoid rings and C–N bond, respectively. The peaks at 1116 and 1045 cm^{-1} can be assigned to the asymmetric and symmetric O=S=O stretching vibrations indicating the existence of a SO_3^- group. The absorption peak at 1732 cm^{-1} can be assigned to the C=O stretching vibration of CSA. The peak depend on C–H stretching of the dopant appeared around 2953 cm^{-1}. In addition, no band due to unreacted and/or reduced DDQ was found in the FT-IR spectrum, indicating that the resulting PANIs/(+)-CSA or (−)-CSA can be absolutely purified by reprecipitation with acetone and maintained its ES state. The spectrum of PANI/(−)-CSA was also similar to that of F-PANI/(+)-CSA. The FT-IR spectrum of F-PANI–EB also showed characteristic peaks at 1603 and 1493 cm^{-1} derived from typical PANI–EB form, in which the peaks should be attributed to C=C ring stretching of quinoid and benzoid structure, respectively. Additionally, each spectrum of F-PANI–EB formed from F-PANI/(+)-CSA or (−)-CSA was inevitably same.

The elemental analysis of the dried F-PANI/(+)- or (−)-CSA showed that the molar ratio of the tetramer unit of emeraldine base and the CSA was approximately 1:2, which suggested that the F-PANI **4** was still fully doped by CSA.

Chiroptical properties of F-PANIs/(+)-CSA and (−)-CSA in *m*-cresol were investigated by means of CD measurement (Fig. 3(a)). As a comparison, the CD spectra of PANIs/(+)-CSA and (−)-CSA in *m*-cresol were shown in Fig. 3(b). In the case of PANI, the CD bands around 330 and 390 nm should be assigned as the bisignate exciton-coupled bands associated with the benzenoid π–π* transition absorption band seen at 350 nm in the UV/vis/near-IR spectra, and the CD band around 450 nm should be also assigned as the bisignate excition-coupled bands associated with the bipolaron absorption band seen at 435 nm in the UV/vis/near-IR spectra, as the similar to the previous reports [23]. The CD spectra of F-PANIs/(+)-CSA and (−)-CSA indicated mirror-imaged characteristic CD bands at wavelengths longer than 320 nm, which are clearly attributed to optical activity in the polymer backbones since there are no CD bands derived from (+)- and (−)-CSA in this region (Fig. 3(a)). As a comparison of the CD spectra between F-PANI and PANI, the following noteworthy different chiroptical property was observed along with blue-shifted CD absorption as the similar cases to the UV/vis/near-IR analyses. Thus, these CD spectra of the F-PANIs and the PANIs were almost mirror imaged: e.g. the CD spectrum of chiral PANI doped with (+)-CSA in *m*-cresol indicated a negative peak around 390 nm and a positive peak around 450 nm, while that of chiral-F-PANI doped with (+)-CSA exhibited a positive peak around 370 nm and a negative peak around 440 nm. Each opposite CD spectra were also observed in the measurements of F-PANI/(−)-CSA and PANI/(−)-CSA. In addition, the peak corresponding to the peak around 330 nm in the case of PANI (the benzenoid π–π* transition absorption band) was not clearly detected due to overlap of the CD peaks derived from the CSA counter anion, which exhibited the CD peak below ca. 320 nm in *m*-cresol.

Based on the interpretation of CD absorption bands of PANI/CSA, the CD band of F-PANI/CSA at 370 nm should be one of bisignate exciton-coupled CD bands associated with the benzenoid π–π* transition absorption band shown at 328 nm in the UV/vis/near-IR spectrum, and the band at 440 nm should be assigned as the bisignate exciton-coupled CD bands corresponding to the polaron absorption band at 404 nm in the UV/vis/near-IR spectrum. In addition, we failed to record the CD bands at the wavelengths longer than ca. 700 nm, since there is the strong absorption of F-PANIs/(+)- and (−)-CSA probably derived from the expected pair of bisignate exciton-coupled CD bands associated with the polaron absorption band in this region.

Since, the Cotton effects in the CD spectrum of F-PANI/(+)- or (−)-CSA are certainly derived from one-handed helical conformation of the chiral F-PANI as the similar to the case of chiral PANI, almost mirror imaged CD spectra of F-PANI and PANI, which are doped with each enantiomer of CSA clearly suggested that only introduction of a fluorine atom at ortho position of aniline drastically induced the CD sign inversion derived from the different chiral conformation, in which the chiral F-PANI/(+)- or (−)-CSA interestingly should have the opposite-handed helical form to chiral PANI/(+)- or (−)-CSA, respectively. In addition, the blue shifted CD absorption band of F-PANI/CSA, compared with that of chiral PANI/CSA, should be depended on the difference of these electronic states as similarly detected in these UV/vis/near-IR measurements of the chiral F-PANI and chiral PANI.

According to the Ikkala's report [46–48], there are four types of interactions in the *m*-cresol solution of PANI/CSA prepared by a common synthetic method: (1) the electrostatic bond of sulfonate ion of the CSA^- anion to the $HN^{\cdot+}$ site of PANI, (2) hydrogen bond of the carbonyl group of the CSA^- anion to NH site of PANI, (3) hydrogen bond of carbonyl group of the CSA^- anion to hydroxyl group of *m*-cresol, and (4) van der Waals interaction (π–π interaction) between phenyl rings of PANI and *m*-cresol. In particular, interaction of hydrogen

bond of carbonyl group of the CSA^- anion to hydroxyl group of *m*-cresol causes to stack of the phenyl rings, resulting in loss of the optical active conformation [i.e. change of non-planar aromatic rings of PANI (compact coil form, helical conformation) to more planar aromatic rings (expanded coil form, random coil conformation)].

Thus, compared with the case of PANI prepared according to the typical synthetic procedure, in the *m*-cresol solution of PANI prepared by our synthetic procedure, the interactions of (a) the electrostatic bond of sulfonate ion of the CSA^- anion to the $HN^{\cdot+}$ site of PANI and (b) hydrogen bond of the carbonyl group of the CSA^- anion to NH site of PANI should be stronger than the interactions of (i) hydrogen bond of carbonyl group of the CSA^- anion to hydroxyl group of *m*-cresol and (ii) van der Waals interaction (π–π interaction) between phenyl rings of PANI and *m*-cresol, leading to maintain the preferred one-sense helical screw. Then, the optical activity of the present chiral F-PANI/CSA in *m*-cresol should also mainly derived from these interactions among the F-PANI backbone, CSA, and *m*-cresol. The difference of conformation between chiral F-PANI and chiral PANI should be depended on the different interaction, presumably derived from the different electronic properties of the ringsubstituent (H vs. F) and/or the different steric hindrance. Additionally, in the present case of chiral F-PANI/CSA, there might also be a hydrogen bonding interaction among the fluorine atom, NH of PANI backbone, and/or hydroxy group of *m*-cresol, leading to induce such different chiroptical property from that of no fluorine-substituted chiral PANI/CSA.

Redoping of F-PANI–EB (**5**) was carried out in *m*-cresol by addition of *m*-cresol solution including an enantiomer of CSA, and the resulting UV/vis/near-IR and FT-IR spectra were identical with those of the initial PANI/CSA. To our surprise, the CD spectrum of the regenerated F-PANI/(+)-CSA in *m*-cresol was also identical with the initial CD spectra of the F-PANI/(+)-CSA, exhibiting CD bands at 374 and 438 nm (Fig. 4), albeit no CD absorption, which strongly implies (almost) loss of the optical active helical conformation (achiral conformation) at least in appearance, was clearly detected in the CD spectrum of F-PANI–EB in *m*-cresol. Thus, the 'memory' of their absolute configurations of the present chiral F-PANIs (**4a** and **4b**) prepared by DDQ mediated polymerization in organic solvents was confirmed during dedoping/redoping cycles in the solution state. The similar regeneration of the Cotton effect was also observed even in the case with F-PANI–EB, which was heated in NMP at 40 °C over 4 days.

We also reported that the dedoped and redoped PANI films of chiral PANI/CSA prepared with DDQ in organic media clearly indicated CD bands in the visible region (see Refs. [22–25]). The 'memory' of helicity in the PANI films was considered to be caused by the steric constraints in the solid state. However, regeneration behavior of CD bands during the redoping process in the *m*-cresol solution has not been reported until now. In addition, as described above, Havinga et al. [29] and Wallace et al. [30] have shown that solutions of PANI/(+)-CSA obtained by analogous doping of achiral EB with (+)-CSA in *m*-cresol never exhibit any visible CD bands. On the basis of these results, the present memory behavior of helicity in the chiral F-PANIs (**4a** and **4b**) in *m*-cresol might be considered as follows: a trace amount of chiral CSA, which was hardly detected by the CD analysis under the present conditions, might be remained in the dedoping state, and then the remaining CSA should work as a trigger to regenerate the chirarity.

Fig. 5 indicates the CD spectra of F-PANIs/(+)-CSA in several polar solvents, such as (a) DMSO, (b) DMF, and (c) NMP. Interestingly, these spectra exhibited different chiroptical properties from that in *m*-cresol: e.g. F-PANIs/(+)-CSA dissolved in *m*-cresol and these polar solvents showed almost mirror-imaged CD spectra, in which the spectra in these polar solvents indicated a negative peak around 370 nm and a positive peak around 440 nm, which should derived from the bisignate exciton-coupled CD bands of F-PANI/(+)-CSA. This different chiroptical property between the case in such polar solvent (DMSO, DMF, or NMP) and the case in *m*-cresol should mainly depend on the solvent nature. Thus, these polar solvents (DMSO, DMF, and NMP) are a hydrogen bonding acceptor, while *m*-cresol is a hydrogen bonding donor. In other words, such polar solutions, which can be act as a hydrogen bonding acceptor, should strongly perturb the above interactions between F-PANI and CSA, leading to the distinct different helical conformation.

The CD spectra of PANIs/(+)-CSA in DMSO, DMF, and NMP, which were prepared by our synthetic procedure with DDQ in organic media, were shown as the inset of Fig. 5. Incidentally, these spectra were not investigated previously. The spectra in DMSO and DMF indicated similar CD absorptions to that in *m*-cresol, which were differed from the case with F-PANI/(+)-CSA. Thus, the helical conformation of PANIs/(+)-CSA dissolved in DMSO and DMF might be maintained by the above interactions between PANI and CSA presumably due to the mentioned hydrogen and electrostatic bonds, although they should be partially perturbed by some bound DMSO or DMF molecules. Meanwhile, the spectra of PANI/(+)-CSA in NMP exhibited different chiroptical properties from those in *m*-cresol, DMSO, and DMF, where the CD sign inversion was also observed. The different CD spectra between F-PANI/(+)-CSA and PANI/(+)-CSA in the various solvents imply that a solvent effect on the PANI's chain largely affected the helical conformations and subsequent chiroptical properties, and that the solvent effect should be strongly dependent upon nature of various organic solvents as well as the structure of PANIs (the ringsubstituent, H vs. F), which should cause the different electronic properties and/or the different steric hindrance. In addition, the hydrogen and electrostatic bonds in the case of chiral F-PANI/CSA might be weak compared with that of chiral PANI/CSA, resulting to smoothly rearrangement of the helical conformation of chiral F-PANI/CSA backbones.

The all Cotton effects observed in the polar solvents such as DMSO, DMF, and NMP became loss within several hours, because dedoping of PANI/CSA should be necessarily carried out, presumably due to basicity of such polar solvent. Then, rearrangement of the chiral conformation of F-PANI/CSA to an

achiral conformation inevitably occurs in such solvents via absolutely deprotonation giving the corresponding EB. However, the similar Cotton effects to those of initial F-PANI/CSA were readily regenerated by addition of an enantiomer of CSA to these F-PANI-polar solvents, and the regenerated Cotton effect was maintained over 2 months.

To investigate real role of solvent effect on the helical conformations as well as chiroptical properties of F-PANIs/(+)-CSA and PANIs/(+)-CSA, CD spectra of F-PANI/(+)-CSA and PANI/(+)-CSA dissolved in cosolvent of *m*-cresol and DMSO at various volume ratios were also recorded (Fig. 6). To prepare the solution, *m*-cresol and DMSO at various volume ratios were well mixed firstly (total volume is 10 mL), and then a specific weight of PANIs/(+)-CSA was added under stirring. The mixture was magnetically stirred until formation of homogeneous solution. Fig. 6(a) shows the result of the F-PANI/(+)-CSA, in which the CD spectra of F-PANI/(+)-CSA dissolved in *m*-cresol/DMSO were significantly different from that of F-PANI/(+)-CSA dissolved in *m*-cresol. The intensities of bisignate exciton-coupled CD bands at 370 nm assigned to F-PANI/(+)-CSA solution in *m*-cresol decreased with increase of the amount of DMSO in the cosolvent, whereas those at 440 nm increased. In particular, the sign inversion of the CD absorptions were observed, when the ratio of DMSO in the *m*-cresol/DMSO cosolvent exceeded 10%. Fig. 6(b) also exhibits the result of the PANI/(+)-CSA, in which the different chiroptical behavior was observed. Thus, the intensities of the bisignate exciton-coupled CD bands at 450 nm assigned to PANI/(+)-CSA solution in *m*-cresol were also decreased with increase with the amount of DMSO in the *m*-cresol/DMSO cosolvent, while those at 400 nm also increased. However, the sign inversion of the CD spectra did not occur even when the ratio of *m*-cresol/DMSO was 80/20 (v/v). These results suggested that the helical conformation of F-PANI/(+)-CSA might be rather flexible than that of PANI/(+)-CSA, since the helical conformation of F-PANI/(+)-CSA was largely affected by solvent effect of DMSO. Incidentally, the similar sign inversion of CD spectra was not observed when the *m*-cresol/DMSO solutions were directly prepared by addition of DMSO to *m*-cresol solution of F-PANI/(+)-CSA, where *m*-cresol may relatively strongly interact with (+)-CSA and then the polymer backbone to prevent the access of DMSO molecules to F-PANI backbone.

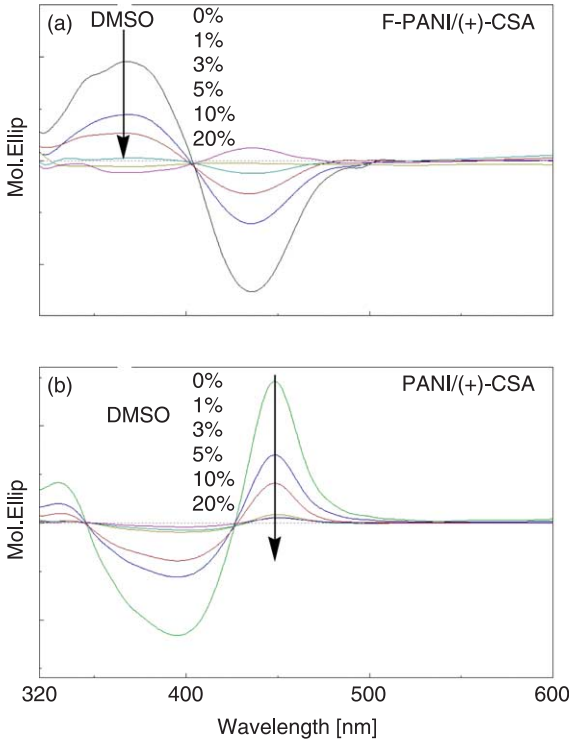


Fig. 6. (a) The CD spectra of F-PANI/(+)-CSA (F-PANI **4a**) dissolved in cosolvent of *m*-cresol and DMSO at various volume ratio, and (b) the CD spectra of PANI/(+)-CSA in the cosolvents.

4. Conclusions

An optically active fluoro-polyaniline, poly(2--fluoropolyaniline) (F-PANI), was smoothly prepared in organic media for the first time by using DDQ and (+)- or (−)-CSA as the electron acceptor and chiral initiator, respectively. The CD spectra of chiral F-PANI in *m*-cresol solution was interestingly found to be almost opposite to that of PANI, although the CD peaks assigned to the bisignate exciton-coupled CD bands of F-PANI/(+)-CSA derived from the benzenoid π–π* transition and the bipolaron were slightly blue shifted compared to those of PANI. Redoping of F-PANI–EB, which has achiral conformation, by addition of an enantiomer of CSA in *m*-cresol caused regeneration of the similar CD absorption bands to those of initial chiral-F-PANI/CSA. This result suggested that the helical conformation of F-PANI–EB prepared by the present synthetic procedure was unexpectedly memorized even during dedoping/redoping cycle in *m*-cresol solution. The CD spectra of F-PANI/(+)-CSA in various polar solvents such as DMSO, DMF, and NMP showed that the helical conformation was largely affected by the solvent effect, in which the sign inversion of the CD spectra was caused. The comparison with the similar investigation of the CD spectra of PANI/(+)-CSA in these polar solvents suggested that degree of the solvent effect leading to inversion of the helical conformation was drastically affected by the ringsubstituent (H vs. F), presumably due to the different electronic properties and/or the different steric hindrance between F-PANI and PANI backbones. Furthermore, comparison of the CD spectra of F-PANI/(+)-CSA dissolved in the cosolvent of *m*-cresol and DMSO at various volume ratio with those of PANI/(+)-CSA also imply that the helical conformation of F-PANI/(+)-CSA might be rather flexible than that of PANI/(+)-CSA. The present results are also interesting, since they enable us to tailor-synthesize a material with specially desired chiroptical properties along with better solution processability. In addition, right and left helical conformation can be readily and selectively synthesized with only using (1*S*)-(+)-CSA, which can be rather easily available than (1*R*)-(−)-CSA, by only change of the cosolvent. Further investigations about the nucleophilic aromatic substitution reaction of the present chiral

F-PANI with various functional groups are now in progress, and the results will be reported elsewhere.

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