# Efficient Anion Recognition Property of Three Dimensionally Clustered Amide Groups Organized on a Poly(phenylacetylene) Backbone

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ABSTRACT: Three-dimensionally organized amide groups have been demonstrated to show a high sensitivity toward anionic guests using poly(phenylacetylene)s with L-leucine and amide functionalities (**poly-PA-Leu**). The **poly-PA-Leu** was prepared from the *N*-(4-ethynylphenylcarbonyl)-L-leucine ethyl ester (**PA-Leu**) using $Rh^+$(2,5-norbornadiene)[($\eta^6$-$C_6H_5$)$B^-$($C_6H_5$)$_3$] (Rh(nbd)$BPh_4$) as a catalyst. The biased helical conformation of **poly-PA-Leu** was demonstrated through Cotton effects in the circular dichroism (CD) spectra. The addition of ammonium salts including acetate, fluoride, benzoate, azide, and bromide ($CH_3COO^-$, $F^-$, $C_6H_5COO^-$, $N_3^-$, and $Br^-$, respectively) into the **poly-PA-Leu** solution intensified the CD responses of the **poly-PA-Leu**, indicative of the polyacetylene helicity changes triggered by anion recognition of the amide groups. The efficient anion binding was observed for **poly-PA-Leu** with $CH_3COO^-$, whose apparent binding constant was estimated to be $1.1 \times 10^3$ ($mol^{-1}\cdot L$). On the other hand, the anions including perchlorate ($ClO_4^-$), nitrate ($NO_3^-$), chloride ($Cl^-$), and iodide ($I^-$) had essentially no effects on both the CD and UV profiles of **poly-PA-Leu**. The guest specificity observed in the CD spectra of **poly-PA-Leu** with counteranions clearly correlated with the guest-basicity.

## Introduction

Recently, in nature or biological processes, the anion recognition event has been discovered to play important and sometimes crucial roles such as DNA recognition, molecular transport, $Cl^-$ channel, and so on. Despite the great importance of anion recognition in nature, on the other hand, in artificial molecular recognition, the molecular design and synthesis of anion receptor still remains a challenging field of chemistry. Therefore, a recent topic in supramolecular chemistry has focused on the host−guest chemistry of anionic species and its applications such as anion templation,[1] anion triggered self-assembly,[2,3] selective ion transport,[4,5] ion-pair recognition,[6] and anion sensing.[7,8] Anion reception chemistry is now becoming popular after a few decades of host−guest chemistry for cationic species. Hence, the molecular design and the synthesis of anion receptors with a high affinity or unique guest signature still remains a challenging task.[9−14]

Among the many anion receptors, the amide group is one of the most widely utilized and promising anion binding sites[15,16] due to its importance even in the naturally occurring anion receptors such as phosphate- or sulfate-binding proteins,[17,18] whereas the isolated amide group possesses a weak affinity toward anionic guests.[19] To achieve an improved amide-based anion receptor, the most important trigger is the multipoint hydrogen-bonding; a three-dimensional layout of the amide group is the key to creating the amide-based anion receptors with a moderate affinity or sensitivity. Usually, scaffolds bearing stiff and directional properties such as calixarene, the steroidal backbone, the cyclic oligo-peptide skeleton, and tris(2-aminoethyl)amine, are used to fix the amide group in the three-dimensionally appropriate conformation for host−guest interactions,[13,15] which features the cooperative hydrogen bonding between the amide groups and anions.

For achieving a noticeable sensitivity toward anion recognition event signaled by certain chemical information, the helical constructs developed from synthetic polymers emerge as the leading candidate, because the helical organization of certain binding sites along the synthetic helical constructs can significantly amplify the guest binding event by changes in the dynamic helical conformation as reported by Yashima and coworkers.[20,21] Furthermore, the helical construct features stiff backbones[22−25] that can fix the amide groups along the polymer main chain in a helical fashion, which should be important for amide-based anion receptors (vide supra). In fact, we previously reported that the *cis*-poly(phenylacetylene) with the urea and L-leucine functionalities as pendant showed the anion responsive property.[26] This finding implied that polyacetylene backbone could act as a facile scaffold for anion recognition system. Therefore, installation of an amide group onto the surface of the synthetic helical constructs would act as a facile anion reception systems.

We now report the well-defined structural design for the amide-based anion receptor with a high sensitivity using poly(phenylacetylene) conjugated to L-leucine through amide groups. The system demonstrates (1) a chiral translation from the pendant leucine to the poly(phenylacetylene) backbones, resulting in the three-dimensional amide organization, and (2) the host−guest interaction between amide groups with counteranion guests and outputting the information about the anion recognition event as the modulation in the helical conformation change (Scheme 1). The *N*-(4-ethynylphenylcarbonyl)-L-leucine ethyl ester (**PA-Leu**) was synthesized and then polymerized in $CHCl_3$ using a rhodium complex as the catalyst to yield the *cis*-poly(phenylacetylene) bearing L-leucine and amide groups (**poly-PA-Leu**). The anion recognition properties were investigated using a series of ammonium salts with variable counteranions, as illustrated in Scheme 1.

## Results and Discussion

**Synthesis and Chiroptical Properties of L-Leucine-Conjugated Poly(phenylacetylene).** To provide a system for counteranion binding, *N*-(4-ethynylphenylcarbonyl)-L-leucine ethyl ester (**PA-Leu**) was prepared and polymerized using $Rh^+$(2,5-

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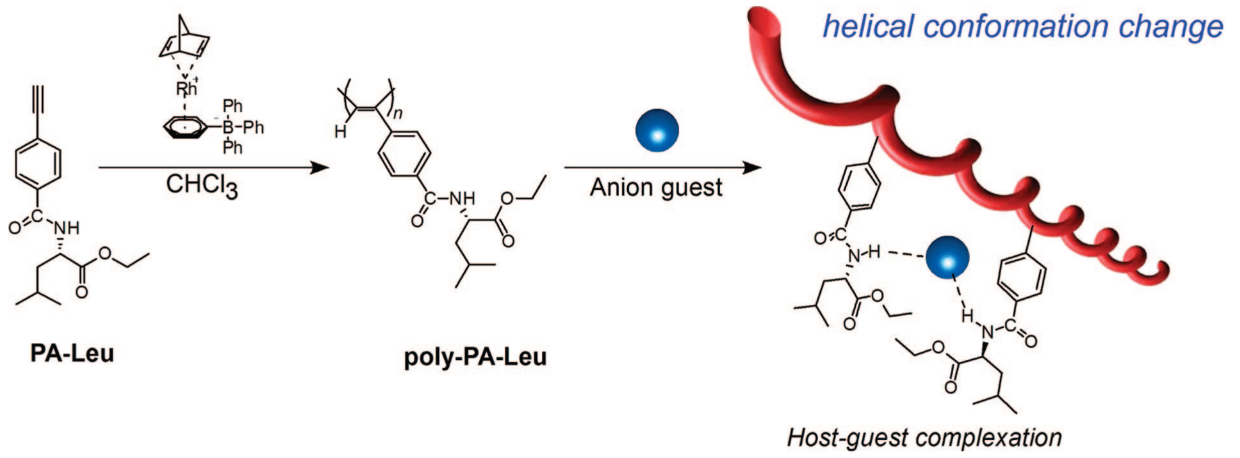
**Scheme 1. Schematic Representation of Anion-Reception Triggered Chiral Adjustment of Polyacetylene Helicity at the Molecular Level**



norbornadiene)[($\eta^6$-$C_6H_5$)$B^-$($C_6H_5$)$_3$] (Rh(nbd)$BPh_4$) as the catalyst.[27] The number average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) of the obtained polymer were $2.8 \times 10^5$ and 2.8, respectively. The $^1$H NMR spectrum of the obtained polymer showed a sharp peak at 5.94 ppm, indicative of the propensity of the *cis*-configuration in the obtained polymer (Figure 1). Thus, the obtained polymer was assigned to the poly(phenylacetylene) bearing amide group as the pendant, **poly-PA-Leu**.

The absorption and chiroptical properties of **poly-PA-Leu** 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-PA-Leu** in DMF at room temperature. Distinctive Cotton effects were observed in the UV−vis wavelength ranging from 300 to 550 nm where the $\pi$-conjugation of the polymer backbone typically appears. The Cotton effects in the polymer backbone absorption clearly indicated that **poly-PA-Leu** presented a biased, one-handed helical conformation directed by the pendant L-leucine groups, which thus showed that the embedded amide functionalities were helically arrayed along the polymer main chain.

As expected, various temperatures and solvents provided the conformational diversity of the helical scaffold due to the dynamic conformation of **poly-PA-Leu**. Figure 3 shows the variable temperature CD and UV−vis experiments in DMF. 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 was 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-PA-Leu** were recorded in various solvents such as DMF, methanol, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and THF (Figure 4). The CD profiles in DMF and methanol were essentially mirror images of that found in HFIP, thus showing that **poly-PA-Leu** has a mirror-imaged, biased helical conformation in these solvents due to the dynamic helical nature of the polyacetylene main chain. In clear contrast, it was found that **poly-PA-Leu** exhibited a very weak UV−vis absorption and no Cotton effect in THF in the range from 300

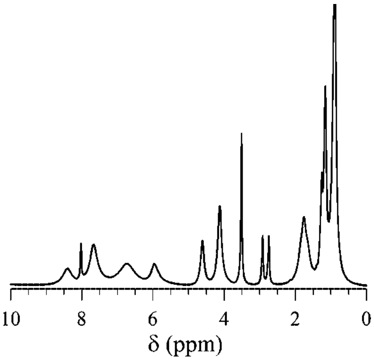


**Figure 1.** $^1$H NMR spectrum of **poly-PA-Leu** in DMF-$d_7$.

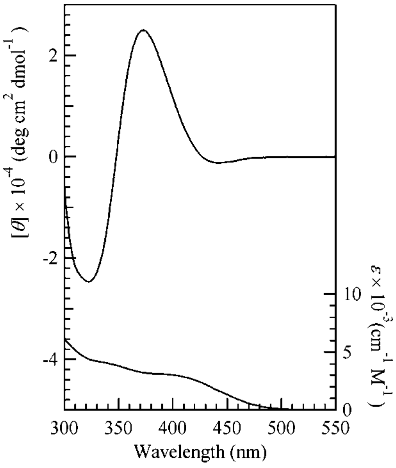


**Figure 2.** CD (upper) and absorption (lower) spectra of **poly-PA-Leu** in DMF at 25 °C ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$).

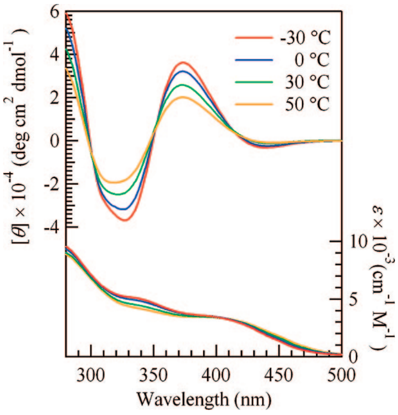


**Figure 3.** CD (upper) and UV absorption (lower) spectra of **poly-PA-Leu** in DMF at various temperatures ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$).

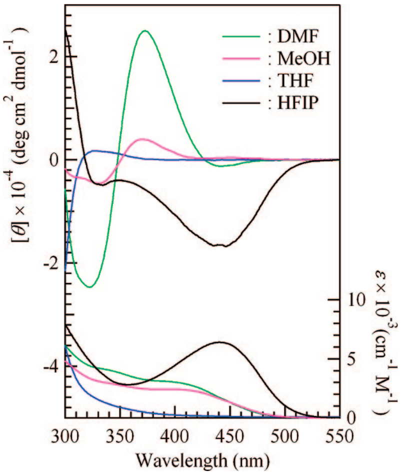


**Figure 4.** CD (upper) and absorption (lower) spectra of **poly-PA-Leu** in various solvents at 25 °C ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$).

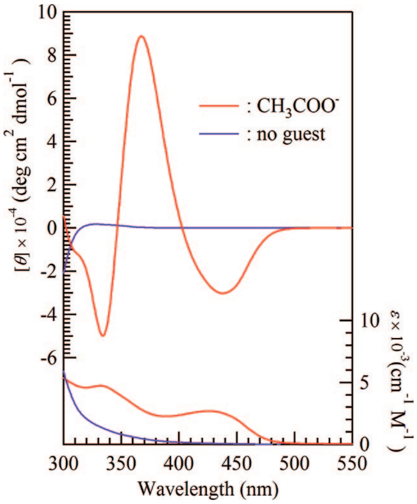


**Figure 5.** CD (upper) and absorption (lower) spectra of **poly-PA-Leu** in THF (blue) with 10 equivalents of TBAA (red) at 25 °C ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$ and [TBAA]/[monomeric unit in **poly-PA-Leu**] = 10).

to 500 nm. The empty profiles in THF demonstrated a nonbiased helical conformation of **poly-PA-Leu** that features equal contents of the right- and left-handed helical structures. Given the perturbation of the CD profiles, the anion recognition experiments were performed in THF. The acquired recognition between the amide groups and the counteranion makes it possible to observe the apparent discrepancy in the chiroptical property of **poly-PA-Leu**, provided that the host−guest interactions can effectively cause a biased helical conformation (Scheme 1).

**The Anion-Binding of poly-PA-Leu.** To provide a preliminary insight into the anion recognition properties of the amide functionalized **poly-PA-Leu**, tetra-*n*-butylammonium acetate (TBAA) was added to the solution of **poly-PA-Leu** in THF because the acetate anion is well-known to form a stable complex with many kinds of anion receptors due to the high basicity of acetate anion. The combination of **poly-PA-Leu** and TBAA promoted a drastic induction in the Cotton effects (Figure 5). The apparent distinction in the UV−vis and CD spectra demonstrated that the anion recognition using **poly-PA-Leu** provided the chiral adjustments of the nonbiased helical conformation accompanied with modulation of the main chain $\pi$-conjugation. The absorptions showed significantly large Cotton effects indicative of the effective propensity of the biased helical conformation of **poly-PA-Leu** (red lines in Figure 5). Given that **poly-PA-Leu** originally had a nonbiased helical conformation (vide supra), we can conclude that the amide-anion recognition gives rise to the preferential formation of the biased helical conformation. The chiral adjustment also provided the helical backbone with effective $\pi$-conjugation properties, and thus the dramatic differences in the UV−vis profiles.

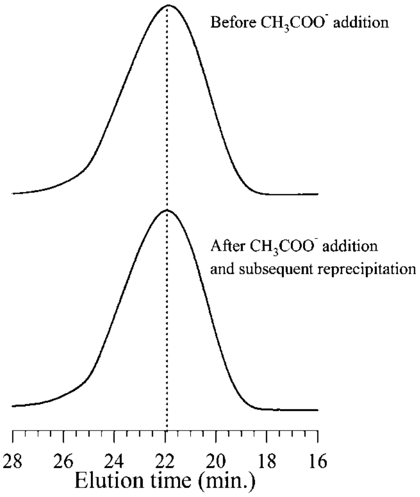


**Figure 6.** SEC traces of **poly-PA-Leu** before (upper) and after (lower) the host−guest interaction with 0.5 equivalents of TBAA in THF at room temperature (eluent; DMF containing 0.01 M LiCl).

To exclude the possibility that changes in the CD profile were due to the changes in the chemical structure of **poly-PA-Leu**, an SEC experiment was performed. First, after 0.5 equivalent of TBAA was added to the THF solution of **poly-PA-Leu**, we gathered the **poly-PA-Leu** by reprecipitation technique. We then carried out SEC measurements of the recovered polymer (lower trace in Figure 6), and no distinct difference from the original SEC trace (upper trace in Figure 6) was observed, showing that the addition of TBAA provided no cross-linking and cleavage of the polymer backbone. These results strongly supported the fact that intensified Cotton effects were promoted by the changes in the helical backbones through the host−guest interaction between the amide groups and acetate anion.

To investigate the guest-selectivity of the anion recognition properties of **poly-PA-Leu**, we employed a series of counteranions including tetra-*n*-butylammonium acetate (TBAA), benzoate (TBAB), nitrate (TBAN), azide ($TBAN_3$), perchlorate ($TBAClO_4$), fluoride (TBAF), chloride (TBACl), bromide (TBABr) and iodide (TBAI). The variable guest experiments highlighted the specific recognition ability of **poly-PA-Leu** as a consequence of the well-defined registration of the amide acceptors. As expected, the addition of a series of tetra-*n*-butylammonium salts demonstrated the breadth and diversity of the CD spectra (Figure 7). The anions including perchlorate ($ClO_4^-$), nitrate ($NO_3^-$), chloride ($Cl^-$), and iodide ($I^-$) anions induced no Cotton effects, and the absorption spectra were same as the polymer blank. On the other hand, the combination of **poly-PA-Leu** and acetate ($CH_3COO^-$), benzoate ($C_6H_5COO^-$), azide ($N_3^-$), fluoride ($F^-$), and bromide ($Br^-$) anions promoted a significant changes in the Cotton effects from the nonactive (blank) to positive second Cotton effects (for $CH_3COO^-$, $C_6H_5COO^-$, $N_3^-$, and $Br^-$) and negative second Cotton effect ($F^-$). The fluoride anion possesses the highest electron density and the smallest ionic radii, which might be the reason why only it induced the negative second Cotton effect. The apparent distinction in the UV−vis and CD spectra should be due to the anion binding of **poly-PA-Leu**, which provided the chiral

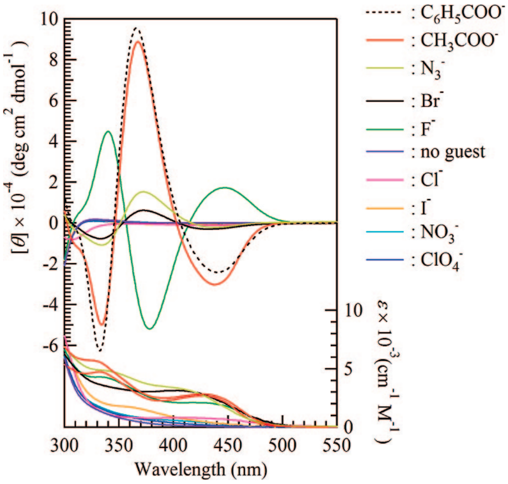


**Figure 7.** CD (upper) and absorption (lower) spectra of **poly-PA-Leu** in THF at 25 °C with various guest molecules ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$ and [guest]/[monomeric unit in **poly-PA-Leu**] = 10).

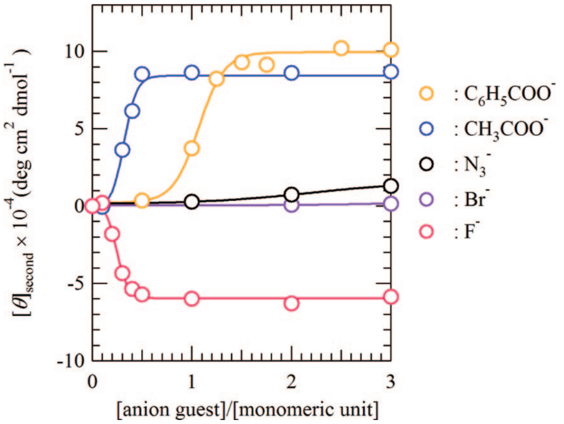


**Figure 8.** Titration curve of the $[\theta]_{second}$ values. The CD measurements of **poly-PA-Leu** with various guest molecules were carried out in THF at 25 °C ([monomeric units of **poly-PA-Leu**] = 3.5 mmol·L$^{-1}$ and [guest]/[monomeric units of **poly-PA-Leu**] = 0−3.0).

**Table 1. Apparent Binding Constants of poly-PA-Leu with Various Anions**[a]

| anion | $K_s$ (M$^{-1}$) |
|---|---|
| $CH_3COO^-$ | 1100 |
| $C_6H_5COO^-$ | 270 |
| $F^-$ | 1200 |
| $N_3^-$ | 120 |
| $Br^-$ | 130 |

[a] Determined from the Hill analysis of CD titration experiments.

adjustments of the nonbiased helical conformation accompanied by modulation of the main chain $\pi$-conjugation. Thus, the system caused a distinct host−guest interaction for only $CH_3COO^-$, $F^-$, $C_6H_5COO^-$, $N_3^-$, and $Br^-$.

In order to clarify the anion-coordination ability in the system, we carried out CD titration experiments for $CH_3COO^-$, $F^-$, $C_6H_5COO^-$, $N_3^-$, and $Br^-$ (Figure 8), and then we estimated the apparent anion-binding constants from the Hill analysis of the CD titration experiments (Table 1). From the titration experiments, we could finally determine the binding selectivity of **poly-PA-Leu**: $CH_3COO^- \sim F^- > C_6H_5COO^- \gg N_3^- \sim Br^-$. Especially, in the cases of $F^-$ and $CH_3COO^-$, the apparent binding constants of **poly-PA-Leu** were up to 1.2 × 10$^3$ M$^{-1}$ and 1.1 × 10$^3$ M$^{-1}$, respectively, which were moderate apparent binding constants as compared to the isolated amide group. More importantly, for the $[CH_3COO^-]$/[monomeric unit] of just 0.5, the guest anion induced saturation in the CD activities (Figure 8), meaning that the efficient anion recognition event was accomplished. Although we could not determine the accurate geometry or binding constant of the host−guest interaction between **poly-PA-Leu** and the acetate anion, the high sensitivity might have a correlation with the polymeric effect of binding sites as in the case of “glycoside-cluster effect”.[28,29]

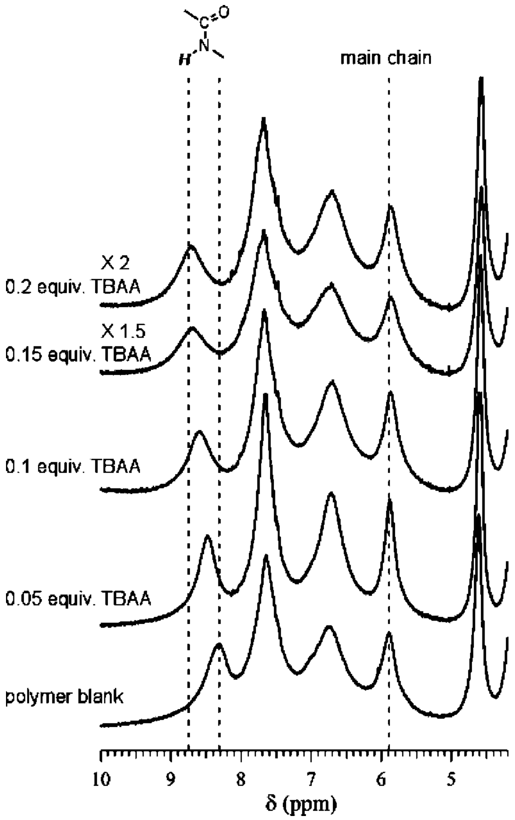


**Figure 9.** $^1$H NMR titration of **poly-PA-Leu** in the presence of TBAA in THF-$d_8$/DMSO-$d_6$ = 10/1 (v/v). ([TBAA]/[monomeric units of **poly-PA-Leu**] = 0−0.2).

Although we confirmed the efficient signaling of **poly-PA-Leu** toward an anionic guest molecule, from only the CD titration, we could not conclude that the changes in the Cotton effect were due to the host−guest interaction. Therefore, to further support that changes in the CD profiles were essentially due to the host−guest interaction between the helically organized amide groups and the anion, we carried out the NMR titration experiments[30] as shown in Figure 9. The addition of acetate anion to the **poly-PA-Leu** solution induced a distinct downfield shift due to host−guest interaction. The change in the NMR spectra was distinctive around the $[CH_3COO^-]$/[monomeric unit] of 0.15, which gave a good correlation with the changes in the CD titration experiment.[31] As previously studied by several groups, the host−guest interaction between an amide and anion induced a distinct downfield shift of the amide proton. Thus, we could conclude that the changes in the CD titration experiment for the system of **poly-PA-Leu** and $CH_3COO^-$ were essentially due to the anion-binding event.[32] As we discussed in the earlier section, the amide group itself shows a weak affinity toward anion guests;[19] thus, the results obtained here provide a novel molecular design for the anion binding motif.

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

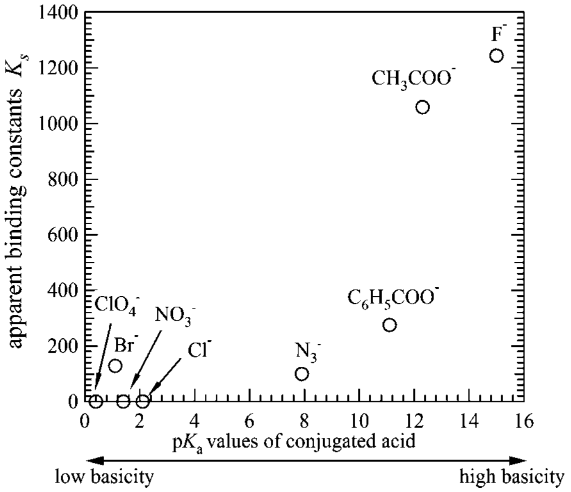


**Figure 10.** Relationship between basicity of anions (acidity of conjugate acids) and apparent binding constants.

interaction of the anion binding site with anionic species. To ensure the anion-binding selectivity of **poly-PA-Leu**, we plotted the relationship between the acidity of the conjugate acid of the employed anionic guests (p$K_a$) and the apparent binding constants ($K_a$), as shown in Figure 10.[33] As expected, a distinct relationship was obviously observed between the basicity and apparent binding-constants, showing that the guest-selectivity was essentially governed by the basicity of the anionic guests. Therefore, the utilization of the polyacetylene backbone as an anion receptor scaffold provided the effective three-dimensional registration of the amide groups in the polymer backbones, thus facilitating the efficient recognition of anionic molecules.

## Conclusions

We have demonstrated an anion receptor system using *cis*-poly(phenylacetylene) with amide and L-leucine functionalities (**poly-PA-Leu**). The efficient anion binding was observed for **poly-PA-Leu** with $CH_3COO^-$, whose apparent binding constant was estimated to be approximately $1.1 \times 10^3$ ($mol^{-1} \cdot L$), whereas the isolated amide group is well-known to show a low affinity toward anionic guests. Thus, by three-dimensionally organizing the amide groups, it is possible to facilitate the efficient molecular recognition of anionic guests. The macromolecular design provides a route to a wide range of sophisticated anion receptor systems comprised of a $\pi$-conjugated polymer backbone as a scaffold.

## Experimental Section

**Materials.** Chloroform for the polymerization was purchased from Kanto Chemicals Co., Inc., and distilled under Ar atmosphere in the presence of $CaH_2$. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was kindly supplied from Central Glass Co. Tetra-*n*-butylammonium nitrate (TBAN), fluoride (TBAF), bromide (TBABr), azide ($TBAN_3$), benzoates (TBAB), and acetate (TBAA) were purchased from Sigma-Aldrich Chemical Co., Inc., and used as received. Tetra-*n*-butylammonium chloride (TBACl), iodide (TBAI), and perchlorate ($TBAClO_4$) were available from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan). *N*,*N*-Dimethylformamide for the spectroscopy (purity >99.7%, water content <0.1%), MeOH for the spectroscopy (>99.7%), and tetrahydrofuran for the spectroscopy (>99.0%) were available from Kanto Chemicals Co., Ltd., and used without further purification. Triphenylphosphine was available from Kanto Chemicals, and used after recrystallization from dichloromethane/diethyl ether. $Rh^+$(2,5-norbornadiene)[($\eta^6$-$C_6H_5$)$B^-$($C_6H_5$)$_3$] ($Rh(nbd)BPh_4$) was prepared in accordance with a previous report.[34] 4-Ethynylbenzoic acid was synthesized according to a previously reported method.[35] 4-(4,6-Dimethoxy-1,3,5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) was available from KOKUSAN Chemical Co., Ltd., and used as received. L-Leucine ethyl ester hydrochloride was purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan), and neutralized to afford L-leucine ethyl ester just before the use.

**Instruments.** The $^1H$ and $^{13}C$ NMR spectra were recorded using JEOL JNM-A400II and JEOL ECP400 instruments. 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 DG-2080−54) equipped with a Shodex Asahipak GF-310 HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 5 $\mu$m; exclusion limit, $4 \times 10^4$) and a Shodex Asahipak GF-7 M HQ column (linear, 7.6 mm × 300 mm; pore size, 20 nm; bead size, 9 $\mu$m; exclusion limit, $4 \times 10^7$) in DMF containing lithium chloride (0.01 M) at the flow rate of 0.4 $mL \cdot min^{-1}$. 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 cell using a Jasco J-720 spectropolarimeter.

**Synthesis of the *N*-(4-Ethynylphenylcarbonyl)-L-leucine Ethyl Ester (PA-Leu).** To a solution of the 4-ethynylbenzoic acid (2.85 g, 19.5 mmol) and DMT-MM (5.94 g, 21.5 mmol) in MeOH (100 mL) was added the L-leucine ethyl ester (3.11 g, 19.5 mmol). After stirring at room temperature for 19 h, the reaction mixture was purified by column chromatography on silica gel with ethyl acetate/hexane (2/7, v/v) to give **PA-Leu** as a white crystal. Yield: 4.22 g (75.0%). $^1H$ NMR ($CDCl_3$): $\delta$ 0.97−1.00 (m, 6H, $-CH_3$), 1.31 (t, 3H, $-OCH_2CH_3$), 1.64−1.68 (m, 1H, $-CH-$), 1.70−1.79 (m, 2H, $-CH-CH_2-$), 3.21 (s, 1H, $-C{\equiv}CH$), 4.20−4.26 (m, 2H, $-OCH_2-$), 4.80−4.86 (m, 1H, $-NH-CH-$), 6.66 (d, $J = 8.13$ Hz, 1H, $-NH-$), 7.54 (d, $J = 8.35$ Hz, 2H, aromatic), 7.75 (d, $J = 8.43$ Hz, 2H, aromatic). $^{13}C$ NMR ($CDCl_3$): $\delta$ 14.0 ($-CH_3$), 21.8 ($-CH_3-$), 22.7 ($-CH_3$), 24.8 ($-CH$), 41.4 ($-CH_2-$), 51.6 ($-CH-$), 61.6 ($OCH_2-$), 76.2 ($-C{\equiv}CH$), 83.6 ($-C{\equiv}CH$), 116.0 (aromatic), 118.9 (aromatic), 132.8 (aromatic), 139.3 (aromatic), 155.3 ($-CO-$(ester)), 175.0 ($-CO-$(amido)). Anal. Calcd for $C_{17}H_{21}O_3N$ (287.35): C, 71.06; H, 7.37; N, 4.87. Found: C, 71.01; H, 7.29; N, 4.86.

**Polymerization.** The polymerization of **PA-Leu** was carried out in a dry flask under an argon atmosphere. Under the argon atmosphere, **PA-Leu** (500 mg, 1.74 mmol) was placed in a flask and dissolved in dry $CHCl_3$ (53.0 mL). To the solution was added a solution of $Rh(nbd)BPh_4$ (20.1 mg, 39.1 $\mu$mol) in dry $CHCl_3$ (5.0 mL). After stirring at room tempreture for 24 h, triphenylphosphine (85.4 mg, 326 $\mu$mol) was added to the reaction mixture. The solution was concentrated and then dissolved in a small amount of THF. A large portion of hexane was then added to the solution. The precipitate was collected and then dried under reduced pressure to give **poly-PA-Leu** as a yellow powder. Yield: 441 mg (88.3%). $M_n = 2.8 \times 10^5$, $M_w/M_n = 2.8$.

**CD Measurements.** CD and UV−vis spectra were measured in a 1-mm quartz cell at 25 °C. The concentration of polymer was calculated on the basis of the monomeric units (3.5 $mmol \cdot L^{-1}$).

**Determination of Binding Constants ($K_s$) on the Basis of the Hill Analysis.** For calculating the apparent binding constant ($K_s$), we used the Hill equation, $\log[Y/(1 - Y)] = n \log|G| + n \log(K_s)$, where $Y$, $G$, and $n$ are fractional saturation, the Hill coefficient, and the concentration of the guest, respectively.[36,37]

**SEC Measurement of Figure 6.** After 0.5 equiv of TBAA was added to the THF solution of **poly-PA-Leu**, we gathered the polymer by reprecipitation technique. We then carried out SEC measurements of the recovered polymer again.

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