Size-Specific, Colorimetric Detection of Counteranions by Using Helical Poly(phenylacetylene) Conjugated to L-Leucine Groups through Urea Acceptors

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Abstract: A colorimetric detection susceptible to the dimensions of guest counteranions has been demonstrated by using poly(phenylacetylene) with L-leucine and urea functionalities (poly-PA-Leu). Poly-PA-Leu was prepared from N-(4-ethynylphenylcarbamoyl)-L-leucine ethyl ester (PA-Leu) by using $[Rh^+\{\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3\}(2,5\text{-norbornadiene})]$ 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 tetra-n-butylammonium acetate, tetra-n-butylammonium chloride, and tetra-n-butylammonium bromide anions (CH_3COO^-, Cl^-, and Br^-), into the poly-PA-Leu solution intensified the CD responses of poly-PA-Leu, which is indicative of the chiral adjustability of anion recognition by using urea groups. In addition, the combination of poly-PA-Leu with the CH_3COO^-, Cl^-, and Br^- anions promoted large redshifts in the absorption spectra, thus providing dramatic color changes from pale yellow to red. Guest dependency in the CD and UV/Vis spectra was clearly correlated with the size of the counteranions. Fundamentally, the addition of tetra-n-butylammonium nitrate, tetra-n-butylammonium hydrogen sulfate, tetra-n-butylammonium perchlorate, tetra-n-butylammonium azide, tetra-n-butylammonium fluoride, and tetra-n-butylammonium iodide anions (NO_3^-, HSO_4^-, ClO_4^-, N_3^-, F^-, and I^-) has no effect on either the CD or UV/Vis profiles of poly-PA-Leu. The guest specificity observed in the CD and UV/Vis spectra clearly demonstrated the guest-dimension selectivity of poly-PA-Leu in counteranion recognition.

Keywords: anion recognition · polymers · sensors · size selectivity · supramolecular chemistry

Introduction

Size-selective molecular recognition requires the sufficient registration of recognition elements for a guest molecule.[1] The recognition ability can be intensified through the well-defined, three-dimensional organization relative to those found in biological macromolecules, such as DNA and RNA.[2,3] The helical constructs developed from synthetic polymers feature adjustable backbones that can modify the characteristics of a helix, such as the helical pitch and screw-sense.[4–7] The adjustability of synthetic helical constructs is advantageous for providing increasingly sophisticated sensing systems. The subtle chemical change in the system significantly outlines the nature of the helical backbones due to the adjustability, thus providing a unique sensitivity and signature of guest molecules.[8] Imparting the surface with synthetic helical constructs with the elements of noncovalent bonding interactions provides new directions for the development of increasingly specific sensing systems.

Poly(phenylacetylene)s provide effective intermediates for adjustable helical constructs to create sensory systems. Yashima et al. showed the detection of guest molecules utilizing a poly(phenylacetylene) containing a pendant β-cyclodextrin; the host–guest complexation of β-cyclodextrin with a guest molecule induced a modulation in the helical pitch and color.[9,10] Recently, we demonstrated metal–cation recognition by using a poly(phenylacetylene) functionalized with polysaccharides. The polysaccharide functionalities permitted the acquisition of metal cations, and the system

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showed a dramatic inversion of the chiroptical property through a host–guest interaction between the polymer and metal cations.[11] The inversed chiroptical properties of the systems exhibited size dependency by the metal cation guests to make them an attractive method for size-specific sensing. In the sensory system based on poly(phenylacetylene) scaffolds, guests can be visualized in the binary mode; the addition of guests makes it possible to modulate not only the UV/Vis, but also the chiroptical properties as a direct consequence of the adjustment of the helical backbones.

We now report the well-defined structural design and synthesis of poly(phenylacetylene) conjugated to L-leucine through urea groups. The system demonstrates 1) a chiral translation from the pendant leucine to the poly(phenylacetylene) backbones, resulting in the three-dimensional urea organization, and 2) the size-specific and colorimetric detection of counteranion guests (Scheme 1). The *N*-(4-ethynylphenylcarbamoyl)-L-leucine ethyl ester (PA-Leu) was synthesized and then polymerized in DMF by using a rhodium complex as the catalyst to yield the *cis*-poly(phenylacetylene) containing L-leucine and urea groups (poly-PA-Leu). The anion-recognition properties were investigated by using a series of ammonium salts with variable counteranions, as illustrated in Scheme 1.

Results and Discussion

Synthesis and chiroptical properties of poly-PA-Leu: To provide a system for counteranion detection, PA-Leu was prepared and polymerized by using [Rh$^+${(η_6-C$_6$H$_5$)B$^-$-(C$_6$H$_5$)$_3$}(2,5-norbornadiene)] ([RhBPh$_4$(nbd)]) as the catalyst. Poly-PA-Leu presents multiple urea functionalities to facilitate the recognition of anionic guests.[12–21] The number-average molecular weight (M_n) and polydispersity (M_w/M_n) of poly-PA-Leu were 2.0×10^5 and 2.4, respectively. The ^{1}H NMR spectrum showed a sharp peak at $\delta=5.63$ ppm, indicative of the propensity of the *cis*-configuration in the poly-PA-Leu (see the Supporting Information).

The absorption and chiroptical properties of poly-PA-Leu were investigated to provide fundamental insights into the scaffold for anion detection. Figure 1 shows the circular dichroism (CD) and 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, the region in which the π conjugation of the polymer backbone typically appears. The Cotton effects in the polymer backbone absorption clearly indicated that poly-PA-Leu presents a biased, one-handed helical conformation directed by the pendant L-leucine groups. The embedded urea functionalities between the L-leucine groups and the polymer backbone were arrayed in a helical fashion.

As expected, variable temperatures and solvents provide the conformational diversity of the helical scaffold due to the dynamic conformation of poly-PA-Leu. Figure 2 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 is presumably due to the suppression of the interconversion between the right-
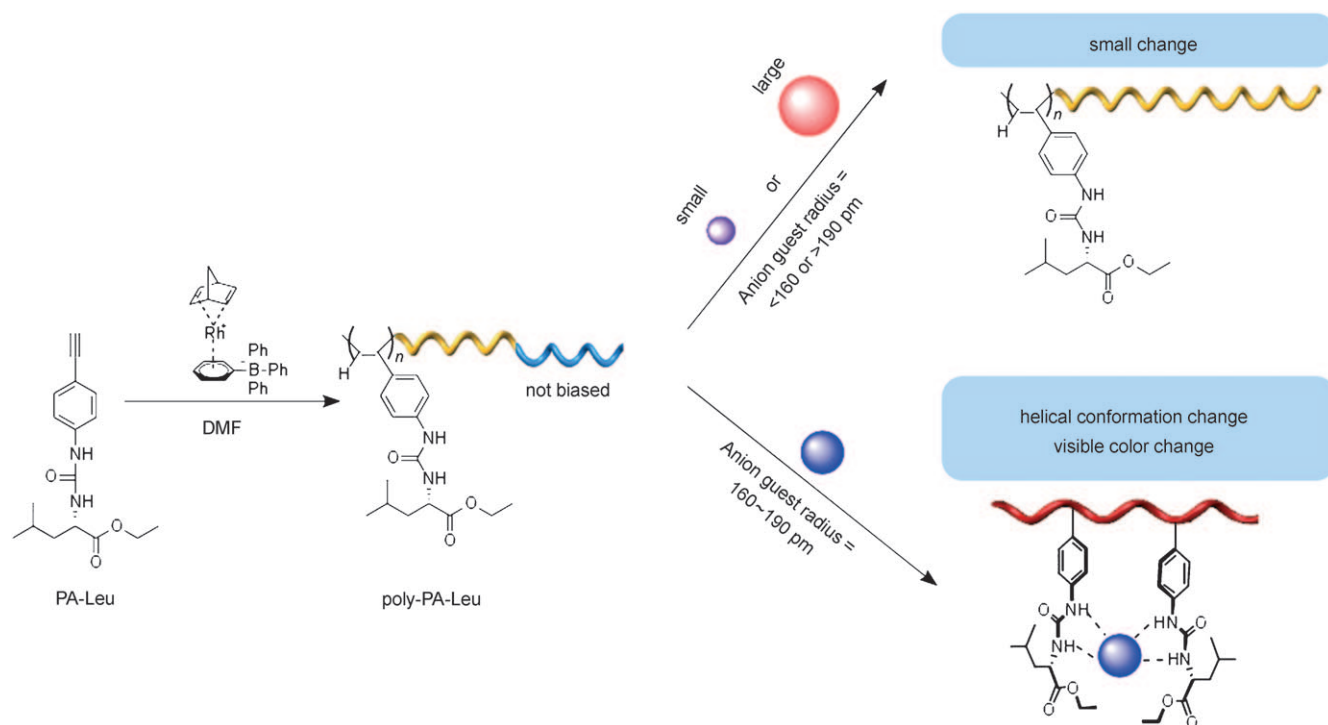
Scheme 1. Schematic representation of size-selective detection for counteranions at molecular level.
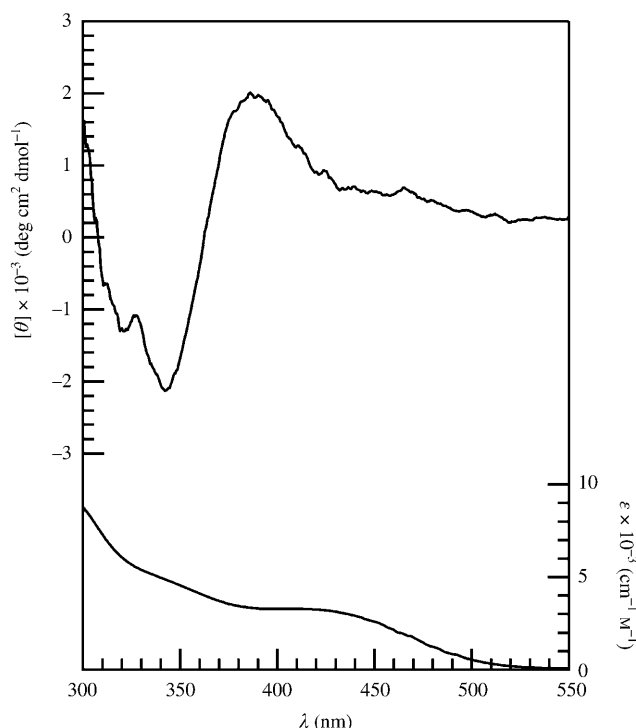
Figure 1. CD (upper) and UV/Vis absorption (lower) spectra of poly-PA-Leu in DMF at 25 °C. [monomeric units of poly-PA-Leu] = 3.3 mmol L^{-1}.
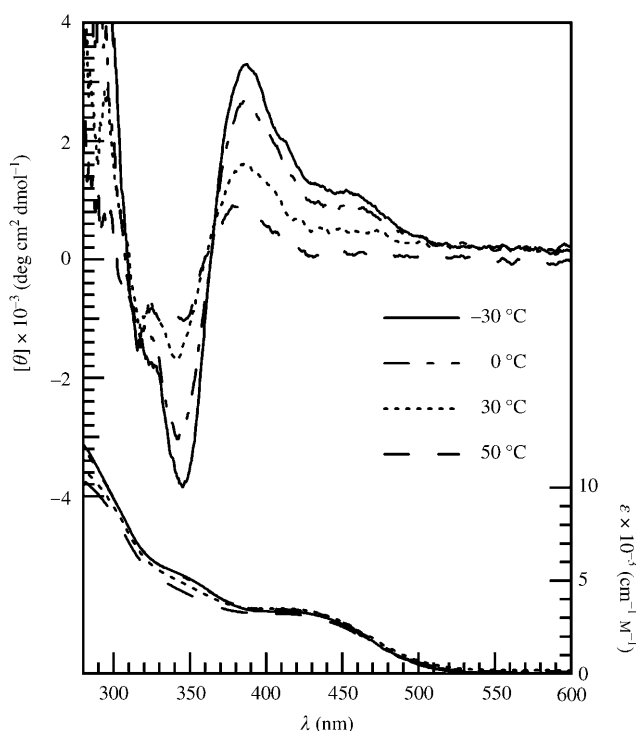

Figure 2. CD (upper) and UV/Vis absorption (lower) spectra of poly-PA-Leu in DMF at various temperatures. [monomeric units of poly-PA-Leu] = 3.3 mmol L^{-1}.

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, dimethylacetoamide (DMAc), *N*-methylpyrrolidone (NMP), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and THF (Figure 3). The CD profiles in DMF and NMP were essen-
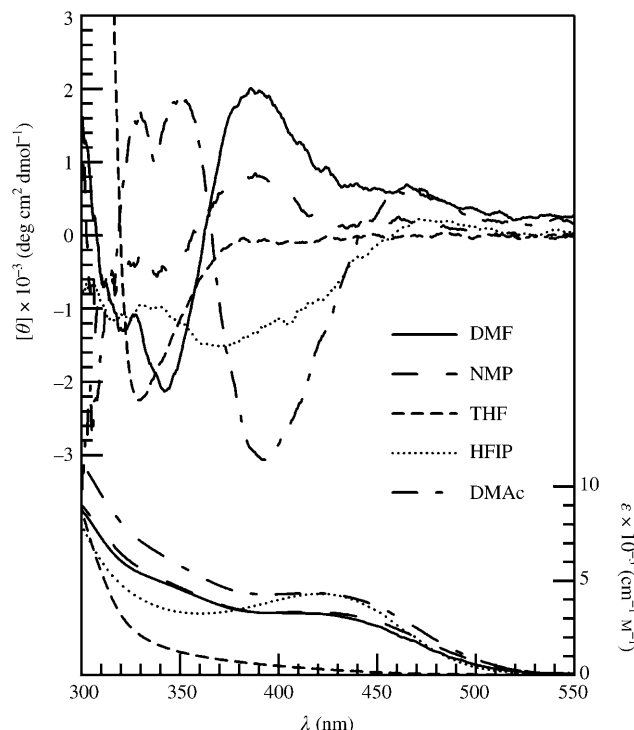

Figure 3. CD (upper) and UV/Vis absorption (lower) spectra of poly-PA-Leu in variable solvents at 25 °C. [monomeric units of poly-PA-Leu] = 3.3 mmol L^{-1}.

tially mirror images of those found in DMAc and HFIP, respectively, 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 of 300 to 500 nm. The empty profiles in THF demonstrate a nonbiased helical conformation of poly-PA-Leu that features equal contents of right- and left-handed helical structures. Given the perturbation of the CD and UV/Vis profiles, the anion-recognition experiments were performed in THF. The acquired recognition between urea groups and the counteranion makes it possible to observe the apparent discrepancy in the chiroptical and optical properties of poly-PA-Leu, provided that the host–guest interactions can effectively provide the biased helical conformation (Scheme 1).

The anion-sensing ability of poly-PA-Leu: To provide a preliminary insight into the anion-recognition properties of the urea-functionalized poly-PA-Leu, tetra-*n*-butylammonium acetate (TBAA) was added to a solution of poly-PA-Leu in

THF, which resulted in the dramatic increase in the CD and UV/Vis spectra. The combination of poly-PA-Leu and TBAA promoted a significant color change in the solution from pale yellow to red, and a drastic induction of the Cotton effects (Figure 4). The apparent distinction in the
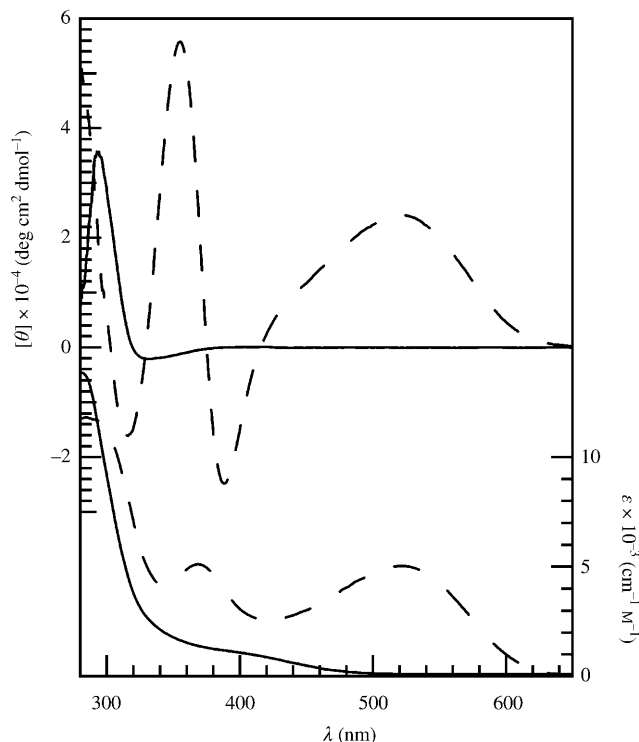

Figure 4. CD (upper) and UV/Vis absorption (lower) spectra of poly-PA-Leu in THF (——) with TBAA (5 equiv; –––) at RT. [monomeric units of poly-PA-Leu] = 3.3 mmol L^{-1} and [TBAA]/[monomeric units of poly-PA-Leu] = 5.

UV/Vis and CD spectra demonstrates that anion recognition by using poly-PA-Leu provided chiral adjustments of the nonbiased helical conformation accompanied by modulation of the main-chain π conjugation. In the UV/Vis spectra, the addition of TBAA resulted in the appearance of extremely distinctive peaks at 370 and 520 nm, which correspond to the backbone π-conjugation transition. The absorptions showed significantly large Cotton effects, which are indicative of the effective propensity of the biased helical conformation of poly-PA-Leu (Figure 4 (–––)). Given that poly-PA-Leu originally had a nonbiased helical conformation (see above), we can conclude that the urea–anion recognition gives rise to the preferential formation of the biased helical conformation. The chiral adjustment also provided the helical backbone with effective π-conjugation properties, and thus the dramatic differences in the UV/Vis profiles.

To focus on the urea–anion interactions, NMR spectroscopy and size exclusion chromatography (SEC) experiments were performed. Figure 5 shows the ^{1}H NMR spectra of poly-PA-Leu in [D$_8$]THF/[D$_7$]DMF (5/1, v/v).[22] The addition of TBAA resulted in broadening of the backbone pro-
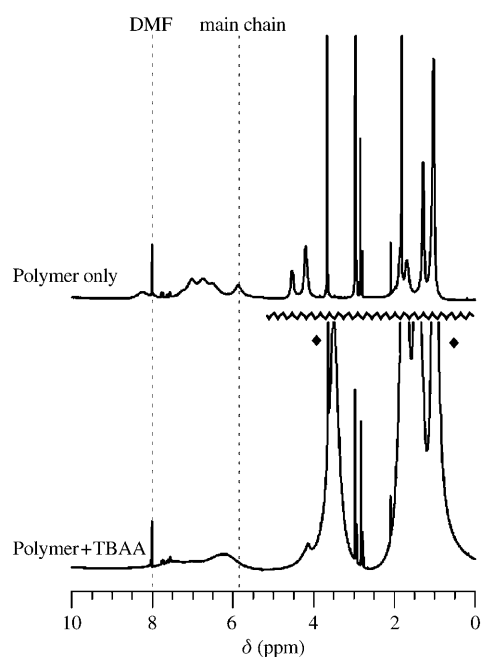

Figure 5. ^{1}H NMR spectra of poly-PA-Leu in the absence (upper) and presence (lower) of TBAA in [D$_8$]THF/[D$_7$]DMF = 5/1 (v/v). [TBAA]/[monomeric units of poly-PA-Leu] = 5. ♦: tetra-n-butylammonium.

tons signals and disappearance of the urea proton signals. The NMR spectroscopy titration results are presumably due to the low mobility of the polymer backbones and confirms the urea–anion recognition.[23] To clarify that addition of anionic molecule to the poly-PA-Leu solution did not affect the polymer structure, we carried out SEC measurements. First, after TBAA (5 equiv) was added to the solution of poly-PA-Leu in THF, we gathered the poly-PA-Leu by a reprecipitation technique. We then carried out SEC measurements on the recovered polymer (lower trace in Figure 6), and no distinct difference from the original SEC trace (upper trace in Figure 6) was observed even after the significant color change, showing that the addition of TBAA provided no cross-linking and cleavage of the polymer backbone. These results strongly supported the observation that significant redshifts and intensified Cotton effects were promoted by the alteration of the helical backbones through urea–anion recognition.

To further investigate the anion-recognition properties of poly-PA-Leu, we employed a series of counteranions, including TBAA, tetra-n-butylammonium hydrogen sulfate (TBAHS), tetra-n-butylammonium nitrate (TBAN), tetra-n-butylammonium azide (TBAN$_3$), tetra-n-butylammonium perchlorate (TBAClO$_4$), tetra-n-butylammonium fluoride (TBAF), tetra-n-butylammonium chloride (TBACl), tetra-n-butylammonium bromide (TBABr), and tetra-n-butylammonium iodide (TBAI). The variable guest experiments highlighted the specific recognition ability of poly-PA-Leu as a consequence of the well-defined organization of the urea acceptors. As expected, the addition of a series of tetra-n-butylammonium salts with variable dimensions demonstrated
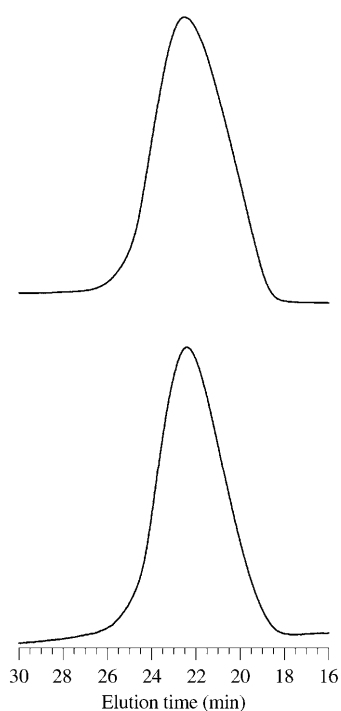
Figure 6. SEC traces of poly-PA-Leu before (upper) and after (lower) the host–guest interaction with TBAA (5 equiv) in THF at RT (eluent: DMF containing 0.01 M LiCl).

the breadth and diversity of the CD and UV/Vis spectra (Figure 7).[24] Depending on changes in the profile when compared with the original obtained in THF, which reflects the ability of each guest molecule to make chiral adjustments, the anionic guests employed were categorized into two groups: redshifting guests and non-redshifting guests.[25] The non-redshifting guests, including the perchlorate (ClO_4^-), hydrogen sulfate (HSO_4^-), nitrate (NO_3^-), azide (N_3^-), fluoride (F^-), and iodide (I^-) anions, showed weak Cotton effects ($\approx 10^3 \, deg \, cm^2 \, dmol^{-1}$), and absorption spectra typical for the poly(phenylacetylene)s (Figure 7a).[26, 27] The extended CD and UV/Vis spectra of poly-PA-Leu for the non-redshifting guests provided specific and definitive signatures to the guest molecules (Figure 7b). The NO_3^-, N_3^-, and F^- anions induced a negative first Cotton effect, and the HSO_4^- and I^- anions induced a positive first Cotton effect in the backbone absorption. In contrast with the original UV/Vis profile of poly-PA-Leu, a distinctive peak was observed in the range from 300 to 550 nm for the NO_3^-, N_3^-, and F^- anions, and from 350 to 450 nm for HSO_4^- and I^-. However, in the case of the perchlorate anion, the UV/Vis and CD spectra of poly-PA-Leu are almost the same as those of the original poly-PA-Leu. Figure 8 shows the color images of the polymer solutions in the presence of the different anionic guests. As a direct consequence of the subtle absorption differences, the solution colors of poly-PA-Leu with non-redshifting guests were a pale orange for NO_3^-, N_3^-, and F^-; yellow for HSO_4^- and I^-; and pale yellow for ClO_4^-. The profile dependency allowed us to qualitatively determine the sensing selectivity of poly-PA-Leu for the

non-redshifting guests as follows: $NO_3^- \approx N_3^- \approx F^- > HSO_4^- \approx I^- > ClO_4^-$.

In sharp contrast to the non-redshifting guests, large changes in both the CD and UV/Vis spectra were observed for the redshifting guests, including Br^-, Cl^-, and CH_3COO^-. A significant redshift was observed in the absorption spectra resulting in the remarkable visible color changes from pale yellow to vivid orange (Br^-) and red (Cl^- and CH_3COO^-) (Figure 8). This result suggests that the redshifting guests provided a significant change in the poly-PA-Leu helical conformation, and thus the extension of the effective π-conjugate length with the biased backbones. The CD studies correlated with the degree of the changed helical conformation. Very strong Cotton effects were developed in the range from 500 to 600 nm in the presence of Br^-, Cl^-, and CH_3COO^- (Figure 7). The magnitude of the first Cotton effect of poly-PA-Leu with Br^- ($[\theta]_{first}$ $1.8 \times 10^3 \, deg \, cm^2 \, dmol^{-1}$) was much smaller than those of Cl^- ($[\theta]_{first} = 1.3 \times 10^4 \, deg \, cm^2 \, dmol^{-1}$) and CH_3COO^- ($[\theta]_{first} = 2.4 \times 10^4 \, deg \, cm^2 \, dmol^{-1}$), showing the unprecedented specificity of poly-PA-Leu to Cl^- and CH_3COO^-. From the CD and UV/Vis studies using a series of ammonium salts, we can finally determine the sensing selectivity of poly-PA-Leu: $CH_3COO^- \approx Cl^- > Br^- \gg NO_3^- \approx N_3^- \approx F^- > HSO_4^- \approx I^- > ClO_4^-$.

The size-selectivity of poly-PA-Leu in counteranion recognition: Given the colorimetric detection demonstrated by using poly-PA-Leu, we focused on providing a preliminary insight into the specificity observed for the three-dimensionally organized urea acceptors along the poly-PA-Leu backbones. As studied by Fabbrizzi and co-workers, the host–guest interaction of the isolated urea with anionic species essentially agrees with the basicity of the anionic guest molecules.[28–30] However, increasingly specific guests (Cl^- and CH_3COO^-) have no consistent basicity, suggesting that the guest selectivity of poly-PA-Leu provides a sophisticated identity in comparison with those of traditional isolated urea systems.[28–30] To ensure that the anion–guest selectivity with poly-PA-Leu was discrete from typical urea systems, we plotted the relationship between the acidity (pK_a) of the conjugate acid of the employed anionic guests and the wavelength for the first Cotton effect in the CD spectra ($\lambda - [\theta]_{first}$), as shown in Figure 9.[31, 32] As expected, no distinct relationship was observed between basicity and guest selectivity, showing that guest selectivity was not dictated by basicity.

We next focused on the relationship between the guest selectivity of poly-PA-Leu and the radius of the anion (Figure 10), providing preliminary evidence for the size selectivity of poly-PA-Leu.[33] The observed profile showed a clear peak with a maximum at an anion radius of around 165 pm. The maximum value in the guest selectivity versus dimension plot demonstrates that the size of the guests significantly dictates the selectivity of poly-PA-Leu rather than the basicity. Furthermore, no distinct relationship between $\lambda - [\theta]_{first}$ and apparent binding constants estimated from Hill
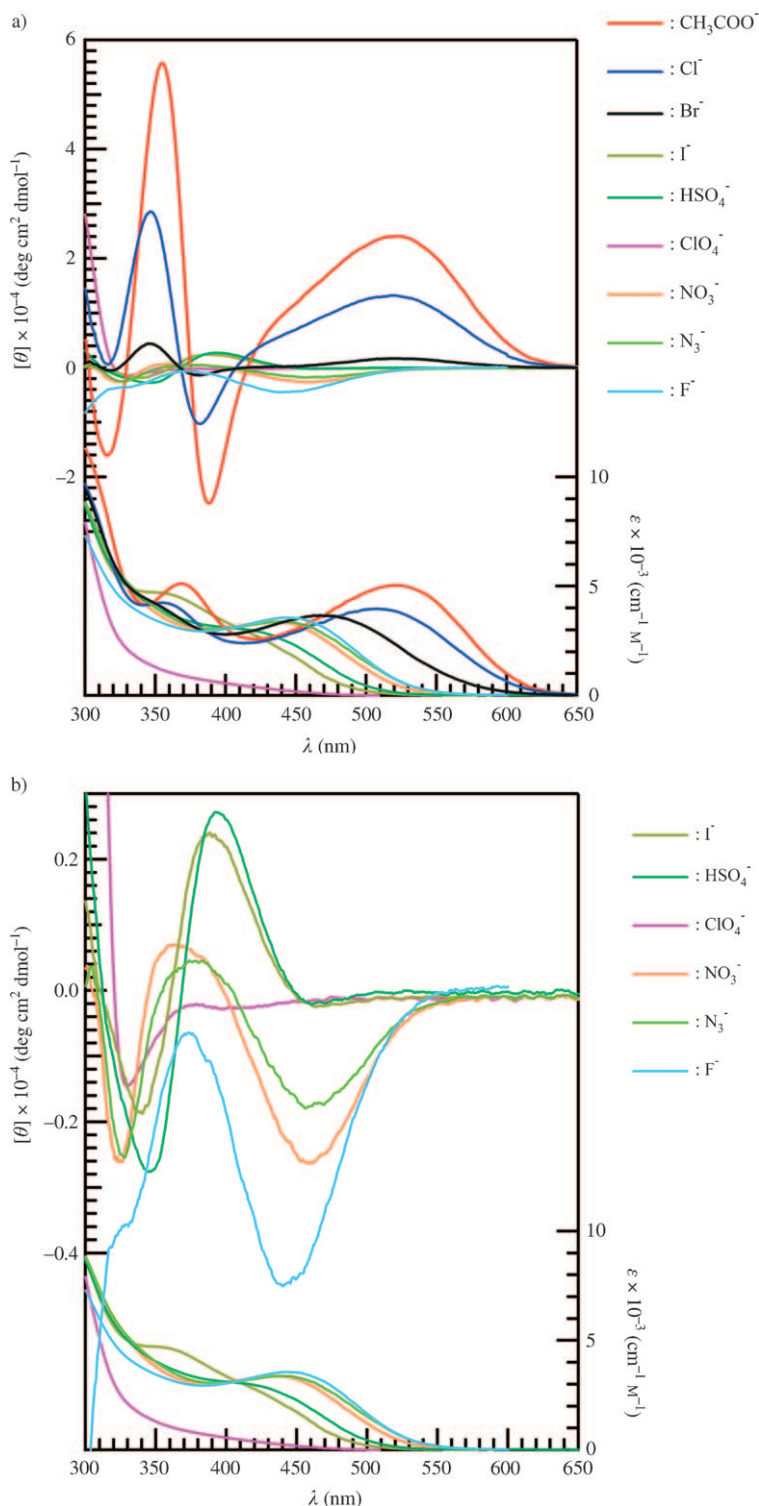
Figure 7. a) CD (upper) and UV/Vis absorption (lower) spectra of poly-PA-Leu in THF at 25 °C with various guest molecules ([monomeric units of poly-PA-Leu] = 3.3 mmol L^{-1} and [guest]/[monomeric unit in poly-PA-Leu] was saturated value.). b) The extended spectra of that given in (a) except for CH$_3$COO$^-$, Cl$^-$, and Br$^-$.

To further investigate whether the anion-sensing property of poly-PA-Leu is dependent on the three-dimensional organization of the urea groups, we prepared the copolymer of phenylacetylene and PA-Leu (poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$)) featuring half the urea functionalities dispersed in the polymer backbones compared with poly-PA-Leu. Figure 11 shows the CD and UV/Vis spectra of poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$) in the presence of TBAA and TBACl as the anion guest in THF. Although the acetate and chloride anions induced a small change in the helical conformation for poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$), essentially no distinct redshift peak was observed (Figure 11). The control experiment clearly showed that the anion-sensing property of poly-PA-Leu is due to the three-dimensionally organized urea groups with anionic guest molecules; the poly-PA-Leu with the two anion guests (Cl$^-$ and CH$_3$COO$^-$) resulted in significant developments in both the CD and absorption spectra (see above). The utilization of the polyacetylene backbone as an anion sensor scaffold provided the effective three-dimensional registration of the urea acceptors in the polymer backbones, thus facilitating the exquisite selectivity specific to the guest dimensions.

Conclusion

We have demonstrated the size-specific, colorimetric detection of anion guests using cis-poly-(phenylacetylene) with urea and L-leucine functionalities (poly-PA-Leu). The observed guest selectivity of poly-PA-Leu is

analysis of the CD titration experiment was observed, which also supported the observation that the guest selectivity of poly-PA-Leu was governed by the guest size (see Figure S-11 in the Supporting information).

different from that of the isolated urea group in that the basicity of the anionic guest molecules is essential. By three-dimensionally organizing urea groups it is possible to facilitate guest size selectivity. The macromolecular design provides a
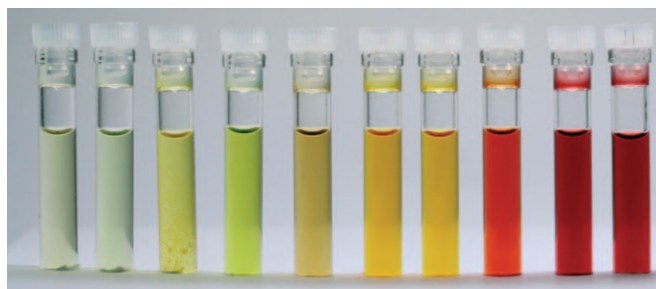
Figure 8. Visible color changes upon the addition of various anionic guests (from left to right: blank, perchlorate, iodide, hydrogen sulfate, fluoride, nitrate, azide, bromide, chloride, and acetate).
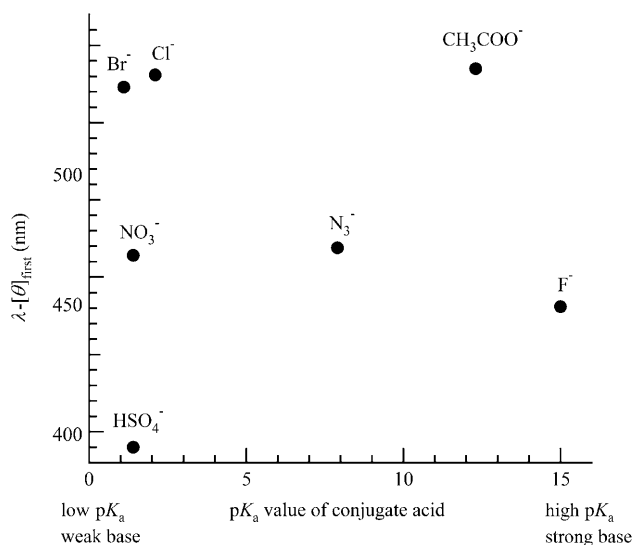

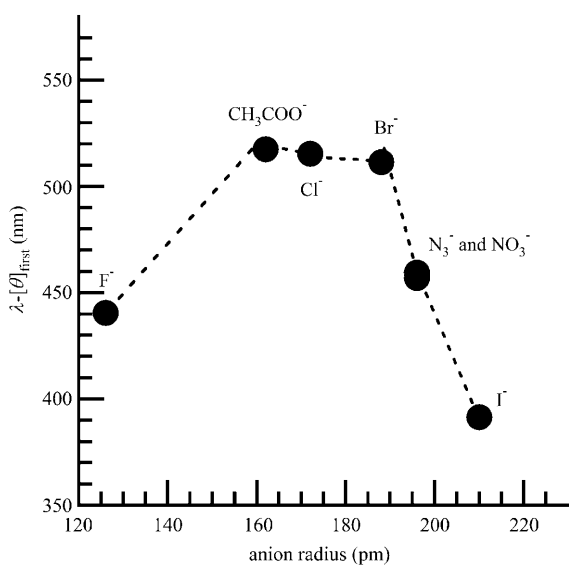Figure 9. Relationship between the basicity of the anion and $\lambda-[\theta]_{first}$.
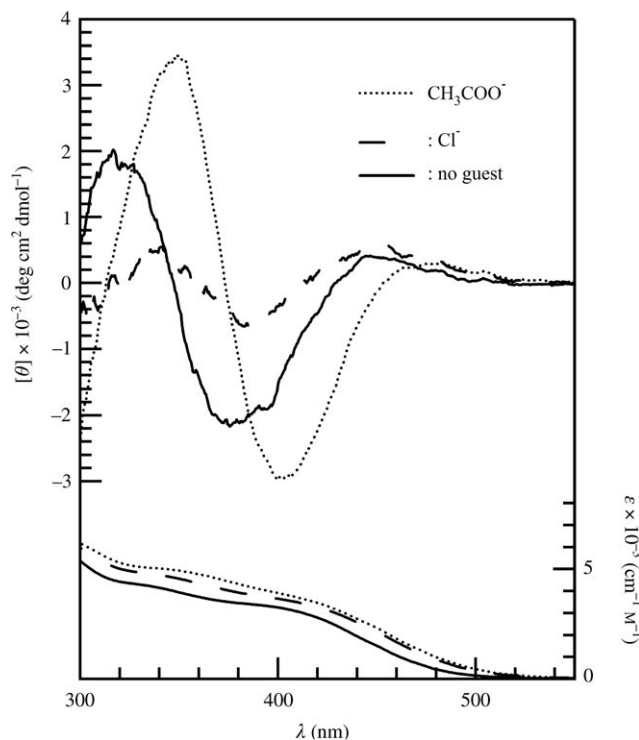
Figure 11. CD (upper) and UV/Vis absorption (lower) spectra of poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$) in the presence of ten equivalents of TBAA or TBACl in THF. [poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$)] = 1 mg mL^{-1}, [TBAA or TBACl]/[poly(PA$_{0.51}$-co-PA-Leu$_{0.49}$)] = 10.

tive organization of the hydrogen-bonding systems is currently being investigated and will be reported in due course.

Experimental Section

Materials: *N*,*N*-Dimethylformamide was purchased from Kanto Chemicals and distilled under reduced pressure. DMAc and NMP were available from Kanto Chemicals and were used as received. HFIP was kindly supplied from Central Glass. TBAN, TBAF, TBABr, and TBAA were purchased from Aldrich Chemical and used as received. TBACl, TBAI, and TBAClO$_4$ were available from Tokyo Kasei Kogyo (TCI, Tokyo, Japan). 4-Ethynylaniline and TBAHS were purchased from Wako Pure Chemical Industries and used without further purification. *N*,*N*-Dimethylformamide for the spectroscopy (purity > 99.7%, water content < 0.1%), and THF for the spectroscopy (> 99.0%) were available from Kanto Chemicals and used without further purification. The *N*-carbonyl-L-leucine ethyl ester was synthesized according to a previous report.[34] [Rh$^+$\{η^6-C$_6$H$_5$)B$^-$(C$_6$H$_5$)$_3$\}(2,5-norbornadiene)] was prepared in accordance with a previous report.[35]

Instruments: The ^{1}H and ^{13}C NMR spectra were recorded by using JEOL JNM-A400II 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 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-7M 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 the 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 CD spectra

Figure 10. Relationship between the radius of the anion and $\lambda-[\theta]_{first}$.

route to a wide range of sophisticated sensory systems comprised of a π-conjugated polymer backbone as a scaffold. The improvement in the detection sensitivity through effec-

were measured in a 1 mm path length cell by using a Jasco J-720 spectro-polarimeter. Preparation of the polymerization solution was carried out in an MBRAUN stainless steel glove box equipped with a gas purification system (molecular sieves and copper catalyst) under a dry argon atmosphere (H_2O, $O_2 < 1$ ppm). The moisture and oxygen contents in the glove box were monitored by MB-MO-SE 1 and MB-OX-SE 1 instruments, respectively.

Synthesis of the *N*-(4-ethynylphenylcarbamoyl)-L-leucine ethyl ester (PA-Leu): 4-Ethynylaniline (3.31 g, 28.3 mmol) was added to a solution of the *N*-carbonyl-L-leucine ethyl ester (4.60 g, 24.9 mmol) in CH_2Cl_2 (100 mL). After stirring at room temperature for 4 h, the reaction mixture was purified by column chromatography on silica gel with ethyl acetate/hexane (10:1–2:1, v/v) as the eluent to give PA-Leu as white crystals (6.05 g, 76.5%). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 0.91$–0.94 (m, 6H; -CH_3), 1.27 (t, $J = 7.11$ Hz, 3H; -OCH$_2$CH_3), 1.46–1.50 (m, 1H; -CH-), 1.58–1.70 (m, 2H; -CH-CH_2-), 3.00 (s, 1H; -C≡CH), 4.13–4.23 (m, 2H; -OCH_2-), 4.50–4.53 (m, 1H; -NH-CH-COO), 6.06 (d, $J = 8.11$ Hz, 1H; CH-NH-CO-NH-Ar), 7.20 (d, $J = 8.63$ Hz, 2H; aromatic), 7.23 (d, $J = 8.47$ Hz, 2H; aromatic), 7.71 ppm (s, 1H; Ar-NH-CO-NH-); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): $\delta = 15.2$ (-CH$_3$), 23.0 (-CH$_3$), 23.9 (-CH$_3$), 26.0 (-CH-), 42.6 (-CH$_2$-), 52.8 (-CH-), 62.8 (OCH$_2$-), 77.4 (-C≡CH), 84.8 (-C≡CH), 117.2 (aromatic), 119.9 (aromatic), 133.7 (aromatic), 140.5 (aromatic), 156.5 (-CO-(ester)), 176.3 ppm (-CO-(urea)); elemental analysis calcd (%) for $C_{17}H_{22}O_3N_2$ (302.37): C 67.53, H 7.33, N 9.26; found: C 67.64, H 7.09, N 9.25.

Polymerization: The polymerization of PA-Leu was carried out in a dry flask under an argon atmosphere. In a glove box (under a moisture- and oxygen-free argon atmosphere; H_2O, $O_2 < 1$ ppm), PA-Leu (600 mg, 2.0 mmol) was weighed into a flask and dissolved in dry DMF (62.2 mL) before a solution of [Rh(BPh$_4$)(nbd)] (20.4 mg, 39.6 μmol) in dry DMF (4.0 mL) was added. After stirring at room tempreture for 24 h, triphenylphosphane (122 mg, 465 μmol) was added to the reaction mixture. The solution was concentrated and then poured into a large amount of acetonitrile (≈ 500 mL). The precipitate was purified by reprecipitation with acetonitrile and then dried under reduced pressure to give poly-PA-Leu as a yellow powder (462 mg, 77.0%). $M_n = 2.0 \times 10^5$; $M_w/M_n = 2.4$.

CD measurements: CD and UV/Vis spectra were measured in a 1 mm quartz cell at room temperature. The concentration of polymer was calculated on the basis of the monomeric units (3.3 mmol L^{-1}).

SEC measurement of Figure 6: After five equivalents of TBAA were added to the solution of poly-PA-Leu, we gathered the polymer by using a reprecipitation technique. We then carried out SEC measurements of the obtained polymer again.

Acknowledgements

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