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ARTICLE

Effect of the Pendant Structure on Anion Signaling Property of Poly(phenylacetylene)s Conjugated to α-Amino Acids through Urea Groups

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ABSTRACT: A colorimetric detection of guest counteranions has been demonstrated using poly(phenylacetylenes)s with urea functionalities and α-amino acids, such as L-leucine, L-glutamic acid, L-aspartic acid, L-phenylalanine, L-isoleucine, and L-alanine (**PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala**, respectively). The polymers were prepared by the polymerization of the *N*-(4-ethynylphenylcarbamoyl)-L-amino acids ethyl ester (**PA-Leu**, **PA-Glu**, **PA-Asp**, **PA-Phe**, **PA-Ile**, and **PA-Ala**) using Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh_4) as the catalyst. The biased helical conformations of all the urea-functionalized polymers were demonstrated through Cotton effects in the circular dichroism (CD) spectra. The addition of various ammonium salts including tetra-*n*-butylammonium acetate (TBAA), benzoate (TBAB), nitrate (TBAN), azide ($TBAN_3$), fluoride (TBAF), chloride (TBACl), and bromide (TBABr) to a solution of all the urea-functionalized polymers intensified the CD responses of the polymers, indicative of the chiral adjustability of the anion recognition using urea groups. The anion signaling property of the urea-functionalized polymers was different from each other. In particular, the signs of the induced Cotton effect for the urea-functionalized polymers in the presence of anions were strongly dependent on the pendant structure of the α-amino acids.

Introduction

Anion reception chemistry,[1] which was brought into the main stream after lagging behind several decades worth of study of cation host−guest chemistry, has been recently explored under a wide range of topics including anion-responsive self-assembly,[2] anion transport,[3] ion-pair recognition,[4] and anion sensing.[5,6] 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 supra molecular chemistry.[7] When we consider anion sensory materials, π-conjugated polymers emerge as important candidates,[8−10] primarily because some of them show not only their optical, but also their inherent chiroptical property coming from the π-conjugated main chain structure, which nominates them as potentially accomplished sensory systems. Among the many π-conjugated polymers, much attention has been paid to polyacetylene derivatives, one important member of the "dynamic helix", because they can output the molecular recognition event by simultaneous changes in not only their optical, but also their chiroptical properties.[11−13]

In fact, we previously found that the *cis*-poly(phenylacetylene) with the urea and L-leucine functionalities as a pendant (**PPA-Leu**) showed the anion responsive property.[14] In this system, the anion-urea host−guest interaction triggered a drastic color change in the polymer solution from pale yellow to red in response to guest anions, such as CH_3COO^-, Cl^-, and Br^-. Furthermore, in the system, an anion recognition event induced a distinct chiroptical property change in the poly(phenylacetylene) backbone. Although **PPA-Leu** showed an anion-signaling property due to its π-conjugated polymer backbone as a chromophore and urea functionality as the anion receptor, the anion distinguishing ability of the system was not sufficient, e.g., CH_3COO^- and Cl^- showed almost the same responses of the color and chiroptical changes. Thus, we should focus on the improvement of the system in order to achieve a more selective anion signaling material.

For polyacetylene derivatives, it is well-known that the structure of the substituent groups on a phenyl ring significantly affected the optical and chiroptical properties even though the difference in structure among the substituent groups was slight.[11−13,15−21] In our anion-sensing system, **PPA-Leu** is composed of three parts, the poly(phenylacetylene) chromophore, urea anion receptor, and chiral element of the α-amino acid residue, in which the substituent group can be very easily replaced from L-leucine by other α-amino acids. Importantly, arraying many of both the structurally and chemically similar sensory materials has recently been shown to make it possible to accomplish a potentially leading sensory system (so-called sensory array), which leads to the system with an advanced anion distinguishing ability using a pattern recognition technique.[22−27] Hence, in order to clarify the scope and limits of the anion responsive property leading to sensory materials, of great interest is to comprehensively elucidate the structural effect of the α-amino acid on the optical and chiroptical properties toward various anionic species.

We now report the diverse synthesis of poly(phenylacetylene)s conjugated to α-amino acids, including L-leucine, L-glutamic acid, L-aspartic acid, L-phenylalanine, L-isoleucine, and L-alanine through urea groups. This article presents (1) the universality of the anion signaling property of urea-functionalized polymers, and (2) the effect of diversity in the pendant structure on the anion signaling property (Scheme 1). *N*-(4-Ethynylphenylcarbamoyl)-L-amino acids ethyl esters (L-leucine, **PA-Leu**; L-glutamic acid, **PA-Glu**; L-aspartic acid, **PA-Asp**; L-phenylalanine, **PA-Phe**;

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Scheme 1. Schematic Representation for Anion-Signaling Event of Poly(phenylacetylene)s Bearing Urea Derivatives of the α-Amino Acids at a Molecular Level

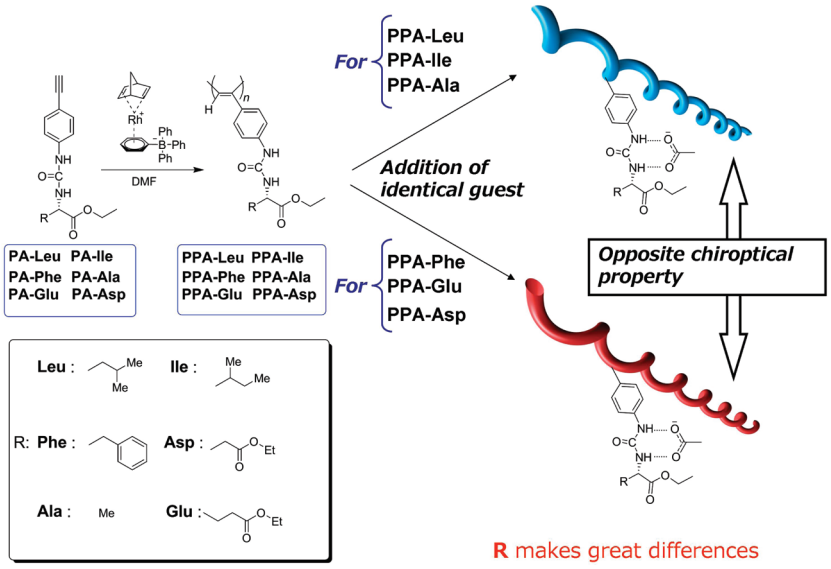

Table 1. Polymerization Results of Urea Functionalized Phenylacetylene Derivatives[a]

monomer	yield (%)	M_n ($\times 10^5$)[b]	M_w/M_n[b]
PA-Leu	77	2.0	2.4
PA-Glu	82	1.7	2.2
PA-Asp	87	1.5	3.9
PA-Phe	82	2.4	3.2
PA-Ile	88	1.7	2.3
PA-Ala	87	3.6	2.2

[a] The polymerization conditions were as follows; temperature, room temperature; [M]/[Rh] = 50; solvent, DMF; [M] = 0.03 mol·L^{-1}. [b] Determined by SEC in DMF containing 0.01 mol·L^{-1} LiCl using polystyrene standards.

L-isoleucine, **PA-Ile**; and L-alanine, **PA-Ala**) were synthesized and then polymerized in DMF using a rhodium complex as the catalyst to yield the *cis*-poly(phenylacetylene)s bearing L-amino acids and urea groups (**PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala**). The anion signaling properties of the obtained polymers were investigated using a series of anions, as illustrated in Scheme 1.

Results and Discussion

Synthesis and Chiroptical Properties of α-Amino Acid Conjugated Poly(phenylacetylene)s. In order to clarify the universality for the anion signaling property of urea-functionalized polymers and the effect of diversity in the structure of the α-amino acid on the anion recognition property, we prepared the *N*-(4-ethynylphenylcarbamoyl)-L-amino acid ethyl ester, which includes the phenylacetylene derivatives of L-leucine (**PA-Leu**), L-glutamic acid (**PA-Glu**), L-aspartic acid (**PA-Asp**), L-phenylalanine (**PA-Phe**), L-isoleucine (**PA-Ile**), and L-alanine (**PA-Ala**). We carried out the polymerization of the monomers using $Rh^+(2,5\text{-norbornadiene})[(\eta_6\text{-}C_6H_5)B^-(C_6H_5)_3]$ (Rh(nbd)BPh$_4$) as the catalyst in DMF, and the polymerization results are summarized in Table 1. All the polymerization reactions of the urea-functionalized phenylacetylene derivatives homogenously proceeded to produce the corresponding polymers. All the obtained polymers had a very high number average molecular weight and moderate polydispersity. Furthermore, the ^{1}H NMR spectra of all the obtained polymers showed sharp peaks at around 5.6 ppm, indicative of the *cis*-configuration in the polyacetylene main chain (see Supporting Information). Therefore, we succeeded in synthesizing poly(phenylacetylene)s bearing urea-functionalities derived from natural α-amino-acids (**PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala**). To investigate the effect of the structure of the α-amino acid in the obtained polymers, we first characterized their solubility toward common organic solvents including DMF, *N*,*N*-dimethylacetoamide (DMAc), *N*-methylpyrrolidone (NMP), DMSO, CH_2Cl_2, MeOH, and THF (Table 2). All the obtained polymers were essentially soluble in extremely polar solvents, such as DMF, DMAc, and NMP, whose solubility was probably due to the urea functionality property to form a strong self-assembly via hydrogen-bonding. On the other hand, the solubility of the obtained polymers toward DMSO, CH_2Cl_2, MeOH, and THF were dependent on the α-amino acids introduced, thus showing that the installed α-amino acid was a key factor to determine the properties of the urea-functionalized polymers.

Table 2. Solubility of Urea Functionalized Poly(phenylacetylene) Derivatives[a]

polymer	DMF	DMAc	NMP	DMSO	CH_2Cl_2	MeOH	THF
PPA-Leu	++	++	++	−	−	−	++
PPA-Glu	++	++	++	++	++	−	++
PPA-Asp	++	++	++	++	++	−	−
PPA-Phe	++	++	++	+	++	−	−
PPA-Ile	++	++	++	−	+	+	−
PPA-Ala	++	++	++	++	−	−	−

[a] Key: ++, soluble, +, partly soluble, −, insoluble.

The absorption and chiroptical properties of the urea-functionalized polymers were investigated in order to provide insights into the structural effect of the α-amino acid on the helical backbone of the poly(phenylacetylene). Figure 1 shows the circular dichroism (CD) and ultraviolet−visible (UV−vis) spectra of all the urea-functionalized polymers in DMF at room temperature. Distinctive Cotton effects were significantly observed in the UV−vis wavelength ranging from 300 to 550 nm, in which the π-conjugation of the polymer backbone typically appears. As expected, the observed Cotton effect of all the urea-functionalized polymers in the polymer backbone absorption was significantly dependent on the structure of the α-amino acid. For example, **PPA-Leu** and **PPA-Glu** showed positive Cotton effects

Table 3. [θ] Values of First Cotton Effects for Urea-Functionalized Polymers in Various Solvents[a]

polymer	DMF	DMAc	NMP
PPA-Leu	$+0.20 \times 10^4$ (390 nm)	-0.31×10^4 (392 nm)	$+0.08 \times 10^4$ (390 nm)
PPA-Glu	$+0.07 \times 10^4$ (360 nm)	-0.18×10^4 (390 nm)	$+0.11 \times 10^4$ (355 nm)
PPA-Asp	-0.24×10^4 (388 nm)	-1.00×10^4 (391 nm)	-1.02×10^4 (394 nm)
PPA-Phe	-0.50×10^4 (395 nm)	-0.78×10^4 (394 nm)	-0.73×10^4 (396 nm)
PPA-Ile	-0.73×10^4 (392 nm)	-0.74×10^4 (393 nm)	-0.51×10^4 (396 nm)
PPA-Ala	-0.97×10^4 (392 nm)	-0.97×10^4 (392 nm)	-1.21×10^4 (394 nm)

[a] CD measurements of urea-functionalized polymers in various solvents were performed at room temperature ([urea-functionalized polymers] = 1.0 mg·mL^{-1}).

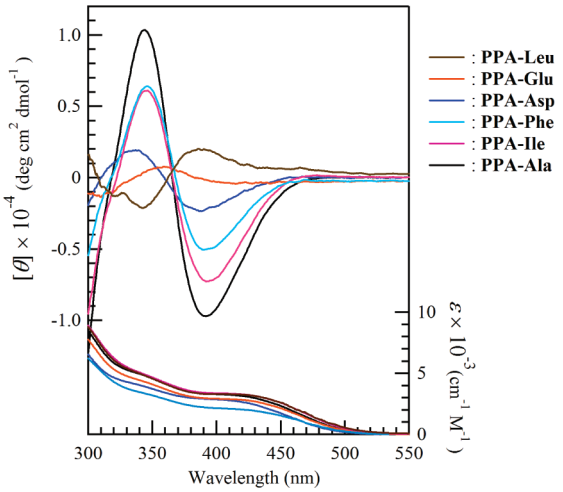

Figure 1. CD (upper) and absorption (lower) spectra of urea-functionalized polymers in DMF at room temperature ([polymer] = 1.0 mg·mL^{-1}).

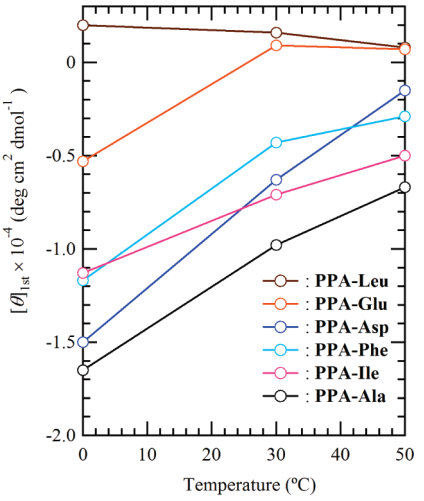

Figure 2. Temperature dependence of the molar ellipticity $[\theta]_{first}$ at the first Cotton effect of urea-functionalized polymers in DMF at various temperatures ([polymer] = 1.0 mg·mL^{-1}).

($+2.0 \times 10^3$ deg cm^2 dmol^{-1} at 390 nm and $+0.7 \times 10^3$ deg cm^2 dmol^{-1} at 360 nm, respectively), while **PPA-Ala** and **PPA-Ile** showed negative ones (-9.7×10^3 deg cm^2 dmol^{-1} at 392 nm and -7.3×10^3 deg cm^2 dmol^{-1} at 392 nm, respectively). Despite the same absolute configuration of the L-amino acids embedded in the polymer pendant, there was a distinct discrepancy among the CD profiles of all the urea-functionalized polymers. For characterizing the structural effect of the α-amino acid on the helical conformation of the poly(phenylacetylene), CD measurements both at variable temperatures and in various solvents were carried out (Figure 2 and Table 3, respectively). Figure 2 shows the variable temperature CD experiments in DMF. The magnitude of the Cotton effects increased as the temperature decreased for all the urea-functionalized polymers, 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. Importantly, there still existed a distinct discrepancy among the CD profiles of all the urea-functionalized polymers, which got larger with the decreasing temperatures. In a fashion similar to the temperature effect on the helical conformation, the solvents had an effect on both the magnitudes and the signs of the induced Cotton effects. Thus, we succeeded in synthesizing poly(phenylacetylene)s featuring diverse α-amino acid groups and urea anion receptors, whose chiroptical property was highly affected by the embedded amino acid residue.

Effect of the Pendant Structure on Anion-Recognition Ability of α-Amino Acid Conjugated Poly(phenylacetylene)s. To provide an insight into the universality for the anion signaling property of urea-functionalized polymers, we next focused on the investigation of the anion responsive properties

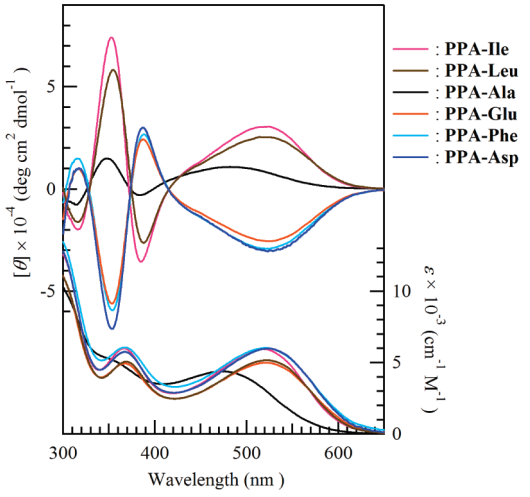

Figure 3. CD (upper) and absorption (lower) spectra of urea-functionalized polymers with CH_3COO^- in THF at 25 °C ([urea-functionalized polymers] = 1.0 mg·mL^{-1} and [TBAA]/[monomeric units of urea-functionalized polymers] = 10).

of the urea-functionalized polymers. Although the polymers, except for **PPA-Leu** and **PPA-Glu**, showed an insolubility in THF probably due to the strong intra- and/or intermolecular hydrogen bonding network (vide supra), we selected THF as the solvent for the anion recognition experiment according to our previous reports.[14,28] The CD and UV spectra of all the urea-functionalized polymers were recorded in the presence of 10 equivalents of tetra-*n*-butylammonium acetate (CH_3COO^-) calculated on the basis of the monomeric unit concentration (Figure 3). In clear contrast to the THF solutions of the polymers themselves, all the polymer solutions in

Table 4. [θ] Values of First Cotton Effects for Urea-Functionalized Polymers with Various Guests in THF[a]

	$[\theta]_{first} \times 10^{-4}$ [deg cm^2 dmol^{-1}] (λ_{first} [nm]) for the employed guest						
polymer	TBAA	TBAB	TBACl	TBABr	TBAF	TBAN	$TBAN_3$
PPA-Leu	+2.54 (515)	+1.71 (531)	+1.40 (521)	+0.175 (509)	−0.0393 (469)	−0.280 (460)	−0.179 (456)
PPA-Glu	−2.57 (526)	+1.81 (532)	−0.830 (512)	−0.332 (486)	−0.285 (454)	−0.141 (458)	−0.240 (386)
PPA-Asp	−3.06 (523)	−3.32 (531)	−0.222 (500)	×[b]	−0.128 (448)	−0.141 (393)	−0.113 (386)
PPA-Phe	−2.92 (522)	−2.95 (532)	−1.60 (505)	+0.504 (513)	−0.283 (461)	−0.152 (473)	−0.304 (459)
PPA-Ile	+3.05 (524)	×	−2.08 (513)	×	×	−0.0744 (474)	−0.0624 (476)
PPA-Ala	+1.08 (483)	+1.50 (511)	−0.712 (486)	×	×	×	×

[a] CD measurements of urea-functionalized polymers in THF were performed at 25 °C ([urea-functionalized polymers] = 1.0 mg·mL^{-1} and [guest]/[monomeric units of the polymers] = 10). [b] × means that polymer was partly soluble to the solution.

the presence of acetate anion provided a homogenously clear solution, probably due to the fact that the acetate anion switched off the noncovalent bonding network. In a similar fashion to the combination of **PPA-Leu** and CH_3COO^-, the combinations of all the urea-functionalized polymers and CH_3COO^- produced the red colored solutions and a drastic induction of the Cotton effects in the region attributed to the polymer backbone absorption. Therefore, the urea-functionalized polyacetylene derivatives featuring diverse α-amino acids universally responded to the anion guests, which triggered the drastic changes in the optical and chiroptical properties for **PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala**. Importantly, we observed a significant distinction in the outputting information toward the CH_3COO^- acquisition among **PPA-Leu**, **PPA-Ala**, **PPA-Phe**, **PPA-Ile**, **PPA-Asp**, and **PPA-Glu**, i.e., **PPA-Leu**, **PPA-Ala**, and **PPA-Ile** triggered the positive first Cotton effects whereas **PPA-Phe**, **PPA-Asp**, and **PPA-Glu** triggered negative ones (Figure 3). For example, **PPA-Ile** showed a very strong positive first Cotton effect ($+3.1 \times 10^4$ deg cm^2 dmol^{-1}) at 524 nm, whereas **PPA-Asp** showed a very strong negative Cotton effect (-3.1×10^4 deg cm^2 dmol^{-1}) at 524 nm. Furthermore, these results make a distinctively unique "fingerprint" for CH_3COO^-. To be more precise, **PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala** showed positive $[\theta]_{first}$, negative one, negative one, negative one, positive one, and positive one, respectively, making a distinct "signature" as (+, −, −, −, +, +) for CH_3COO^-. Thus, these results showed that a simple change of the pendant structure in the urea-functionalized poly(phenylacetylene)s could provide a unique signature for certain anionic guests, which should be important for the pattern recognition of anionic guests.

Because we found that all the urea-functionalized poly(phenylacetylene)s made a unique signature for CH_3COO^-, we finally focused on a preliminary pattern recognition toward anionic guests using both the urea-functionalized poly(phenylacetylene)s and a series of anions including acetate (CH_3COO^-), benzoate ($C_6H_5COO^-$), nitrate (NO_3^-), azide (N_3^-), fluoride (F^-), chloride (Cl^-), and bromide (Br^-) as their tetra-*n*-butylammonium salts in THF ([guest]/[urea] = 10, the guest concentration was calculated on the basis of the monomer concentration).[29,30] Table 4 shows the value of the first Cotton effect ($[\theta]_{first}$) and the wavelength for the first Cotton effect in the CD spectra (λ-$[\theta]_{first}$). As expected from the above preliminary experiments, the combination of a series of anions and urea-functionalized polymers including **PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala** demonstrated the breadth and diversity of the CD and UV−vis spectra as a consequence of the differences in the pendant structure of the α-amino acids. In a similar fashion to CH_3COO^-, unique patterns between the anionic guests and employed urea-functionalized polymers were observed for all the employed guests. As an example of $C_6H_5COO^-$, an anion structurally similar to CH_3COO^-, **PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala** showed positive $[\theta]_{first}$, positive one, negative one, negative one, heterogeneous solution, and positive one respectively, making a distinct "signature" as (+, +, −, −, × , +) for $C_6H_5COO^-$. This signature is distinctively different from that for CH_3COO^-, which in turn realized a distinct discrimination between the CH_3COO^- and $C_6H_5COO^-$ anions using the urea-functionalized poly(phenylacetylene)s. In a fashion similar to carboxylate anions, there existed a distinct discrepancy in the patterns of the chiroptical properties for a urea-functionalized poly(phenylacetylene) among the halogen anions. Thus, using the very simple system comprised of the urea-functionalized poly(phenylacetylene)s featuring the diverse pendant structure of α-amino acids, it was clearly possible to distinguish the anions including CH_3COO^-, $C_6H_5COO^-$, F^-, Cl^-, and Br^-. Although a distinct discrimination between NO_3^- and N_3^- could not be obtained, these results suggest the urea-functionalized poly(phenylacetylene)s as potentially accomplished sensory array system for the detection of anionic guests.

Conclusions. In summary, we have demonstrated an anion signaling system using *cis*-poly(phenylacetylene) with the urea and amino acid functionalities (**PPA-Leu**, **PPA-Glu**, **PPA-Asp**, **PPA-Phe**, **PPA-Ile**, and **PPA-Ala**). The anion signaling property turned out to be a universal phenomenon for urea-functionalized poly(phenylacetylene)s. In addition, we discovered that the anion signaling property of the polymers was strongly governed by the pendant structures. By arraying these polymers, it is possible to distinguish the anionic guests by a pattern recognition technique. This system provides a potential application to a wide range of sensory array systems.

Experimental Section

Materials. *N*,*N*-Dimethylformamide was purchased from Kanto Chemicals Co., Inc., and distilled under reduced pressure. *N*,*N*-Dimethylformamide, *N*,*N*-dimethylacetoamide, and *N*-methylpyrrolidone were available from Kanto Chemicals Co., Ltd., and used as received. Tetra-*n*-butylammonium azide ($TBAN_3$), nitrate (TBAN), fluoride (TBAF), bromide (TBABr), benzoate (TBAB) and acetate (TBAA) were purchased from Aldrich Chemical Co., Inc., and used as received. Tetra-*n*-butylammonium chloride (TBACl) was available from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan). 4-Ethynylaniline was purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. *N*,*N*-Dimethylformamide (purity >99.7%, water content <0.1%), and THF for the spectral analysis (>99.0%) were available from Kanto Chemicals Co., Ltd., and used without further purification. The *N*-carbonyl-L-amino acid ethyl esters were synthesized according to a previous report.[31] $Rh^+(2,5\text{-norbornadiene})[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ ($Rh(nbd)BPh_4$) was prepared in accordance with a previous report.[32] The synthesis of **PPA-Leu** was previously reported.[14]

Instruments. The ^{1}H and ^{13}C NMR spectra were recorded 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-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 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 circular dichroism (CD) spectra were measured in a 1-mm path length cell 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-Ethynylphenylcarbamoyl)-L-isoleucine Ethyl Ester (PA-Ile). To a solution of the *N*-carbonyl-L-isoleucine ethyl ester (7.50 g, 40.5 mmol) in CH_2Cl_2 (40 mL) was added 4-ethynylaniline (5.66 g, 48.3 mmol). After stirring at room temperature overnight, the reaction mixture was washed with HCl(aq). The combined organic layer was dried with $MgSO_4$, which gave the crude product. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (2/5, v/v) to give **PA-Ile** as a white crystal. Yield: 9.86 g (80.6%). Mp = 139 °C. $[\alpha]_D$ = +47.5° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.84−0.96 (m, C*H*$_3$CH$_2$CH(C*H*$_3$)−, 6H), 1.11−1.24 (m, CH$_3$C*H*$_2$CH(CH$_3$)−, 1H), 1.29 (t, *J* = 7.1 Hz, C*H*$_3$CH$_2$O−, 3H), 1.36−1.46 (m, CH$_3$C*H*$_2$CH(CH$_3$)−, 1H), 1.87−1.94 (m, CH$_3$CH$_2$C*H*(CH$_3$)−, 1H), 3.01 (s, C*H*≡CPh−, 1H), 4.15−4.29 (m, CH$_3$C*H*$_2$O−, 2H), 4.55 (dd, J_1 = 4.9 Hz, J_2 = 8.7 Hz, −C*H*COO, 1H), 5.96 (d, *J* = 8.7 Hz, −N*H*CONH−Ar, 1H), 7.25 (d, *J* = 8.5 Hz, Ar, 2H), 7.36 (d, *J* = 8.5 Hz, Ar, 2H,) 7.44 (s, −NHCON*H*−Ar, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 11.8, 14.3, 15.7, 25.3, 38.2, 57.5, 61.7, 76.4, 83.8, 116.4, 119.2, 133.1, 139.5, 155.2, 174.1. Anal. Calcd for $C_{17}H_{22}O_3N_2$ (302.37): C, 67.53; H, 7.33; N, 9.26. Found: C, 67.45; H, 7.47; N, 9.32.

Synthesis of the *N*-(4-ethynylphenylcarbamoyl)-L-alanine ethyl ester (PA-Ala). To a solution of the *N*-carbonyl-L-alanine ethyl ester (2.17 g, 15.2 mmol) in CH_2Cl_2 (30 mL) was added 4-ethynylaniline (1.88 g, 16.0 mmol). After being stirred at room temperature overnight, the reaction mixture was washed with HCl(aq). The combined organic layer was dried with $MgSO_4$, which gave the crude product. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (3/4, v/v) to give **PA-Ala** as a white crystal. Yield: 3.71 g (94.1%). Mp = 134 °C. $[\alpha]_D$ = +40.1° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.28 (t, *J* = 7.1 Hz, C*H*$_3$CH$_2$O−, 3H), 1.40 (d, *J* = 7.2 Hz, C*H*$_3$CH−, 3H), 3.01 (s, C*H*≡CPh−, 1H), 4.16−4.24 (m, CH$_3$C*H*$_2$O−, 2H), 4.53 (m, −C*H*COO, 1H), 6.01 (d, *J* = 7.5 Hz, −N*H*CONH−Ar, 1H), 7.23 (d, *J* = 8.7 Hz, Ar, 2H), 7.33 (d, *J* = 8.7 Hz, Ar, 2H), 7.54 (s, −NHCON*H*−Ar, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 18.8, 49.0, 61.9, 76.5, 83.7, 116.4, 119.3, 133.1, 139.4, 155.0, 174.9. Anal. Calcd for $C_{14}H_{16}N_2O_3$ (260.29): C, 64.60; H, 6.20; N, 10.76. Found: C, 64.60; H, 6.25; N, 10.78.

Synthesis of the *N*-(4-Ethynylphenylcarbamoyl)-L-phenylalanine Ethyl Ester (PA-Phe). To a solution of the *N*-carbonyl-L-phenylalanine ethyl ester (3.38 g, 15.4 mmol) in CH_2Cl_2 (30 mL) was added 4-ethynylaniline (2.12 g, 18.1 mmol). After stirring at room temperature overnight, the reaction mixture was washed with HCl(aq). The combined organic layer was dried with $MgSO_4$, which gave the crude product. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (2/5, v/v) to give **PA-Phe** as a white crystal. Yield: 4.59 g (88.3%). Mp = 134 °C. $[\alpha]_D$ = +105.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.22 (t, *J* = 7.1 Hz, C*H*$_3$CH$_2$O−, 3H), 2.89−3.07 (m, −C*H*$_2$Ph, C*H*≡CPh−, 3H), 4.07−4.19 (m, CH$_3$C*H*$_2$O−, 2H), 4.78 (m, −C*H*COO, 1H), 6.03 (d, *J* = 8.0 Hz, −N*H*CONH−Ar, 1H), 7.10−7.30 (m, Ar, 9H), 7.61 (s, −NHCON*H*−Ar, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.2, 38.3, 54.2, 61.8, 76.5, 83.7, 116.3, 119.3, 127.2, 128.6, 129.4, 133.0, 136.1, 139.3, 155.1, 173.4. Anal. Calcd for $C_{20}H_{20}N_2O_3$ (336.38): C, 71.41; H, 5.99; N, 8.33. Found: C, 71.39; H, 6.02; N, 8.33.

Synthesis of the *N*-(4-Ethynylphenylcarbamoyl)-L-aspartic Acid Diethyl Ester (PA-Asp). To a solution of the *N*-carbonyl-L-aspartic acid diethyl ester (2.41 g, 11.2 mmol) in CH_2Cl_2 (40 mL) was added 4-ethynylaniline (1.56 g, 13.3 mmol). After being stirred at room temperature overnight, the reaction mixture was washed with HCl(aq). The combined organic layer was dried with $MgSO_4$, which gave the crude product. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/2, v/v) to give **PA-Asp** as a white crystal. Yield: 2.76 g (74.1%). Mp = 132 °C. $[\alpha]_D$ = +61.2° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.20−1.26 (m, C*H*$_3$CH$_2$O−, 6H), 2.90−3.09 (m, −C*H*$_2$C═O, C*H*≡CPh−, 3H), 4.06−4.26 (m, CH$_3$C*H*$_2$O−, 4H), 4.90−4.95 (m, −NHC*H*COO, 1H), 6.51 (d, *J* = 8.4 Hz, −N*H*CONH−Ar, 1H), 7.23 (d, *J* = 8.7 Hz, Ar, 2H), 7.30 (d, *J* = 8.7 Hz, Ar, 2H), 8.02 (s, −PhN*H*C═O, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 13.9$_9$, 14.0$_2$, 36.9, 49.4, 61.1, 62.0, 76.3, 83.6, 116.0, 118.9, 132.8, 139.5, 155.1, 171.5, 172.4. Anal. Calcd for $C_{17}H_{20}N_2O_5$ (332.35): C, 61.44; H, 6.07; N, 8.43. Found: C, 61.33; H, 6.07; N, 8.36.

Synthesis of the *N*-(4-Ethynylphenylcarbamoyl)-L-glutamic Acid Diethyl Ester (PA-Glu). To a solution of the *N*-carbonyl-L-glutamic acid diethyl ester (4.36 g, 19.0 mmol) in CH_2Cl_2 (80 mL) was added 4-ethynylaniline (2.67 g, 22.8 mmol). After stirring at room temperature overnight, the reaction mixture was washed with HCl(aq). The combined organic layer was dried with $MgSO_4$, which gave the crude product. The crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1/2, v/v) to give **PA-Glu** as a white crystal. Yield: 5.77 g (87.9%). Mp = 76 °C. $[\alpha]_D$ = +29.8° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.21−1.30 (m, C*H*$_3$CH$_2$O−, 6H), 1.95−2.50 (m, −CH−C*H*$_2$C*H*$_2$−COO−, 4H), 3.01 (s, C*H*≡CPh−, 1H), 4.09−4.22 (m, CH$_3$C*H*$_2$O−, 4H), 4.55−4.61 (m, −NHC*H*COO, 1H), 6.04 (d, *J* = 8.0 Hz, −N*H*CONH−Ar, 1H), 7.26−7.38 (m, Ar, 4H), 7.54 (s, −NHCON*H*−Ar, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 14.4$_1$, 14.4$_5$, 28.0, 30.8, 52.9, 61.2, 62.2, 76.7, 83.9, 116.7, 119.5, 133.3, 139.6, 155.3, 173.6, 173.7. Anal. Calcd for $C_{18}H_{22}N_2O_5$ (346.38): C, 62.42; H, 6.40; N, 8.09. Found: C, 62.31; H, 6.38; N, 8.02.

Polymerization of the Urea-Functionalized Phenylacetylene Derivatives. The polymerizations of the urea-functionalized phenylacetylene derivatives were carried out in DMF using Rh^+(2,5-norbornadiene)[(η^6-C_6H_5)B^-(C_6H_5)$_3$] (Rh(nbd)BPh$_4$) as the catalyst. A typical procedure is described below.

The polymerization of **PA-Ile** was carried out in a dry flask under an argon atmosphere. In an argon atmosphere, **PA-Ile** (600 mg, 1.98 mmol) was weighed into a flask and dissolved in dry DMF (62.0 mL). To the solution was added a solution of Rh(nbd)BPh$_4$ (22.7 mg, 40.7 μmol) in dry DMF (4.0 mL). After this was stirred at room temperature for 24 h, triphenylphosphine (52.0 mg, 200 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 acetonitrile and then dried under reduced pressure to give **PPA-Ile** as a yellow powder. Yield: 529 mg (88.2%). $M_n = 1.7 \times 10^5$; M_w/M_n = 2.3.

For the other monomers, we used the following solvents for the reprecipitation: MeOH (**PPA-Ala**), 2-propanol (**PPA-Phe**), EtOH (**PPA-Asp**), and diethyl ether (**PPA-Glu**).

CD Measurements. The CD and UV−vis spectra were measured in a 1 mm quartz cell ([polymer] = 1.0 mg·mL^{-1}).

The concentration of guest was calculated based on the monomeric units of the polymer.

Supporting Information Available: Figures showing ^{1}H NMR spectra of the obtained polymers in DMF-d_7 and CD spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Caltagirone, C.; Gale, P. A. *Chem. Soc. Rev*. **2009**, *38*, 520–563.
(2) Maeda, H. *Chem.—Eur. J*. **2008**, *14*, 11274–11282.
(3) Davis, A. P.; Sheppard, D. N.; Smith, B. D. *Chem. Soc. Rev*. **2007**, *36*, 348–357.
(4) Gale, P. A. *Coord. Chem. Rev*. **2003**, *240*, 191–221.
(5) Anzenbacher, P.; Nishiyabu, R.; Palacios, M. A. *Coord. Chem. Rev*. **2006**, *250*, 2929–2938.
(6) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev*. **2003**, *103*, 4419–4476.
(7) Sessler, J. L.; Gale, P. A.; Cho, W.-S. *Anion Receptor Chemistry*; Royal Society of Chemistry: Cambridge, U.K., **2006**.
(8) Swager, T. M. *Acc. Chem. Res*. **1998**, *31*, 201–207.
(9) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev*. **2000**, *100*, 2537–2574.
(10) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev*. **2007**, *107*, 1339–1386.
(11) Lam, J. W. Y.; Tang, B. Z. *Acc. Chem. Res*. **2005**, *38*, 745–754.
(12) Yashima, E.; Maeda, K. *Macromolecules* **2008**, *41*, 3–12.
(13) Masuda, T. *J. Polym. Sci., Part A: Polym. Chem*. **2007**, *45*, 165–180.
(14) Kakuchi, R.; Nagata, S.; Sakai, R.; Otsuka, I.; Nakade, H.; Satoh, T.; Kakuchi, T. *Chem.—Eur. J*. **2008**, *14*, 10259–10266.
(15) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J*. **2004**, *10*, 42–51.
(16) Sanda, F.; Araki, H.; Masuda, T. *Macromolecules* **2005**, *38*, 10605–10608.
(17) Sanda, F.; Terada, K.; Masuda, T. *Macromolecules* **2005**, *38*, 8149–8154.
(18) Suzuki, Y.; Tabei, J.; Shiotsuki, M.; Inai, Y.; Sanda, F.; Masuda, T. *Macromolecules* **2008**, *41*, 1086–1093.
(19) Otsuka, I.; Hongo, T.; Nakade, H.; Narumi, A.; Sakai, R.; Satoh, T.; Kaga, H.; Kakuchi, T. *Macromolecules* **2007**, *40*, 8930–8937.
(20) Cheuk, K. K. L.; Lam, J. W. Y.; Li, B. S.; Xie, Y.; Tang, B. Z. *Macromolecules* **2007**, *40*, 2633–2642.
(21) Cheuk, K. K. L.; Li, B. S.; Lam, J. W. Y.; Xie, Y.; Tang, B. Z. *Macromolecules* **2008**, *41*, 5997–6005.
(22) Collins, B. E.; Anslyn, E. V. *Chem.—Eur. J*. **2007**, *13*, 4700–4708.
(23) Anslyn, E. V. *J. Org. Chem*. **2007**, *72*, 687–699.
(24) Wang, Z.; Palacios, M. A.; Anzenbacher, P. *Anal. Chem*. **2008**, *80*, 7451–7459.
(25) Zyryanov, G. V.; Palacios, M. A.; Anzenbacher, P. *Angew. Chem., Int. Ed*. **2007**, *46*, 7849–7852.
(26) Palacios, M. A.; Nishiyabu, R.; Marquez, M.; Anzenbacher, P. *J. Am. Chem. Soc*. **2007**, *129*, 7538–7544.
(27) Palacios, M. A.; Wang, Z.; Montes, V. A.; Zyryanov, G. V.; Anzenbacher, P. *J. Am. Chem. Soc*. **2008**, *130*, 10307–10314.
(28) Kakuchi, R.; Nagata, S.; Tago, Y.; Sakai, R.; Otsuka, I.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42*, 1476–1481.
(29) Because we previously discovered that 10 equiv of guest was enough to induce the distinct changes in the both optical and chiroptical property of polyacetylene main chain, we set the guest concentration as [guest]/[urea] = 10. For detailed CD titration experiments, please see ref 14.
(30) All the CD figures in the presence of 10 equivalent of guest were listed in the Supporting Information. With respect to **PPA-Leu**, the CD data was previously reported in ref 14.
(31) Knólker, H. J.; Braxmeier, T. *Synlett* **1997**, 925–928.
(32) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **1995**, *28*, 6662–6666.