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ARTICLE

Optical and Chiroptical Output of Anion Recognition Event Using Clustered Sulfonamide Groups Organized on Poly(phenylacetylene) Backbone

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ABSTRACT: Three-dimensionally organized sulfonamide groups have been demonstrated to show an anion signaling ability using poly(phenylacetylene) with L-aspartic acid and sulfonamide functionalities (**poly-1**). The polymerization of *N*-(4-ethynylphenylsulfonyl)-L-aspartic acid diethyl ester (**1**) was carried out using Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh_4) as a catalyst to afford **poly-1**. The biased helical conformation of **poly-1** was demonstrated through Cotton effects in the circular dichroism (CD) spectra. The addition of the anions including perchlorate (ClO_4^-), nitrate (NO_3^-), azide (N_3^-), and bromide (Br^-) anions had fundamentally no effect on both the CD and UV profiles of **poly-1**. On the other hand, the addition of the anions including acetate and fluoride anions (CH_3COO^- and F^-) into the **poly-1** solution intensified the CD responses of the **poly-1**, showing that the anion recognition of sulfonamide groups induced distinct changes in the poly(phenylacetylene) backbone. In addition, a distinct red shift was observed for **poly-1** in the presence of these two anions; i.e., the λ_{max} value for CH_3COO^- changed from 408 to 447 nm, and that for F^- changed from 408 to 482 nm. The guest specificity observed in the solution color change of **poly-1** with counteranions clearly correlated with the guest basicity.

Introduction

The anion reception chemistry,[1−6] which was brought to the mainstream after lagging behind several decades of cation host−guest chemistry, has recently been deeply explored under a wide range of topics including anion templation,[7] anion-responsive self-assembly,[8] anion transport,[9] ion-pair recognition,[10] and anion sensing.[11,12] Despite many anionic species playing indispensable roles in bioactive systems, the detection of anionic molecules still remains a challenge. Therefore, the development of anion sensors is an important subject for supramolecular chemists.

Among the many anion receptors, the sulfonamide group has emerged as a leading candidate for anion binding sites due to its high acidity of the NH protons as compared to other anion receptors such as amide or urea groups.[13,14] However, the isolated sulfonamide group has been scarcely utilized because the isolated sulfonamide group is not enough to accomplish a strong anion-recognition event.[15] For achieving the improved sulfonamide-based anion receptor, the most important trigger is the multipoint hydrogen bonding; a three-dimensional layout of the sulfonamide group is the key to creating the sulfonamide-based anion receptors with an adequate affinity or sensitivity.[16] Usually, scaffolds bearing stiff and directional properties such as calixarene,[17] the steroidal backbone,[9,18] the benzene ring,[19] and tris(2-aminoethyl)amine[20] are used to fix the sulfonamide groups in the three-dimensionally appropriate conformation for the host−guest interactions, which features the cooperative hydrogen bonding between the sulfonamide groups and anions. However, when we consider the sensory material, the utilization of such scaffold molecules suffer from their synthesis because we have to introduce chromophores into a scaffold, which is usually complicated from the viewpoint of organic synthesis.

Previously, we discovered that the *cis*-poly(phenylacetylene) with the urea anion receptors as a pendant (**PPA-Urea**) showed the anion responsive property.[21] In this system, the anion−urea host−guest interaction triggered a drastic color change of the polymer solution from pale yellow to red in response to guest anions such as CH_3COO^-, Cl^-, and Br^-. Furthermore, in the system, the guest selectivity of the **PPA-Urea** was different from the isolated urea groups provably due to a three-dimensional layout of urea anion receptors. More recently, we found that *cis*-poly(phenylacetylene) with the amide anion receptors as a pendant (**PPA-Amide**) showed high sensitivity toward anionic guests.[22] Importantly, the isolated amide group shows weak affinity toward anionic guests,[23] whereas the **PPA-Amide** showed a distinct anion-binding ability. Thus, we first discovered that the polyacetylene backbone served as not only a signaling component but also the structural scaffold for the anion recognition unit. Therefore, installation of a sulfonamide group onto the surface of the synthetic helical constructs would act as a facile anion sensing systems with unique guest selectivity.

We now report the synthesis of poly(phenylacetylene)s conjugated to natural α-amino acid through sulfonamide groups. In order to increase the solubility of the polymer, we employed L-aspartic acid as the pendant structure because we can introduce two functional groups easily at the carboxylic acid. This article presents (1) a three-dimensional sulfonamide organization clustered on poly(phenylacetylene) backbones and (2) the colorimetric detection of counteranion guests through the anion recognition of the sulfonamide groups (Scheme 1). The *N*-(4-ethynylphenylsulfonyl)-L-aspartic acid diethyl ester (**1**) was synthesized and then polymerized in $CHCl_3$ using a rhodium

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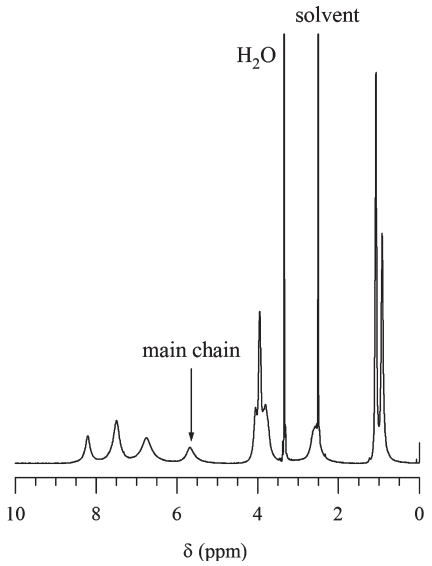


Figure 1. ^{1}H NMR spectrum of **poly-1** in DMSO-d_6.

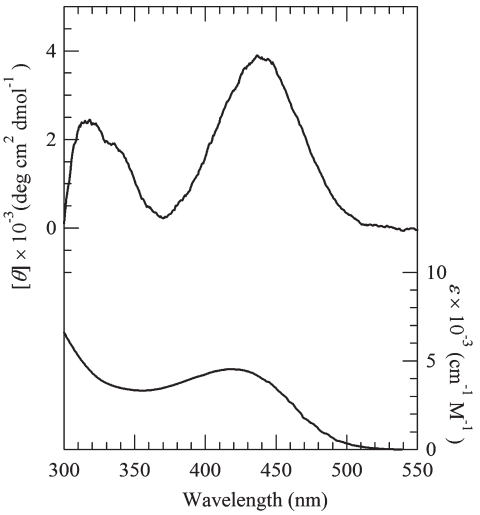
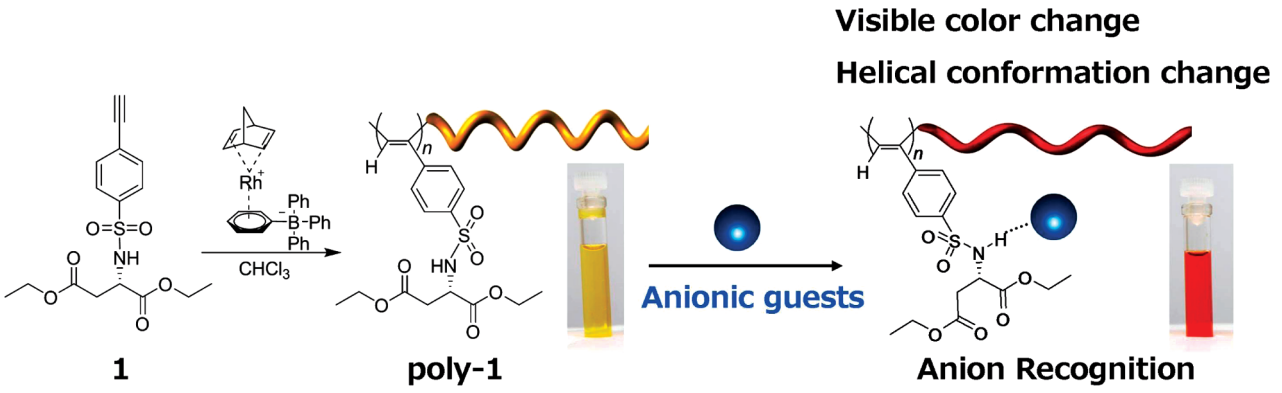


Figure 2. CD (upper) and absorption (lower) spectra of **poly-1** in $CHCl_3$ at 25 °C ([**poly-1**] = 1.0 mg mL^{-1}).

Scheme 1. Schematic Representation of the Anion Reception Triggered Helical Conformation Change of Polyacetylene Helicity at a Molecular Level



complex as the catalyst to yield the *cis*-poly(phenylacetylene)s bearing L-aspartic acid and sulfonamide groups (**poly-1**). The anion signaling properties of the obtained polymers were investigated using a series of ammonium salts with variable counteranions, as illustrated in Scheme 1.

Results and Discussion

Synthesis and Chiroptical Properties of Sulfonamide-Conjugated Poly(phenylacetylene). To provide a system for counteranion signaling, the *N*-(4-ethynylphenylsulfonyl)-L-aspartic acid diethyl ester (**1**) was prepared and polymerized using $Rh^+(2,5\text{-norbornadiene})[(\eta_6\text{-}C_6H_5)B^-(C_6H_5)_3]$ ($Rh(nbd)BPh_4$) as the catalyst. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of **poly-1** were 1.9×10^5 and 2.4, respectively. The ^{1}H NMR spectrum showed a sharp peak at 5.68 ppm, indicative of the *cis*-configuration in **poly-1** (Figure 1).[24,25]

The absorption and chiroptical properties of **poly-1** were investigated for the purpose of providing fundamental insights into the scaffold for anion binding. Figure 2 shows the circular dichroism (CD) and ultraviolet−visible (UV−vis) spectra of **poly-1** in $CHCl_3$ at 25 °C. Distinctive Cotton effects were observed in the UV−vis wavelength ranging from 300 to 550 nm where the π-conjugation of the polymer backbone typically appears. The Cotton effects in the polymer backbone absorption clearly indicated that the **poly-1** presents a biased, one-handed helical conformation directed by the pendant L-aspartic acid groups, which in turn showed that the embedded sulfonamide functionalities were helically arrayed along the polymer main chain.

As expected, the temperature and solvent have an effect on the conformational diversity of the helical scaffold due to the dynamic conformation of the **poly-1**.[26−30] Figure 3 shows the temperature dependence of the molar ellipticity at the first Cotton effect ($[\theta]_{first}$) of **poly-1** in $CHCl_3$. The magnitude of the Cotton effects increased as the temperature decreased, reflecting the enhanced thermodynamic stability of the dynamic helical structures at lower temperatures. The enhanced stability is presumably due to the suppression of the interconversion between the right- and left-handed helices at low temperatures. The thermodynamic stability also reflected the polarity and hydrogen-bonding ability of the solvents. The CD and UV−vis spectra of **poly-1** were recorded in various solvents such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), $CHCl_3$, DMSO, and THF (Figure 4). The CD profiles in HFIP and $CHCl_3$ were essentially mirror images of those found in DMSO and THF, thus showing that **poly-1** has a mirror-imaged, biased helical conformation in these solvents. Thus, **poly-1** is revealed to have a flexible main chain that was affected by external stimuli. Hence, an anion recognition event is supposed to have an effect on both the optical and chiroptical properties of **poly-1** rising from the π-conjugated helical polymer backbone (Scheme 1).

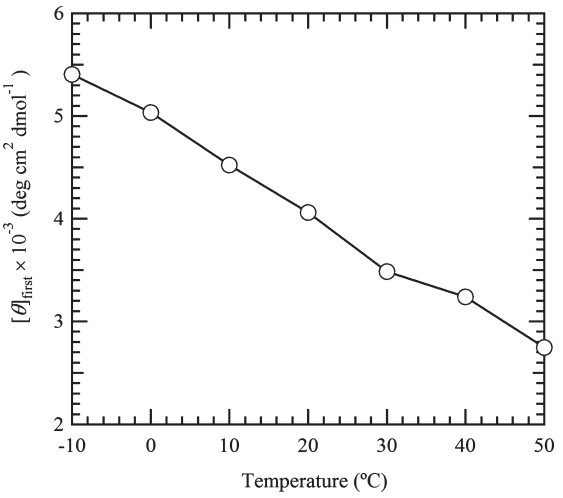


Figure 3. Temperature dependence of the molar ellipticity $[\theta]_{first}$ at the first Cotton effect of **poly-1** in $CHCl_3$ ([**poly-1**] = 1.0 mg mL^{-1}).

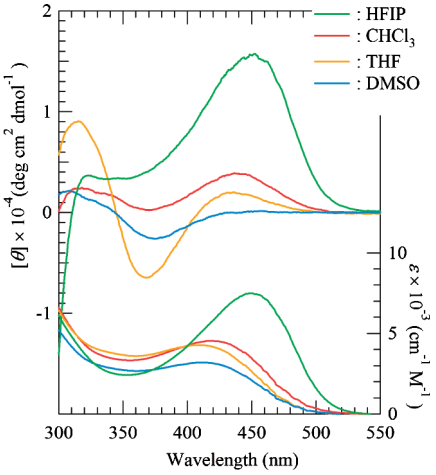


Figure 4. CD (upper) and absorption (lower) spectra of **poly-1** in various solvents at 25 °C ([**poly-1**] = 1.0 mg mL^{-1}).

Anion-Signaling Ability of Poly-1. To provide an insight into the anion recognition properties of the sulfonamide functionalized **poly-1**, the tetra-*n*-butylammonium fluoride (TBAF) was added to the solution of **poly-1** in THF because fluoride anion was well-known to make a stable complex with any kind of anion receptors due to its high basicity. On the basis of our previous study in which THF was the suitable solvent for the anion acquisition of **PPA-Urea**, we used THF as the solvent.[21] The combination of **poly-1** and TBAF promoted drastic changes in not only the Cotton effects but also the UV absorption (Figure 6A). To be more precise, in the absence of F^-, the clear split-type Cotton effects appeared in the range from 300 to 500 nm (Figure 6A). On the other hand, in the presence of F^-, the large Cotton effects newly appeared in the range from 450 to 600 nm (Figure 6A). Accordingly, a distinct red shift was observed in the UV spectra, which corresponded to the shift in the λ_{max} from 408 nm (blank) to 482 nm. This distinct discrepancy in the λ_{max} well reflected the color change of the polymer solution (Figure 6B). Thus, the chiral adjustment also provided the helical backbone with effective π-conjugation properties and thus the dramatic differences in the UV−vis profiles. To the best of our knowledge, except for a few examples, it is still rare that the host−guest interaction induces simultaneous changes in the helical conformation and the solution color for the poly (phenylacetylene) derivatives.

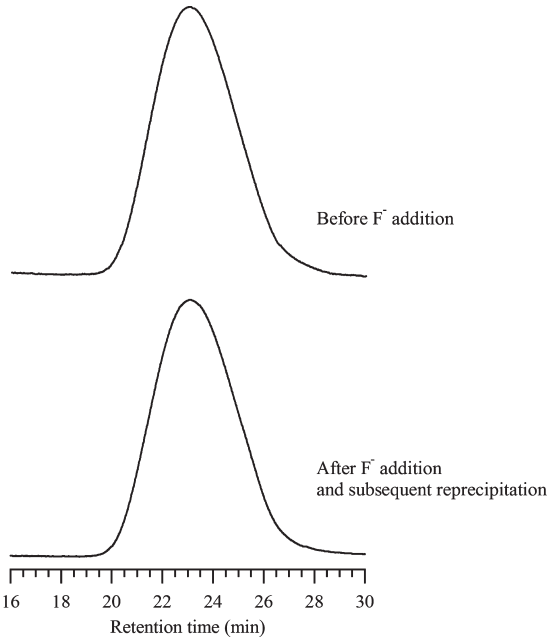


Figure 5. SEC traces of **poly-1** before (upper) and after (lower) the sulfonamide−anion interaction with 5 equiv of TBAF in THF at room temperature (eluent; DMF containing 0.01 M LiCl).

To exclude the possibility that changes in the CD and UV profile were due to the changes in the chemical structure of **poly-1**, additional SEC, NMR, and CD experiments were performed. First, after 5 equiv of TBAF was added to the THF solution of **poly-1**, we gathered the **poly-1** using the reprecipitation technique. We then carried out SEC measurements of the recovered polymer (lower trace in Figure 5), and no distinct difference from the original SEC trace (upper trace in Figure 5) was observed, showing that the addition of TBAF provided no cross-linking and cleavage of the polymer backbone. We checked the direct chemical structure of **poly-1** in THF-d_8 with 1 equiv of TBAF, which revealed that no distinct peaks due to degradation were observed (see Supporting Information).[31] Furthermore, we carried out the CD and UV−vis measurements of **poly-1** in the presence of TBAF in THF/MeOH (95/5, v/v) (Figure 6A). As a result, just 5% of MeOH was enough to switch off the drastic color and chiroptical property change of **poly-1** triggered by the F^- addition, meaning that sulfonamide−anion interaction played a crucial role in the drastic color change. These results strongly supported the fact that intensified Cotton effects and the drastic color changes were triggered by the sulfonamide−anion interaction through the hydrogen bonding and/or deprotonation process.[13,32−34] In order to give an insight into the mechanistic aspect for the color change of **poly-1**, we carried out the ^{1}H NMR titration experiment. Because of the extreme broadening of **poly-1** in the presence of the TBAF, we measured the ^{1}H NMR spectra of monomer **1** in THF-d_8 in the absence and the presence of various amounts of TBAF (see Supporting Information, Figures S-13 and S-14). On the basis of the fact that peaks due to phenyl ring of **1** shifted upfield with increasing amount of TBAF, the sulfonamide−anion interaction was estimated to be through the deprotonation process.[13,33,35,36]

To investigate the guest selectivity of the anion recognition properties of **poly-1**, we employed a series of the anions guests as their tetra-*n*-butylammonium salts, including fluoride (TBAF), acetate (TBAA), nitrate (TBAN), azide ($TBAN_3$), perchlorate ($TBAClO_4$), and bromide (TBABr).[37]

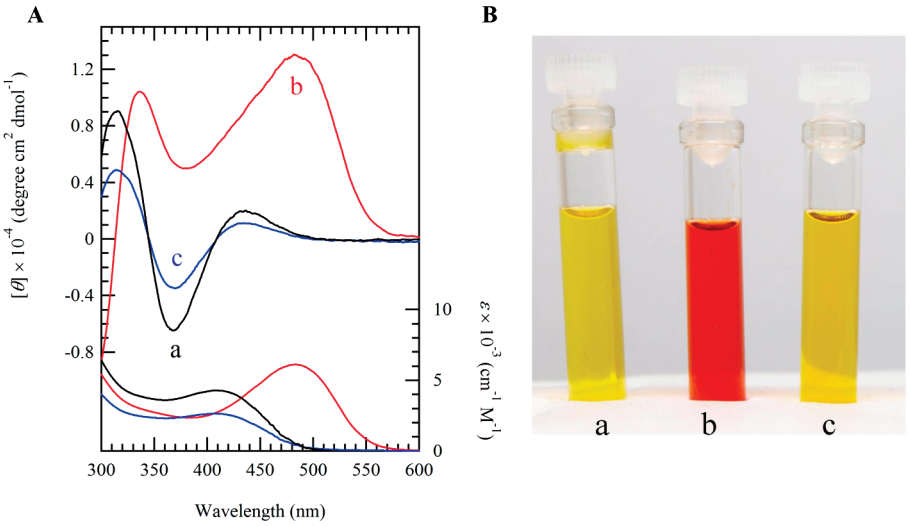


Figure 6. (A) CD (upper) and absorption (lower) spectra of **poly-1**: (a) in THF at 25 °C, (b) with 5 equiv of TBAF in THF at 25 °C, (c) with 5 equiv of TBAF in THF/MeOH (95/5, v/v) at 25 °C. (B) Visible color of **poly-1** in each condition. The experimental conditions were as follows: the concentration of monomeric units of **poly-1** was 2.8 mmol L^{-1}, and the ratio of guest to monomeric unit in **poly-1** was 5.

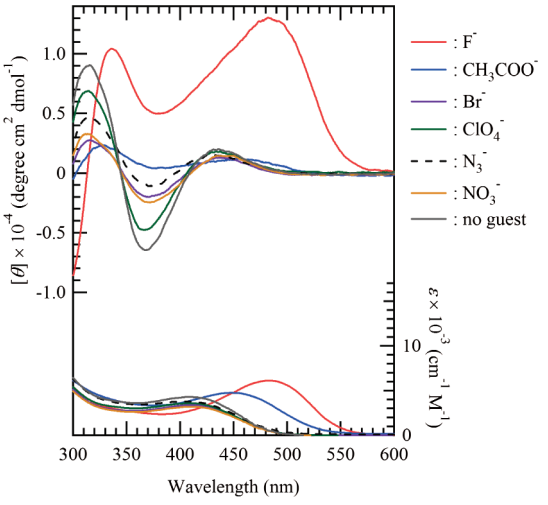


Figure 7. CD (upper) and absorption (lower) spectra of **poly-1** in THF at 25 °C with various guest molecules ([monomeric units of **poly-1**] = 2.8 mmol L^{-1} and [guest]/[monomeric unit in **poly-1**] was a saturated value).

The variable guest experiments highlighted the specific recognition ability of **poly-1** as a consequence of the well-defined registration of the sulfonamide acceptors. As expected, the addition of a series of anions demonstrated the breadth and diversity of the CD spectra (Figure 7). Although the anions including perchlorate (ClO_4^-), nitrate (NO_3^-), azide (N_3^-), and bromide (Br^-) induced small changes in the Cotton effects, no distinct red shift was observed in the absorption spectra. On the other hand, the combination of **poly-1** and acetate (CH_3COO^-) and fluoride (F^-) anions promoted significant changes in both the Cotton effects and the UV absorption (for the solution color change, please see Figure 8). To be more precise, in the CD spectra, the addition of CH_3COO^- induced positive new Cotton effects (1.2×10^3 deg cm^2 $dmol^{-1}$) at 457.5 nm, and that of F^- also produced a positive one (1.3×10^4 deg cm^2 $dmol^{-1}$) at 482 nm. Although the magnitude of the newly appearing Cotton effect for CH_3COO^- was smaller than that for F^-, it is a clear observation that only these two anions (CH_3COO^- and F^-) produced a new Cotton effect. In addition, a distinct red shift was observed; the λ_{max} value for CH_3COO^- changed from 408 to 447 nm, and that for F^- changed from 408 to 482 nm. Thus, the system caused a distinct sulfonamide−anion interaction for only CH_3COO^- and F^-.

We finally focused on the investigation about what factor dictates the guest signature in the system. In the field of anion reception chemistry, the basicity of the anionic guest molecules is one of the most important factors to determine the host−guest interaction of the anion binding site with anionic

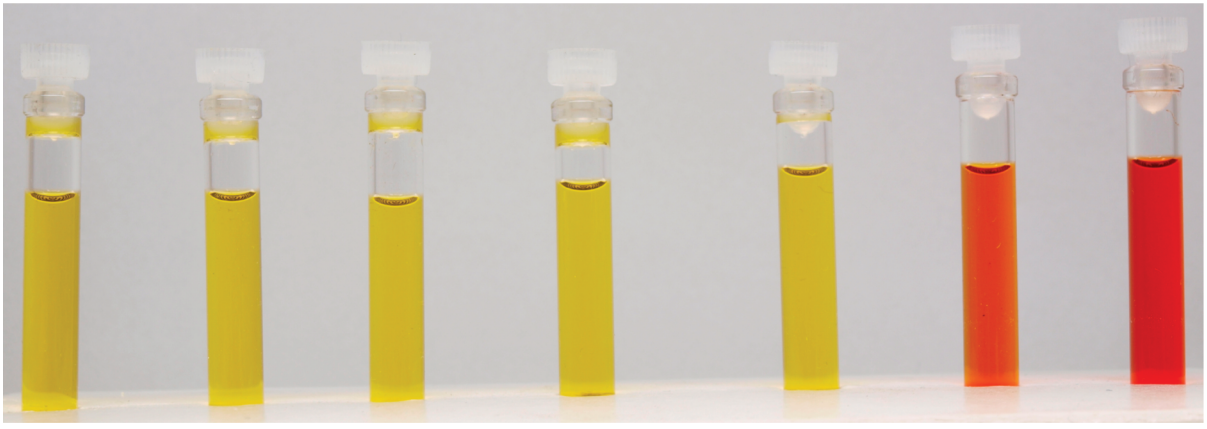


Figure 8. Visible color changes upon the addition of various anionic guests (from left to right: blank, perchlorate, nitrate, bromide, azide, acetate, and fluoride).

species.[34,36,38] The anion guests can be roughly classified into two groups, namely (1) basic anions including CH_3COO^- and F^- and (2) less basic anions including ClO_4^-, NO_3^-, N_3^-, and Br^-. As precisely studied by many researchers, the higher the basicity that the anion gets, the stronger a host−guest interaction of anionic guest with anion receptors generally tends to get. As expected, a distinct relationship was obviously observed between the basicity and color change in the polymer solution. To be more precise, less basic anions did not affect both the optical and chiroptical properties of **poly-1**. On the other hand, two basic anions, namely CH_3COO^- and F^-, induced the drastic visible color changes (vide supra), thus showing that the guest selectivity was essentially governed by the basicity of the anionic guests. Therefore, we succeeded in achieving the anion signaling using **poly-1** and revealed that the guest specificity observed in the anion responsive property of **poly-1** with counteranions clearly correlated with the guest basicity.

Conclusions

In summary, we have demonstrated the colorimetric and chiroptical detection of anion guests using *cis*-poly(phenylacetylene) with the sulfonamide and L-aspartic acid functionalities (**poly-1**). By three-dimensionally organizing sulfonamide groups, it is possible to give the anion sensing property to the polyacetylene derivatives. The guest selectivity of **poly-1** was obviously turned out to relate with the basicity of anionic guest molecules. To the best of our knowledge, this is the first demonstration of giving anion signaling property toward a π-conjugated polymer using its main chain as a chromophore and the sulfonamide group as an anion recognition unit.

Experimental Section

Materials. The chloroform for the polymerization was purchased from Kanto Chemicals Co., Inc., and distilled under an Ar atmosphere in the presence of CaH_2. The 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was kindly supplied from the Central Glass Co. The tetra-*n*-butylammoniums azide ($TBAN_3$), nitrate (TBAN), fluoride (TBAF), bromide (TBABr), and acetate (TBAA) were purchased from the Sigma-Aldrich Chemical Co., Inc., and used as received. The 4-iodobenzenesulfonyl chloride and tetra-*n*-butylammonium perchlorate ($TBAClO_4$) were available from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan). The triphenylphosphine was available from Kanto Chemicals and used after recrystallization from dichloromethane/diethyl ether. Bis(triphenylphosphine)palladium(II) dichloride was purchased from Aldrich Chemicals Co., Inc., and used as received. The (trimethylsilyl)acetylene was kindly supplied from Shinetsu Chemical Co., Ltd. (Tokyo, Japan). The Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh_4) was prepared in accordance with a previous study.[25]

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded using JEOL JNM-A400II and JEOL-ECP-400 instruments. The size exclusion chromatography (SEC) was performed at 40 °C using a Jasco high-performance liquid chromatography (HPLC) system (PU-980 Intelligent HPLC pump, CO-965 Column oven, RI-930 Intelligent RI detector, and Shodex DEGAS KT-16) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 5 μm; exclusion limit, 4×10^4) and a Shodex Asahipak GF-7 M HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 9 μm; exclusion limit, 4×10^7) in DMF containing lithium chloride (0.01 M) at a flow rate of 0.4 mL min^{-1}. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. The circular dichroism (CD) spectra were measured in a 1 mm path length using a Jasco J-720 spectropolarimeter. The melting points of the compounds were determined by the differential scanning calorimetry (DSC) analysis using a Bruker AXS DSC 3100 SA under a nitrogen atmosphere. The optical rotations were measured with a Jasco DIP-1000 digital polarimeter.

Synthesis of the *N*-(4-Iodophenylsulfonyl)-L-aspartic Acid Diethyl Ester. To a stirred mixture of aspartic acid diethyl ester (5.00 g, 26.4 mmol) and triethylamine (7.3 mL) in CH_2Cl_2 (70 mL) was slowly added a solution of 4-iodobenzenesulfonyl chloride (8.78 g, 29.0 mmol) in CH_2Cl_2 (25 mL) under a N_2 atmosphere, and the reaction mixture was stirred for 1 h. After the conversion of starting material was checked by ^{1}H NMR, solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, and the solution was washed with HCl aqueous solution, $NaHCO_3$ aqueous solution, and water. The extracts were dried using anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/2, v/v) to give *N*-(4-iodophenylsulfonyl)-L-aspartic acid diethyl ester as white solid. Yield: 9.91 g (82.4%); mp 70 °C; $[\alpha]_D = +37.6°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, J = 7.08 Hz, 3H, −$OCHH_2CH_3$), 1.24 (t, J = 7.14 Hz, 3H, −$OCHH_2CH_3$), 2.81−3.01 (m, 2H, EtOCO−CH_2−CH−NH), 4.02−4.17 (m, 5H, −OCH_2CH_3 and CH_3CH_2O−CH−NH), 5.75 (d, J = 8.29 Hz, 1H, SO_2NH), 7.59 (d, J = 8.54 Hz, 2H, Ar), 7.87 (d, J = 8.72 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.1, 37.9, 52.2, 61.3, 62.3, 66.6, 100.2, 128.65, 138.3, 139.6, 169.7, 170.2. Anal. Calcd for $C_{14}H_{18}O_6NSI$ (455.27): C, 36.93; H, 3.99; N, 3.09; S, 7.04. Found: C, 36.95; H, 3.93; N, 3.13; S, 7.12.

Synthesis of the *N*-[4-(Trimethylsilylethynyl)phenylsulfonyl]-L-aspartic Acid Diethyl Ester. To a mixture of *N*-(4-iodophenylsulfonyl)-L-aspartic acid diethyl ester (9.20 g, 20.2 mmol), triphenylphosphine (87.6 mg, 334 μmol), bis(triphenylphosphine)palladium(II) dichloride (112 mg, 160 μmol), and copper(I) iodide (91.4 mg, 480 μmol) in degassed DMF/NEt_3 (28 mL /80 mL) was added (trimethylsilyl)acetylene (4.80 mL, 34.1 mmol) under a nitrogen atmosphere. After stirring at room temperature for 22 h, reaction mixture was evaporated under reduced pressure. The residue was dissolved in dichloromethane, and the solution was washed with HCl aqueous solution. The extracts were dried using anhydrous $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica gel with ethyl acetate/hexane (1/2, v/v) to give *N*-[4-(trimethylsilylethynyl)phenylsulfonyl]-L-aspartic acid diethyl ester as pale yellow syrup. Yield: 8.53 g (99.2%); $[\alpha]_D = +53.5°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 9H, −$SiCH_3$), 1.14 (t, J = 7.14 Hz, 3H, −$OCHH_2CH_3$), 1.24 (t, J = 7.15 Hz, 3H, −$OCHH_2CH_3$), 2.79−2.98 (m, 2H, EtOCO−CH_2−CH−NH), 4.03−4.16 (m, 5H, −OCH_2CH_3 and CH_3CH_2O−CH−NH), 5.83 (d, J = 8.23 Hz, 1H, SO_2NH), 7.56 (d, J = 8.66 Hz, 2H, Ar), 7.81 (d, J = 8.66 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ −0.3, 13.8, 14.0, 37.9, 52.1, 61.2, 62.2, 98.5, 103.0, 127.0, 127.9, 132.3, 139.2, 169.7, 170.1. Anal. Calcd for $C_{19}H_{27}O_6NSSi$ (425.57): C, 53.62; H, 6.39; N, 3.29; S, 7.53. Found: C, 53.33; H, 6.42; N, 3.21; S, 7.43.

Synthesis of the *N*-(4-Ethynylphenylsulfonyl)-L-aspartic Acid Diethyl Ester (1). To a solution of *N*-[4-(trimethylsilylethynyl) phenylsulfonyl]-L-aspartic acid diethyl ester (7.76 g, 18.2 mmol) in MeOH (6.0 mL) and THF (300 mL) was added 1 M TBAF THF solution (6.0 mL, 6.0 mmol). After stirring at room temperature for 1 h, the reaction was quenched by saturated NH_4Cl aqueous solution. The solvent was removed under vacuum. The residue was treated with water and extracted with dichloromethane, and the extracts were dried over anhydrous $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel with ethyl acetate/hexane (2/3, v/v) to give **1** as a pale yellow solid. Yield: 5.73 g (89.1%); mp 74 °C; $[\alpha]_D = +47.1°$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.13 (t, J = 7.26 Hz, 3H, −$OCHH_2CH_3$), 1.24 (t, J = 7.12 Hz, 3H, −$OCHH_2CH_3$),

2.80−3.00 (m, 2H, EtOCO−CH_2−CH−NH), 3.27 (s, 1H, −C≡CH), 4.01−4.19 (m, 5H, −OCH_2CH$_3$ and CH$_3$CH_2O−CH−NH), 5.81 (d, J = 8.36 Hz, 1H, SO$_2$NH), 7.60 (d, J = 8.48 Hz, 2H, Ar), 7.84 (d, J = 8.42 Hz, 2H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 14.0, 37.9, 52.2, 61.2, 62.2, 80.7, 81.9, 126.9, 127.1, 132.6, 139.8, 169.7, 170.2. Anal. Calcd for $C_{16}H_{19}O_6NS$ (353.39): C, 54.38; H, 5.42; N, 3.96; S, 9.07. Found: C, 54.33; H, 5.48; N, 3.94; S, 9.05.

Polymerization. The polymerization of **1** was carried out in a dry flask under an argon atmosphere. Under argon atmosphere, **1** (1.0 g, 2.8 mmol) was weighed into a flask and dissolved in dry $CHCl_3$ (26.3 mL). To the solution was added a solution of Rh(nbd)BPh$_4$ (20.1 mg, 39.1 μmol) in dry $CHCl_3$ (2.0 mL). After stirring at room temperature for 24 h, triphenylphosphine (85.4 mg, 326 μmol) was added to the reaction mixture. The solution was concentrated and then poured into a large amount of acetonitrile. The precipitate was purified by reprecipitation using diethyl ether and then dried under reduced pressure to give **poly-1** as a yellow powder. Yield: 949 mg (94.9%). $M_n = 1.9 \times 10^5$, $M_w/M_n = 2.4$.

CD Measurements. CD and UV−vis spectra were measured in a 1 mm quartz cell. The concentration of polymer was calculated on the basis of the monomeric units (2.8 mmol L^{-1}).

SEC Measurement of Figure 5. After 5 equiv of TBAF was added to the solution of **poly-1**, we gathered the polymer by reprecipitation technique. We then carried out SEC measurements of the recovered polymer again.

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Supporting Information Available: Detailed CD titration experiments of the **poly-1** and ^{1}H NMR spectra of **1** in THF-d_8 in the absence and presence of various amounts of TBAF. This material is available free of charge via the Internet at http://pubs.acs.org.

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