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ARTICLE

# Efficient Colorimetric Anion Detection Based on Positive Allosteric System of Urea-Functionalized Poly(phenylacetylene) Receptor

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ABSTRACT: Poly(phenylacetylene) with rationally designed urea groups was demonstrated to be a superior anion receptor possessing both a colorimetric response ability and a positive homotropic allosteric binding mode. The target polymer, poly(phenylacetylene) with [bis(trifluoromethyl)phenyl]urea pendants (poly-**1**), was synthesized by the stereoselective polymerization with $Rh(nbd)BPh_4$ (nbd = norbornadiene) in high yield. The anion sensing ability of poly-**1** was evaluated using the tetra-*n*-butylammonium (TBA) salts of a series of anions in THF. Upon the addition of anions such as $CH_3CO_2^-$, $C_6H_5CO_2^-$, $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $N_3^-$, and $HSO_4^-$, the yellow color of the THF solution of poly-**1** immediately turned to a different color depending on the types of anions, indicating the anion recognition capability of poly-**1**. The $^1H$ NMR titrations of poly-**1** by using increasing amounts of $CH_3CO_2^-$ revealed that the colorimetric response of poly-**1** was considered to be the direct consequence of the hydrogen-bonding complex formation between the urea functionality and the anions. Interestingly, during the course of the determination of the anion-binding affinity, we encountered highly cooperative binding ability of poly-**1**. The Hill plot analysis provided an exceptional positive cooperativity, e.g., 8.4 of Hill coefficient in the complexation between poly-**1** and $C_6H_5CO_2^-$. This result clearly indicated that this binding mode was based on a positive homotropic allosterism, in which the partially formed urea/anion complex units in the polymer chain should produce a change in the whole main chain conformation, facilitating further anion binding. Additionally, by comparing the anion binding of poly-**1** with that of previously prepared urea-functionalized poly(phenylacetylene) (poly-**2**), an enhanced anion binding ability based on two electron-withdrawing $-CF_3$ groups was found to be essential to realize such cooperativity.

## Introduction

Anions have been recognized as a significant analyte in diverse fields including environmental, industrial, biological, and medical ones.[1] Therefore, a reliable, robust, and highly sensitive anion sensor has been increasingly in demand.[2−7] In particular, a colorimetric anion sensor has been recently appreciated because of its capability that allows a simple and quick analysis and even naked-eye detection.[2,3,5] For example, Sessler et al. achieved the fabrication of a number of colorimetric anion sensors by simply using commercially available chemicals.[8] Anzenbacher et al. established a reliable method for multianion sensing based on the pattern recognition of colorimetric sensor arrays.[9] Although such sophisticated colorimetric anion sensors have already been developed, further improvement in the detection sensitivity is still desired.

For the realization of a highly efficient anion detection, one of the rational approaches should be the construction of a positive homotropic allosteric system.[10,11] This system rests on the cooperative binding process, in which the initial molecular binding facilitates the subsequent interactions, thus providing an efficient sensing ability. Although the system is ubiquitously seen in nature as an efficient information transduction process, it is highly difficult to artificially prepare the appropriate receptor molecule with the positive homotropic allosterism. Therefore, only limited examples have been known as the anion recognition with such a cooperative binding mode, in which small molecular receptor bearing several binding sites is employed.[12−15] Considering that the positive allosteric system essentially needs to possess dynamic multiple binding sites, a polymeric receptor would be a rational candidate because (1) the introduction of a great number of binding sites (more than 100) into one molecule is synthetically easy and (2) the initial guest-binding event influences the subsequent complexation through the conformational change of the whole polymer chain. In particular, by adopting a $\pi$-conjugated polymer as such receptor polymer, the optical output ability is highly expected as well as the cooperative binding.[16−23]

On the basis of this concept, we have investigated the anion recognition ability of poly(phenylacetylene) receptors.[24−27] Among them, poly(phenylacetylene)s with amino acid-derived urea pendants were found to exhibit a drastic anion-induced colorimetric response, in which the resulting color was varied depending on the employed anion.[24,26] However, the desired positive allosteric binding was not achieved probably due to the low binding ability of the urea receptor. In order to enhance the binding affinity, a rational molecular design must be required in receptor units.

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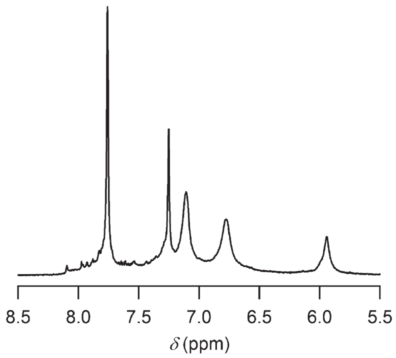
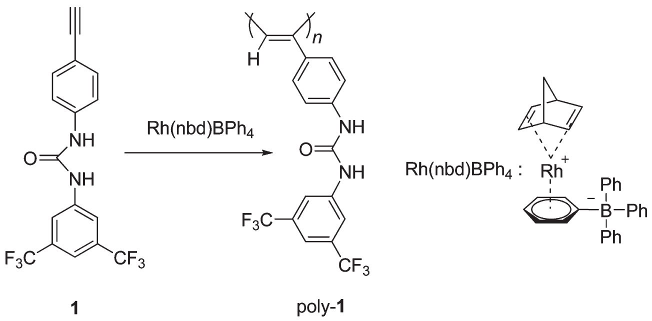


**Figure 1.** $^1$H NMR spectrum of poly-**1** in $CD_3OD$ at ambient temperature.

**Scheme 1. Synthesis of Urea-Functionalized Poly(phenylacetylene) (Poly-1)**



We have now designed poly(phenylacetylene) with [bis(trifluoromethyl)phenyl]urea pendants (poly-**1**), which emerges as an ideal candidate because of the expectation that the electron-withdrawing $-CF_3$ substituents will enhance the hydrogen-bonding ability of urea functionalities.[28,29] The UV−vis and $^1$H NMR measurements in the presence of a series of anions have been carried out to elucidate the colorimetric anion sensing of poly-**1**, providing insight into positive allosteric binding based on the rationally designed polymeric receptor.

## Results and Discussion

The polymerization of **1** was carried out using Rh(nbd)$BPh_4$ in dry THF at ambient temperature to produce the desired poly(phenylacetylene) with [bis(trifluoromethyl)phenyl]urea pendants (poly-**1**) in 89% yield (Scheme 1). The molecular weight and polydispersity of poly-**1** were determined to be $1.7 \times 10^5$ and 1.8 based on the SEC measurement, respectively. In the $^1$H NMR spectrum of poly-**1**, the signal corresponding to the main chain proton was observed at 5.94 ppm along with those due to aromatic protons at 7.76, 7.25, 7.11, and 6.78 ppm, indicating that poly-**1** possessed the *cis* configuration as the main chain stereoregularity (Figure 1).

The anion sensing ability of poly-**1** was evaluated using the tetra-*n*-butylammonium (TBA) salts of a series of anions in THF. Poly-**1** exhibits a yellow color due to the $\pi$-conjugated system in the main chain structure. Upon the addition of almost all anions, the yellow polymer solution immediately turned to a different color depending on the types of anions, as shown in Figure 2a. For more detailed discussions, UV−vis measurements of poly-**1** were performed in the presence of these anions. As shown in Figure 2b, a large bathochromic shift was observed for $CH_3CO_2^-$, $C_6H_5CO_2^-$, $F^-$, $Cl^-$, $Br^-$, $NO_3^-$, $N_3^-$, and $HSO_4^-$, though $ClO_4^-$ apparently produced no spectral change. Interestingly, the anion recognition of poly-**1** provides a different absorption spectrum basically depending on the kinds of anions, which is the reason for the color variation. Although poly-**1** seems to bind to almost all the above anions without articulate selectivity under this condition, the multicolor response capability allows a rough discrimination of the anions by the naked eye.

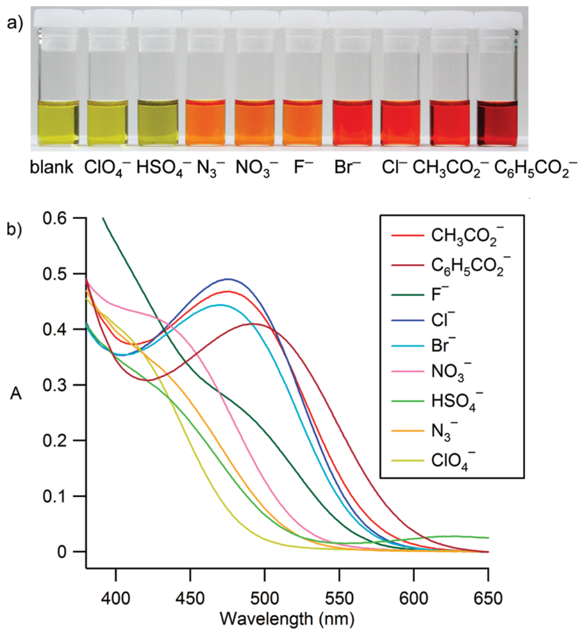


**Figure 2.** (a) Photograph of THF solutions and (b) absorption spectra of poly-**1** in the presence of TBA salts of a series of anions ([monomeric units of poly-**1**] = 1.3 mM in photograph and 130 $\mu$M in absorption spectra, [anion]/[monomeric units of poly-**1**] = 5).

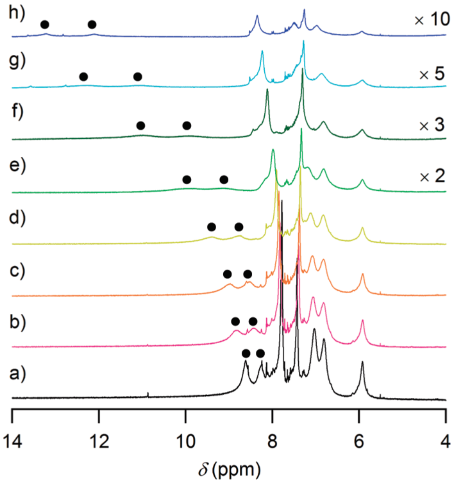


**Figure 3.** $^1$H NMR spectra of poly-**1** in the presence of (a) 0, (b) 0.05, (c) 0.1, (d) 0.2, (e) 0.3, (f) 0.5, (g) 0.7, and (h) 1.0 equiv of tetra-*n*-butylammonium acetate in THF-$d_8$. Closed circles show the peaks due to the urea protons.

In anion reception chemistry, a color change of a urea receptor molecule has been known to be based on a complex formation with an anion or anion-induced deprotonation.[30−33] To provide an insight into the colorimetric response of poly-**1**, we performed $^1$H NMR titrations of poly-**1** in the presence of increasing amounts of $CH_3CO_2^-$ (Figure 3). In the $^1$H NMR spectrum, a remarkable broadening was observed in the signals due to the urea, main chain, and aromatic protons of poly-**1**. Additionally, a downfield shift in the urea protons reflects the establishment of a hydrogen bond interaction with $CH_3CO_2^-$.[34] These results indicated that the colorimetric response of poly-**1** was considered to be the direct consequence of the supramolecular complex formation between the urea functionality and various anions.

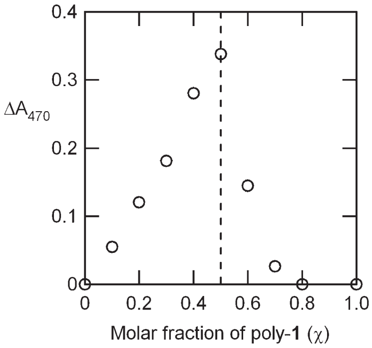


**Figure 4.** Job's plots upon mixing of THF solutions of poly-**1** and $CH_3CO_2^-$, obtained by means of UV−vis spectroscopy. The total concentration of monomeric units of poly-**1** and $CH_3CO_2^-$ was kept constant at 260 $\mu$M.

In order to further elucidate this complex formation, the stoichiometry of the poly-**1**/$CH_3CO_2^-$ system was determined by means of continuous-variation plots (Job's plots), in which the variation of the absorbance at 470 nm was plotted against the molar fraction of the monomeic units of poly-**1** ($\chi$) (Figure 4). Although the shape of plots was not symmetrical because of the cooperativity that is described later, the maximum value was clearly observed at 0.5 of $\chi$, which indicated that the urea receptor in poly-**1** and $CH_3CO_2^-$ formed the 1:1 complex.

To understand the binding ability of poly-**1**, an absorption titration experiment was conducted using $CH_3CO_2^-$. By adding $CH_3CO_2^-$, the absorption corresponding to the polymer backbone gradually red-shifted and the $\lambda_{max}$ reached 466 nm when 1.0 equiv of $CH_3CO_2^-$ was added to the system (Figure 5a). Figure 5b shows the plots of the absorbance at 470 nm as a function of the $CH_3CO_2^-$ amount. The saturation in the absorption change was produced by the addition of almost an equimolar amount of $CH_3CO_2^-$ relative to the urea units of poly-**1**, implying that the efficient anion reception event was accomplished. More importantly, the resulting titration curve displayed a sigmoidal curvature, indicative of a cooperative binding mode.[10,11] Thus, this binding process was analyzed using the Hill equation, which is a suitable equation for determining both the binding constant and cooperativity in the case of a cooperative binding system.[35] The monomer unit-based apparent association constant ($K_a$) and Hill coefficient ($n$) of this binding system was determined to be 11 500 $M^{-1}$ and 8.0, respectively (the inset of Figure 5b). The resulting $K_a$ value obviously indicates that poly-**1** possesses a superior binding ability to $CH_3CO_2^-$.[36] More importantly, an exceptional $n$ value was observed in this binding system, implying a positive homotropic allosterism. The $n$ value describes the cooperativity in the binding process and the values greater than one are obtained in the case of positive allosteric binding mode, in which the initial guest-binding facilitates further complex formation. Given the observed large $n$ value, it is obvious that the cooperative and positive allosteric binding occurs between poly-**1** and $CH_3CO_2^-$, thus providing the increasing anion binding ability. For this binding system, the partially formed urea/$CH_3CO_2^-$ complex units in the polymer chain should produce a change in the whole main chain conformation, which is more suitable for further $CH_3CO_2^-$ binding. Therefore, the binding ability of poly-**1** nonlinearly increases with the increasing amount of $CH_3CO_2^-$ bound to poly-**1**. The observed positive allosteric binding mode is definitely attributable to the molecular feature that cooperative conformation change of the polymer backbone is actualized. A similar cooperative conformation change has been particularly observed for helical poly(phenylacetylene)s,[37] which is the so-called chiral amplification via the sergeants and soldiers principle.[38,39] Given the scarcity of such highly cooperative conformational change for the polymeric receptor, poly(phenylacetylene) backbone should be important for the observed allosteric anion-binding capability of poly-**1**. The inherent rigidity and stiffness of the poly(phenylacetylene) backbone may contribute to the exceptional cooperativity.

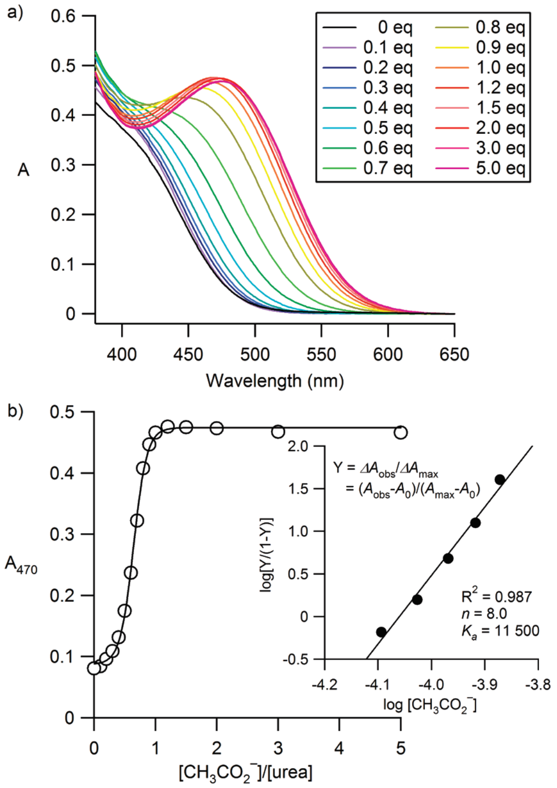


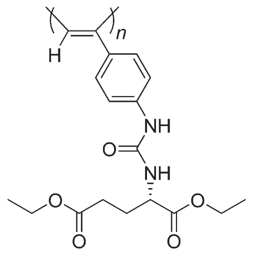
**Figure 5.** (a) UV−vis absorption titration and (b) the resulting titration curve of poly-**1** with $CH_3CO_2^-$ in THF ([monomeric units of poly-**1**] = 130 $\mu$M, [$CH_3CO_2^-$]/[monomeric units of poly-**1**] = 0−5.0). Inset shows the Hill plot analysis of this complexation.

We further examined the effect of the molecular design of poly-**1** on the anion binding affinity by comparison to that of poly(phenylacetylene) featuring urea receptors derived from L-glutamic acid (poly-**2**), which is one of the polymers that we previously reported.[40] The change in the absorption spectrum with the addition of $CH_3CO_2^-$ and the resulting titration curve are shown in Figure S1 of the Supporting Information. Poly-**2** exhibited a bathochromic shift similar to poly-**1** upon the addition of $CH_3CO_2^-$. However, the spectral change was gradual, and thus more than 15 equiv of $CH_3CO_2^-$ was necessary for completing the change. On the basis of the Hill analysis, the $K_a$ and $n$ values of this binding system were found to be 2800 $M^{-1}$ and 1.3, respectively, which were both significantly lower than those for poly-**1**. In particular, the resulting $n$ value indicates little cooperativity in the binding process between poly-**2** and $CH_3CO_2^-$. These results suggest that the both binding ability and cooperativity were remarkably enhanced for the newly designed poly-**1**.

The most reasonable explanation in the improvement of the binding ability of poly-**1** is the rational molecular design of the urea moiety. Two electron-withdrawing $-CF_3$ groups probably endow the urea receptor with a more robust and efficient hydrogen-bonding ability, thus enabling the improved anion binding affinity. For realization of the highly cooperative binding, the rational molecular design of the receptor units was therefore clarified to be indispensable as well as the inherent nature of the poly(phenylacetylene) backbone.

Finally, we carried out the absorption titration experiment and Hill analysis for all the anions in order to elucidate the binding

**Chart 1. Structure of Poly-2**



poly-**2**

**Table 1. Apparent Association Constant ($K_a$) and Hill Coefficient ($n$) of the Complexation of Poly-1 with Various Anions[a]**

| anion | $K_a$ ($M^{-1}$) | $n$ |
|---|---|---|
| $CH_3CO_2^-$ | 11500 | 8.0 |
| $C_6H_5CO_2^-$ | 11700 | 8.4 |
| $F^-$ | 6500 | 2.6 |
| $Cl^-$ | 9100 | 3.6 |
| $Br^-$ | 5300 | 1.6 |
| $NO_3^-$ | 4900 | 1.4 |
| $N_3^-$ | 12300 | 1.4 |
| $HSO_4^-$ | 11500 | 1.4 |

[a] Determined from absorption titrations by using the Hill equation.

ability of poly-**1** to other anions (see Supporting Information; Figures S3–S5). In the resulting titration curve, the amount of anion for reaching to the saturation and the curve profile highly depended on anions. The $K_a$ and $n$ values could be determined for anions except for $ClO_4^-$ by using the Hill analysis, and the resulting values are summarized in Table 1. Poly-**1** was found to possess good binding affinities to these anions, of which the $K_a$ values ranged from 4900 to 12 300, suggesting that poly-**1** was a suitable receptor for all these anions. Moreover, a positive allosteric binding similar to the case of $CH_3CO_2^-$ was observed for $C_6H_5CO_2^-$, $F^-$, and $Cl^-$, though almost no cooperativity was found for $Br^-$, $NO_3^-$, $N_3^-$, and $HSO_4^-$. In particular, the poly-**1**/$C_6H_5CO_2^-$ complex exhibited the highest $n$ value of 8.4. The observed $n$ value increased in the order of $NO_3^- \approx N_3^- \approx HSO_4^- < Br^- < F^- < Cl^- \ll CH_3CO_2^- < C_6H_5CO_2^-$. The important point to note is that the order is not well explained by only the binding constant.

For the anion recognition chemistry, the binding affinity is generally dictated by the basicity of anions, which increases in the order of $ClO_4^- < HSO_4^- \approx Br^- \approx NO_3^- < Cl^- < N_3^- < C_6H_5CO_2^- < CH_3CO_2^- < F^-$.[41] However, neither the $K_a$ nor $n$ values well correlated with the basicity of the anions. Considering that good relationship was also not observed between the colorimetric response of poly-**1** and the basicity of the employed anions, other factor should be concerned in this anion recognition event. In the both processes of the colorimetric response and the cooperative anion binding, the polymer conformation change plays a crucial role as well as the anion binding at the urea functionalities. Therefore, the anion size, which has a significant effect in the polymer conformation change, could be considered as one of the prime factors in this anion recognition. Although the exact mechanism has yet to be revealed, the anion specificity in the colorimetric response and the cooperative binding were clearly demonstrated in this examination. Further investigation is currently being conducted to clarify this mechanism, which includes the evaluation of anion recognition of poly(phenylacetylene) bearing bulkier pendants.

## Conclusions

We demonstrated the efficient colorimetric anion sensing based on the highly cooperative binding ability of urea-functionalized poly(phenylacetylene). The introduction of electron-withdrawing $-CF_3$ groups realized a significant enhancement in the binding ability without disturbing the capability of showing the color variation depending on the types of anions. A detailed investigation clarified that both the poly(phenylacetylene) scaffold and the enhanced hydrogen bonding ability of the urea receptor were essential for the exceptional cooperativity. The concept of this cooperative anion binding is applicable to other polymer and supramolecular receptor that are possessing dynamic multipoint binding sites. Therefore, we believe that the demonstrated positive allosterism based on the poly(phenylacetylene) receptor will contribute to the further design of reliable and highly sensitive anion sensor materials.

## Experimental Section

**Materials.** 3,5-Bis(trifluoromethyl)phenyl isocyanate, tetra-*n*-butylammonium azide, nitrate, fluoride, bromide, benzoate, and acetate were purchased from Aldrich Chemical Co., Inc., and used as received. Tetra-*n*-butylammonium chloride and perchlorate were available from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan). 4-Ethynylaniline and tetra-*n*-butylammonium hydrogen sulfate were purchased from Wako Pure Chemical Industries, Ltd., and used without further purification. Dry THF was available from Kanto Chemicals Co., Ltd., and used without further purification. $Rh^+$(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.[42] The synthesis of poly-**2** has already been reported.[26] The number-average molecular weight and polydispersity of poly-**2** are $1.7 \times 10^5$ and 2.2, respectively.

**Instruments.** The $^1H$ and $^{13}C$ NMR spectra were recorded using a JEOL JNM-A400II instrument. 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 $\mu$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 a flow rate of 0.4 mL $min^{-1}$. The number-average molecular weight ($M_n$) and polydispersity ($M_w/M_n$) of the polymer were calculated on the basis of a polystyrene calibration. The ultraviolet–visible (UV–vis) spectrum was measured using a Jasco V-550 spectrophotometer equipped with a Jasco ETC-505T temperature controller. 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.

**Synthesis of 1-(4-Ethynylphenyl)-3-[3,5-bis(trifluoromethyl)-phenyl]urea (1).** To a solution of 3,5-bis(trifluoromethyl)phenyl isocyanate (4.40 g, 17.3 mmol) in dry THF (45 mL) was added a solution of 4-ethynylaniline (2.12 g, 18.1 mmol) in dry THF (25 mL) at room temperature under a $N_2$ atmosphere. The reaction mixture was stirred overnight. After the removal of the solvent, the residue was dissolved in ethyl acetate and washed with 1 N HCl, followed by water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated to dryness. The residue was purified by recrystallization from acetonitrile to give **1** as a solid. Yield = 6.26 g (97.5%); mp 156 °C. $^1H$ NMR (400 MHz, DMSO-$d_6$, $\delta$): 9.44 (s, 1H, $-NH-CO-$), 9.19 (s, 1H, $-NH-CO-$), 8.14 (s, 2H, aromatic), 7.64 (s, 1H, aromatic), 7.52 (d, $J$ = 8.8 Hz, 2H, aromatic), 7.42 (d, $J$ = 8.7 Hz, 2H, aromatic), 4.06 (s, 1H, $HC{\equiv}C-$). $^{13}C$ NMR (100 MHz, DMSO-$d_6$, $\delta$): 153.14, 142.58, 140.64, 133.34, 131.65 (q, $J$ = 33 Hz), 124.21 (q, $J$ = 273 Hz), 119.5, 119.10, 116.26, 115.45, 84.50, 80.49. Anal. Calcd for $C_{17}H_{10}F_6N_2O$: C, 54.85; H, 2.71; N, 7.53. Found: C, 54.51; H, 2.94; N, 7.42.

**Polymerization.** The polymerization of **1** was carried out in a dry Shlenk flask under an argon atmosphere. Under an Ar atmosphere, **1** (1.00 g, 2.69 mmol) was weighed into a flask and dissolved in dry THF (85.5 mL). To the solution was added a solution of Rh(nbd)BPh$_4$ (27.6 mg, 53.7 $\mu$mol) in dry THF (4.0 mL). After stirring at room temperature for 24 h, to the reaction mixture was added triphenylphosphine (84.6 mg, 322 $\mu$mol). The solution was concentrated and then poured into a large amount of CH$_2$Cl$_2$. The precipitate was purified by reprecipitation with CH$_2$Cl$_2$ and then dried under reduced pressure to give poly-**1** as a black powder. Yield: 887 mg (88.7%). $M_n = 1.7 \times 10^5$, $M_w/M_n = 1.8$.

**Typical Experimental Procedure for UV−vis Absorption Measurements.** All UV−vis absorption measurements were performed in dry THF. The concentrations of poly-**1** and poly-**2**, which were calculated on the basis of the monomeric units, were 130 $\mu$M for all the measurements. A typical experimental procedure is described as follows: Stock solutions of poly-**1** (537 $\mu$M) and tetra-*n*-butylammonium acetate (TBAA) (1.34 mM) in THF were prepared in flasks equipped with stopcocks, respectively. The poly-**1** solution (1 mL) and the TBAA solution (0.4 mL) were transferred to a vial, and then the resulting mixture was diluted with dry THF (2.6 mL) to give the sample solution, of which [monomeric units of poly-**1**] and [TBAA]/[monomeric units of poly-**1**] were adjusted to be 130 $\mu$M and 1.0, respectively. The UV−vis absorption spectrum of the resulting sample solution was measured in a glass cell with a 10 mm path length at 25 °C.

**Absorption Titrations and Hill Plots.** Sample solution with varying anion amount was prepared in accordance with the above procedure, and the absorption spectra were taken to determine the change. The titration curve was obtained by plotting the absorbance at the proper wavelength versus the [anion]/[urea] ratio. The binding data were further analyzed using the Hill equation: $\log(Y/(1-Y)) = n \log[\text{anion}] + n \log K_a$, where $Y$, $K_a$, and $n$ represent the fractional saturation of the host, the apparent microscopic association constant, and the Hill coefficient, respectively. The $Y$ value was calculated by the following equation: $Y = \Delta A_{obs}/\Delta A_{max} = (A_{obs} - A_0)/(A_{max} - A_0)$, where $A_0$, $A_{obs}$, and $A_{max}$ represent the inherent absorbance of polymer sample, the absorbance in the presence of anion guests, and the maximum absorbance obtained when the absorption change was completed at the selected wavelength. The $K_a$ and $n$ values were determined from the slope and $Y$-intercept in the resulting Hill plots. The $K_a$ value estimated in this calculation means the apparent binding constant of one urea receptor unit, that is, the monomeric unit in the cases of poly-**1** and poly-**2**.

**Job's Plots.** THF solutions of poly-**1** and TBAA were mixed to prepare sample solution with varying molar fractions of the monomeic units of poly-**1** ($\chi$) from 0 to 1. The total concentration of monomeric units of poly-**1** and CH$_3$CO$_2^-$ was kept constant at 260 $\mu$M. UV−vis measurement of each sample was performed. Absorbance at 470 nm were normalized to the variation of absorbance ($\Delta A_{470}$) with the following equation: $\Delta A_{470} = A_{obs} - \chi A_0$, where $A_0$ is absorbance of poly-**1** itself in THF at 260 $\mu$M ($\chi = 1$). Job's plots were obtained by plotting $\Delta A_{470}$ values against $\chi$.

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**Supporting Information Available:** UV−vis absorption titration of poly-**1** and poly-**2** in the presence of TBA salts of anions and the resulting Hill plots. 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* (2), 520–563.
(2) Martinez-Manez, R.; Sancenon, F. *Chem. Rev.* **2003**, *103* (11), 4419–4476.
(3) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250* (23−24), 3094–3117.
(4) Gale, P. A.; Quesada, R. *Coord. Chem. Rev.* **2006**, *250* (23−24), 3219–3244.
(5) Anzenbacher, P., Jr.; Nishiyabu, R.; Palacios, M. A. *Coord. Chem. Rev.* **2006**, *250* (23−24), 2929–2938.
(6) Davis, A. P. *Coord. Chem. Rev.* **2006**, *250* (23−24), 2939–2951.
(7) Katayev, E. A.; Ustynyuk, Y. A.; Sessler, J. L. *Coord. Chem. Rev.* **2006**, *250* (23−24), 3004–3037.
(8) Miyaji, H.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2001**, *40* (1), 154–157.
(9) Palacios, M. A.; Nishiyabu, R.; Marquez, M.; Anzenbacher, P. *J. Am. Chem. Soc.* **2007**, *129* (24), 7538–7544.
(10) Takeuchi, M.; Ikeda, M.; Sugasaki, A.; Shinkai, S. *Acc. Chem. Res.* **2001**, *34* (11), 865–873.
(11) Shinkai, S.; Ikeda, M.; Sugasaki, A.; Takeuchi, M. *Acc. Chem. Res.* **2001**, *34* (6), 494–503.
(12) Takeuchi, M.; Shioya, T.; Swager, T. M. *Angew. Chem., Int. Ed.* **2001**, *40* (18), 3372–3376.
(13) Hirata, O.; Takeuchi, M.; Shinkai, S. *Chem. Commun.* **2005**, *30*, 3805–3807.
(14) dos Santos, C. M. G.; McCabe, T.; Watson, G. W.; Kruger, P. E.; Gunnlaugsson, T. *J. Org. Chem.* **2008**, *73* (23), 9235–9244.
(15) Willans, C. E.; Anderson, K. M.; Potts, L. C.; Steed, J. W. *Org. Biomol. Chem.* **2009**, *7* (13), 2756–2760.
(16) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94* (2), 349–372.
(17) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100* (7), 2537–2574.
(18) Hill, D. J.; Mio, M. J.; Prince, R. B.; Hughes, T. S.; Moore, J. S. *Chem. Rev.* **2001**, *101* (12), 3893–4012.
(19) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101* (12), 4013–4038.
(20) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101* (12), 4039–4070.
(21) Thomas, S. W.; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107* (4), 1339–1386.
(22) Yashima, E.; Maeda, K.; Nishimura, T. *Chem. Eur. J.* **2004**, *10* (1), 42–51.
(23) Yashima, E.; Maeda, K. *Macromolecules* **2008**, *41* (1), 3–12.
(24) Kakuchi, R.; Nagata, S.; Sakai, R.; Otsuka, I.; Nakade, H.; Satoh, T.; Kakuchi, T. *Chem. Eur. J.* **2008**, *14* (33), 10259–10266.
(25) Kakuchi, R.; Nagata, S.; Tago, Y.; Sakai, R.; Otsuka, I.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42* (5), 1476–1481.
(26) Kakuchi, R.; Tago, Y.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42* (13), 4430–4435.
(27) Kakuchi, R.; Kodama, T.; Shimada, R.; Tago, Y.; Sakai, R.; Satoh, T.; Kakuchi, T. *Macromolecules* **2009**, *42* (12), 3892–3897.
(28) Amendola, V.; Boiocchi, M.; Colasson, B.; Fabbrizzi, L. *Inorg. Chem.* **2006**, *45* (16), 6138–6147.
(29) Nishiyabu, R.; Anzenbacher, P. *Org. Lett.* **2006**, *8* (3), 359–362.
(30) Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *Org. Biomol. Chem.* **2005**, *3* (8), 1495–1500.
(31) Jose, D. A.; Kumar, D. K.; Ganguly, B.; Das, A. *Tetrahedron Lett.* **2005**, *46* (32), 5343–5346.
(32) Amendola, V.; Esteban-Gomez, D.; Fabbrizzi, L.; Licchelli, M. *Acc. Chem. Res.* **2006**, *39* (5), 343–353.
(33) Gale, P. A. *Acc. Chem. Res.* **2006**, *39* (7), 465–475.
(34) Boiocchi, M.; Del Boca, L.; Gomez, D. E.; Fabbrizzi, L.; Licchelli, M.; Monzani, E. *J. Am. Chem. Soc.* **2004**, *126* (50), 16507–16514.
(35) The binding data were analyzed using the Hill equation: $\log(Y/(1-Y)) = n \log[\text{anion}] + n \log K_a$, where $Y$ is the fractional saturation of the host, $K_a$ is the apparent microscopic association constant, and $n$ is the Hill coefficient. See: Connors, K. A. *Binding Constants: the Measurement of Molecular Complex Stability*; Wiley: New York, 1987; pp 59−65.
(36) One reviewer of this paper pointed out the possibility that the newly developed absorbance at 470 nm corresponds not to the quantity of anion bound to polymer but to the extent of conformational change. This is definitely sensible. In fact, Yashima et al. have reported amplification of circular dichroism (CD) signal based on cooperative conformational change of polymer chain.[37] However, we think such possibility is excluded by the following reasons: (1) Poly-**1** shows the colorimetric response by the addition of anions, in which conformational change of poly-**1** actually plays crucial roles as well as the complex formation. However, the colorimetric response is unexplainable by only the conformation change of poly-**1**. In contrast to CD signals, abosorption change should be ascribable to the complex formation event. (2) In anion recognition chemistry,

a number of small molecular receptors with chromophores show the colorimetric response as a direct consequence of anion recognition event, in which the color change is considered to be based on the complex formation. Therefore, the colorimetric response of poly-**1** would correlate closely with the anion recognition. (3) The Job's plots as shown in Figure 4 provided additional important information on the colorimetric response of poly-**1**. The Job's plots showed the maximum value at 0.5 of $\chi$. If the signal amplification based on the cooperative conformation change occurs, the $\Delta A_{470}$ values in the range from 0.5 to 1.0 should be much higher due to the signal amplification effect. Therefore, we believe that the absorbance at 470 nm is almost identical with the quantity of anion bound to the polymer. At least, the determination of the apparent binding constant and cooperativity using this absorbance is considered to be appropriate.

(37) Nonokawa, R.; Yashima, E. *J. Am. Chem. Soc.* **2003**, *125* (5), 1278–1283.

(38) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268* (5219), 1860–1866.

(39) Green, M. M.; Park, J. W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38* (21), 3139–3154.

(40) Due to the good solubility in THF, poly-**2** was employed to compare the anion binding ability. See ref 26.

(41) The acid−base equilibrium constants in DMSO were used as an alternative. For $F^-$: (a) Frederick, G. B. *Acc. Chem. Res.* **1988**, *21*, 456–463. For other anions: (b) Izutsu, K. *Acid-Base Dissociation Constants in Dipolar Aprotic Solvents*; Blackwell: London, 1990.

(42) Kishimoto, Y.; Itou, M.; Miyatake, T.; Ikariya, T.; Noyori, R. *Macromolecules* **2002**, *28* (19), 6662–6666.