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Strict Size Specificity in Colorimetric Anion Detection Based on Poly(phenylacetylene) Receptor Bearing Second Generation Lysine Dendrons

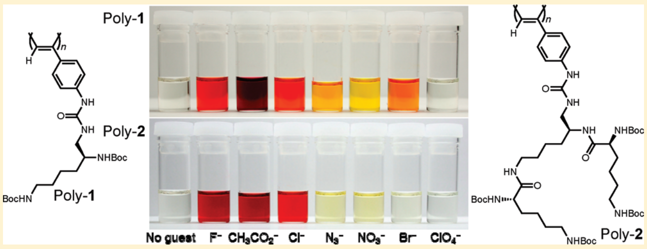
Ryosuke Sakai,[†,§] Naoya Sakai,[†] Toshifumi Satoh,[†] Wen Li,[‡] Afang Zhang,[‡] and Toyoji Kakuchi*,[†]

[†]Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

[‡]Department of Polymer Materials, Shanghai University, Shanghai 201800, China

S *Supporting Information*

ABSTRACT: Poly(phenylacetylene) bearing second generation lysine dendrons through urea groups (poly-**2**) was demonstrated to be a superior anion receptor possessing strict size specificity in colorimetric anion detection. On the basis of the comparison of the colorimetric response behavior between poly-**2** and poly-**1**, which is poly(phenylacetylene) bearing first generation lysine dendrons, the size of the pendant dendron was implied to dictate the selectivity in the colorimetric anion detection. Various instrumental analyses including ^{1}H NMR, light scattering, and viscosity measurements concluded that the conjugation of the bulky G2 dendrons in the vicinity of the urea receptors plays a crucial role in imparting the strict size specificity in the anion-sensing ability of poly-**2**.



INTRODUCTION

The fabrication of a reliable, robust, and efficient anion sensor has been increasingly in demand because anions are significant analytes in diverse fields including environmental, industrial, biological, and medical uses.[1,2] For such sensory materials, the design and construction of synthetic receptors with selective anion detection ability is highly required.[3−19] However, the realization of such selective and specific anion binding has been recognized as a remarkably challenging task because of the diversity in the chemical and physical properties of anions, which includes basicity, size, and shape. Therefore, considerable effort has been devoted recently to exploring the rational design of receptor molecules for any target anions, which led to developing several effective strategies for selective anion detection, e.g., the fine-tuning of binding site, utilization of macrocyclic receptor molecules, and three-dimensional arrangement of multiple binding sites.[20−36] For example, Beer and colleague have succeeded in selective luminescent sensing of hydrogensulfate by using a rhenium(I)−bipyridyl-based rotaxane, in which the unique interlocked structural cavity plays an important role in the selectivity.[21] Flood et al. have realized selective recognition of Cl^- and Br^- for a series of macrocyclic [3$_4$]triazolophane receptors, in which the fixed size of the central cavity provides a means for the selective recognition.[26] Sessler and co-workers have reported that a pyrrolyl-based triazolophane bearing both CH and NH donor groups exhibits a preferential binding ability for pyrophosphate anions.[34]

We previously reported the colorimetric anion detection based on urea-functionalized poly(phenylacetylene)s, in which the color change was dependent on the anions employed.[37−39] The detailed investigations suggested that the observed colorimetric response was dictated by the anion size. For these polymers, the polymer backbone probably acts as a scaffold for the three-dimensional organization of the multiple urea binding sites, which might impart a size-selective anion-binding ability based on the steric hindrance.[40−49] Although such a receptor design that leverages a macromolecular scaffold might be one of the successful examples for size-specific anion detection, further improvement in the anion selectivity is still desired to realize a reliable and sophisticated anion sensor.

For the enhancement and adjustment of the size specificity in anion recognition, one of the rational approaches should be the fine-tuning of the steric factor in the vicinity of the binding sites. For the modulation of such a steric factor, the dendron emerges as an ideal candidate for the bulky substituent capable of spatially regulating the receptor environment because significant performance has already been proven in a wide variety of chemistry fields including supramolecular chemistry.[50−53] In fact, dendronized polymers, which are linear polymers bearing dendrons at each repeating unit on the polymer chain, often exhibit a unique behavior due to the three-dimensional bulkiness of the pendant dendrons.[54−76] Therefore, the conjugation of bulky dendrons in the vicinity of the urea groups on the poly(phenylacetylene) receptor is highly expected to influence the selectivity in colorimetric anion detection.

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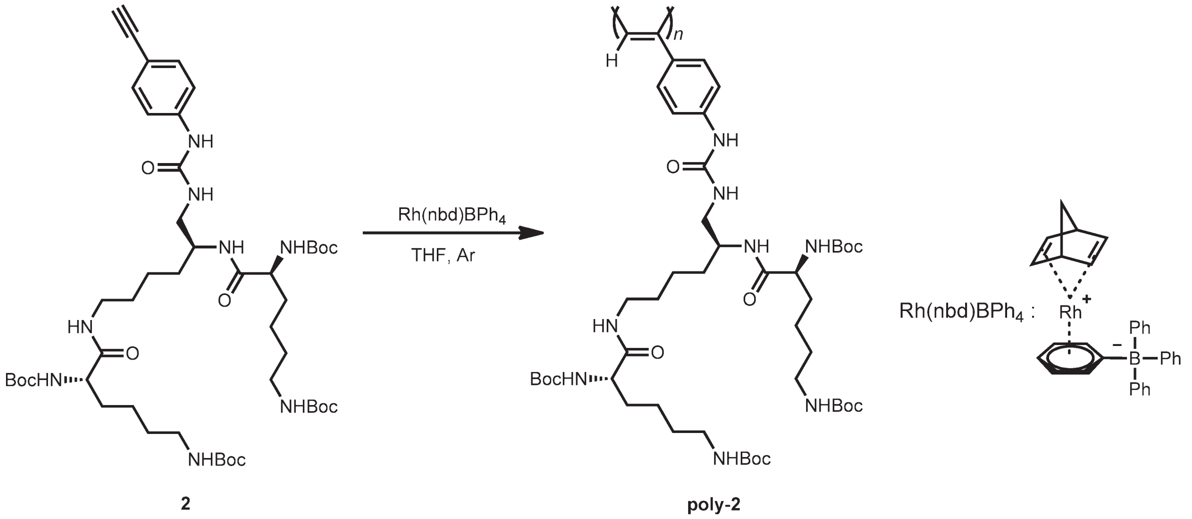
Scheme 1. Synthesis of Poly(phenylacetylene) Bearing G2 Lysine Dendrons (Poly-2)



We have now designed poly(phenylacetylene) bearing second generation lysine dendrons through a urea group (poly-**2**) as a novel anion receptor with colorimetric detection ability (Scheme 1). The morphology of poly-**2** in solution was determined by the NMR, static light scattering, and viscosity measurements. Circular dichroism (CD) and UV−vis analyses in the presence of a series of anions were carried out to clarify the specificity in the colorimetric anion sensing of poly-**2**. This result was compared with those for poly(phenylacetylene) featuring first generation lysine dendrons (poly-**1**) and urea-deficient poly(phenylacetylene) (poly-**11**), providing insight into the strict size specificity in the colorimetric anion detection of poly-**2**.

EXPERIMENTAL SECTION

Materials. All chemicals were purchased from commercial sources and used without further purification unless otherwise noted. Bis-Boc-lysinol (**3**),[77] 4-ethynylbenzoic acid,[78] and Rh^+(2,5-norbornadiene)-$[(\eta^6\text{-}C_6H_5)B^-(C_6H_5)_3]$ ($Rh(nbd)BPh_4$)[79] were prepared in accordance with previous reports.

Instruments. The ^1H and ^{13}C NMR spectra were recorded using a JEOL JNM-A400II and JEOL JNM-EX270 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 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 polystyrene calibration. The specific rotations were measured in THF using a Jasco DIP 1000 digital polarimeter with a Na lamp (wavelength, 589 nm). A circular dichroism (CD) spectrum was obtained using a JASCO J-720 spectropolarimeter equipped with a Jasco ETC-505T temperature controller. The melting points were measured by the differential scanning calorimetry (DSC) analysis using a Bruker AXS DSC 3100 SA under a nitrogen atmosphere. The absolute molecular weight and viscosity of polymer samples were determined by SEC in THF at 40 °C using an Agilent 1100 series instrument equipped with two Shodex KF-804 L columns (linear, 8.0 mm × 300 mm; exclusion limit, 4×10^5; bead size, 7 μm), a DAWN 8 multiangle laser light scattering (MALLS) detector (Wyatt Technology, Santa Barbara, CA), a Viscostar viscosity detector (Wyatt Technology), and an Optilab rEX refractive index detector (Wyatt Technology). The Mark−Houwink−Sakurada constant (α) was estimated by ASTRA 5.1.6.0 software (Wyatt Technology).

Synthesis of 4. A solution of methanesulfonyl chloride (MsCl) (2.41 g, 21.4 mmol) in 10 mL of dichloromethane (DCM) was added dropwise to a mixture of **3** (3.5 g, 10.5 mmol) and triethylamine (TEA) (5.33 g, 52.7 mmol) in DCM (120 mL) at −10 °C. After stirring for 2 h, MeOH was added to quench the reaction. After washing with pure water, the organic phase was dried over $MgSO_4$ and then evaporated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (2/1, v/v) to give **4** as a colorless oil. Yield: 2.5 g (58%). ^1H NMR ($CDCl_3$): δ (ppm) = 1.31−1.62 (m, 24H, CH_2 + CH_3), 3.05−3.17 (m, 5H, CH_2 + CH_3), 3.82−3.84 (m, 1H, CH_2), 4.16−4.30 (m, 2H, CH_2 + CH), 4.64−4.80 (br, 2H, NH). HRMS (ESI): m/z calcd for $C_{17}H_{34}N_2O_7S$ $[M + H]^+$: 411.2159. Found: 411.2161.

Synthesis of 5. A mixture of **4** (2.50 g, 6.09 mmol) and NaN_3 (1.19 g, 18.27 mmol) in DMF (30 mL) was stirred overnight at 55 °C. After evaporation, the residue was dissolved in DCM and washed with brine. The organic phase was dried over $MgSO_4$, and the solvent then evaporated. The residue was purified by column chromatography on silica gel with hexane/ethyl acetate (6/1, v/v) to give **5** as a colorless oil. Yield: 1.7 g (78%). ^1H NMR ($CDCl_3$): δ (ppm) = 1.37−1.48 (m, 24H, CH_2 + CH_3), 3.09−3.11 (m, 2H, CH_2), 3.32−3.41 (m, 2H, CH_2), 3.68 (m, 1H, CH), 4.58−4.61 (d, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 23.03, 23.36, 27.30, 27.81, 28.76, 28.82, 30.21, 31.97, 32.29, 40.49, 50.60, 55.23, 79.52, 80.07, 155.80, 156.48. HRMS (ESI): m/z calcd for $C_{16}H_{31}N_5O_4Na$ $[M + Na]^+$: 380.2268. Found: 380.2265.

Synthesis of 6. To a solution of **5** (1.60 g, 4.48 mmol) in THF (40 mL) was added 25% HCl(aq) (10 mL) at 0 °C, and the reaction mixture was stirred for 26 h at room temperature. The solvent was removed in vacuo to give **6** as a colorless oil. Yield: 1.00 g (97%). ^1H NMR (CD_3OD): δ (ppm) = 1.34−1.53 (m, 2H, CH_2), 1.67−1.74 (m, 4H, CH_2), 2.94−2.97 (m, 2H, CH_2), 3.56−3.60 (m, 1H, CH_2), 3.61−3.3.65 (m, 1H, CH_2), 3.77−3.81 (dd, 1H, CH). ^{13}C NMR (CD_3OD): δ (ppm) = 23.03, 23.36, 27.30, 27.81, 28.76, 28.82, 30.21, 31.97, 32.29, 34.90, 40.49, 50.60, 55.23, 79.52, 80.07, 155.80, 156.48. HRMS (ESI): m/z calcd for $C_6H_{16}N_5$ $[M + H]^+$: 158.1400. Found: 158.1397.

Synthesis of 7. To a mixture of **6** (1.0 g, 4.34 mmol) and diisopropylethylamine (DIPEA) (5.6 g, 43.0 mmol) in DMF (25 mL) was slowly added a solution of Boc-Lys(Boc)-ONp (**9**) (5.07 g, 10.9 mmol) in DCM (40 mL) at −15 °C. After stirring overnight, the reaction mixture was washed with brine, and then the organic phase was dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (1/1 and 1/2, v/v) to give **7**. Yield: 3.20 g (91%). ^1H NMR ($CDCl_3$): δ (ppm) = 1.24−1.52 (m, 50 H, CH_2 + CH_3), 1.57−1.74 (m, 4H, CH_2), 3.08−3.10 (m, 4H, CH_2), 3.30−3.39 (m, 2H, CH_2), 3.91 (br, 1H, CH), 4.08−4.10 (m, 1H, CH), 4.24−4.25 (m, 1H, CH), 4.77 (br, 2H, NH), 5.59 (br, 1H, NH), 5.91 (br, 1H, NH), 7.01 (br, 1H, NH), 7.10 (br, 1H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 21.60, 22.96, 23.11, 28.53, 28.55, 28.59, 29.60, 29.81, 30.61, 31.04, 31.56, 32.73, 36.60, 37.80, 40.37, 48.87, 54.14, 54.60, 54.93, 79.12, 80.01, 80.09, 156.22, 156.42, 156.63, 162.67, 173.40, 173.69. HRMS (ESI): *m*/*z* calcd for $C_{38}H_{71}N_9O_{10}Na$ $[M + Na]^+$: 836.5216. Found: 836.5211.

Synthesis of G2-NH$_2$ (8). A mixture of **7** (3.10 g, 3.81 mmol) and PPh_3 (1.50 g, 5.72 mmol) in THF (120 mL) and water (20 mL) was stirred overnight at 50 °C. After evaporation of THF, DCM was added to dissolve the organic compounds. The organic phase was separated, further washed with water, and dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel with DCM/MeOH (15/1 and 10/1, v/v) to give **8** as a colorless form. Yield: 2.60 g (86%). ^1H NMR (CD_3OD): δ (ppm) = 1.24−1.51 (m, 50 H, CH_2 + CH_3), 1.64−1.84 (m, 4H, CH_2), 2.73−2.77 (m, 2H, CH_2), 3.09−3.36 (m, 5H, CH_2), 3.39−3.40 (m, 1H, CH_2), 3.73 (br, 1H, CH_2), 3.84 (br, 1H, CH), 4.10−4.13 (m, 2H, CH), 4.78 (br, 1H, NH), 4.91 (br, 1H, NH), 5.68 (br, 1H, NH), 5.76 (br, 1H, NH), 6.88 (br, 1H, NH), 6.96 (br, 1H, NH). ^{13}C NMR (CD_3OD): δ (ppm) = 21.43, 23.27, 28.80, 28.86, 29.91, 29.99, 31.50, 32.41, 38.54, 40.53, 54.61, 54.96, 79.41, 80.25, 156.68, 171.53, 173.51. HRMS (ESI): *m*/*z* calcd for $C_{38}H_{73}N_7O_{10}Na$ $[M + Na]^+$: 810.5311. Found: 810.5323.

Synthesis of G2 Monomer (2). To a solution of 4-ethynylaniline (112 mg, 951 μmol) in DCM (5.0 mL) was added 1,1′-carbonyldiimidazole (CDI) (175 mg, 1.08 mmol). After stirring at room temperature for 18 h, a solution of **8** (596 mg, 756 μmol) in DCM (4.0 mL) was added to the reaction mixture, which was further stirred at room temperature for 22 h. The solution was removed under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/MeOH (27/2, v/v) to give **2** as a pale yellow solid. Yield: 621 mg (87.6%); mp =107 °C. $[\alpha]_D$ = −45.7°. ^1H NMR ($CDCl_3$): δ (ppm) 1.22−1.57 (m, 50 H, CH_2 + CH_3), 1.58−1.85 (m, 4H, CH_2), 3.00 (s, 1H, C≡CH), 2.90−3.46 (m, 8H, CH_2), 3.89 (m, 1H, CH−), 4.12 (br, 2H, CH), 4.77 (br, 1H, NH), 5.13 (br, 1H, NH), 5.77−5.97 (br, 3H, −NH), 6.86−7.10 (br, 2H, NH), 7.38 (m, 4H, aromatic), 8.20 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) 21.65, 22.81, 28.31, 28.35, 28.42, 28.47, 31.87, 37.97, 40.08, 43.70, 48.59, 54.37, 54.84, 83.88, 79.10, 79.80, 115.07, 118.07, 132.82, 140.44, 155.90, 156.05, 173.36, 173.57. HRMS (ESI): *m*/*z* calcd for $C_{47}H_{78}N_8O_{11}Na$ $[M + Na]^+$: 953.5688. Found: 953.5681. Anal. calcd for $C_{47}H_{78}N_8O_{11}\cdot{}^3/_4H_2O$: C, 59.76; H, 8.48; N, 11.86. Found: C, 59.87; H, 8.58; N, 11.83.

Synthesis of G1-NH$_2$ (10). A mixture of **5** (1.80 g, 5.04 mmol) and PPh_3 (1.98 g, 7.55 mmol) in THF (50 mL) and water (10 mL) was stirred overnight at 50 °C. After evaporation, the residue was dissolved in DCM and washed with brine. The organic phase was dried over $MgSO_4$. The residue was purified by column chromatography on silica gel with DCM/MeOH (10/1, v/v) to give **10** as a pale yellow oil. Yield: 1.42 g (85%). ^1H NMR ($CDCl_3$): δ (ppm) = 1.43−1.48 (m, 22H, CH_2+CH_3), 1.83−1.99 (m, NH_2), 2.10−2.16 (m, 2H, CH_2), 2.64−2.77 (m, 2H, CH_2), 3.07−3.11 (m, 2H, CH), 3.53 (br, 1H, CH), 4.71−4.80 (m, 2H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 23.45, 25.89, 28.82, 30.20, 32.78, 40.58, 46.25, 52.94, 53.82, 68.33, 79.38, 79.57, 156.51, 156.58. HRMS (ESI): *m*/*z* calcd for $C_{16}H_{34}N_3O_4$ $[M + H]^+$: 332.2544. Found: 332.2550.

Synthesis of G1 Monomer (1). To a solution of 4-ethynylaniline (309 mg, 2.64 mmol) in DCM (14.0 mL) was added CDI (485 mg, 2.99 mmol). After stirring at room temperature for 18 h, a solution of **10** (683 mg, 2.06 mmol) in DCM (11.0 mL) was then added to the reaction mixture, which was further stirred at room temperature for 22 h. The solution was removed under reduced pressure. The residue was purified by column chromatography on silica gel with DCM/ethyl acetate (1/1, v/v) to give **1** as a white solid. Yield: 737 mg (75.3%); mp =123 °C. $[\alpha]_D$ = −4.12°. ^1H NMR ($CDCl_3$): δ (ppm) = 1.43−1.48 (m, 24H, CH_2 + CH_3), 3.01 (s, 1H, C≡CH), 3.10 (m, 2H, CH_2), 3.28 (m, 2H, CH_2), 3.57 (br, 1H, CH), 4.73 (s, 1H, NH), 5.13 (s, 1H, NH), 5.94 (s, 1H, NH), 7.38 (m, 4H, aromatic), 7.77 (s, 1H, NH). ^{13}C NMR ($CDCl_3$): δ (ppm) = 22.49, 28.34, 28.43, 29.85, 31.62, 39.65, 44.08, 51.65, 79.36, 79.55, 83.74, 115.52, 118.55, 132.87, 140.09, 156.23, 156.61. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{38}N_4O_5Na$ $[M + Na]^+$: 497.2740. Found: 497.2744. Anal. calcd for $C_{25}H_{38}N_4O_5$: C, 63.27; H, 8.07; N, 11.81. Found: C, 63.31; H, 8.02; N, 11.72.

Synthesis of Monomer 11. To a mixture of **3** (292 mg, 0.878 mmol), 4-ethynylbenzoic acid (191 mg, 1.31 mmol), and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (106 mg, 0.361 mmol) in DCM (5.0 mL) was added *N*,*N*′-diisopropylcarbodiimide (DIC) (170 mg, 1.35 mmol) under a N_2 atmosphere. The reaction mixture was stirred for 40 h at room temperature and was then filtered. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel with hexane/ethyl acetate (3/2, v/v) to give **11** as a white powder. Yield: 253 mg (62.6%); mp =105 °C. $[\alpha]_D$ = −10.9°. ^1H NMR ($CDCl_3$): δ = 1.35−1.65 (m, 24H, CH_2 + CH_3), 3.12 (m, 2H, CH_2), 3.25 (s, 1H, C≡CH), 4.00 (m, 1H, CH_2), 4.30 (m, 2H, CH_2 + CH), 4.62 (br, 2H, NH), 7.55 (d, *J* = 8.5 Hz, 2H, aromatic), 7.99 (d, *J* = 8.6 Hz, 2H, aromatic). ^{13}C NMR ($CDCl_3$): δ = 22.92, 28.32, 28.41, 29.79, 31.47, 40.12, 49.50, 67.16, 77.20, 79.56, 80.15, 82.74, 126.90, 129.56, 129.88, 132.08, 155.55, 156.03, 165.78. HRMS (ESI): *m*/*z* calcd for $C_{25}H_{36}N_2O_6Na$ $[M + Na]^+$: 483.2471. Found: 483.2502. Anal. calcd for $C_{25}H_{36}N_2O_6\cdot{}^1/_5H_2O$: C, 64.69; H, 7.90; N, 6.04. Found: C, 64.67; H, 7.96; N, 6.10.

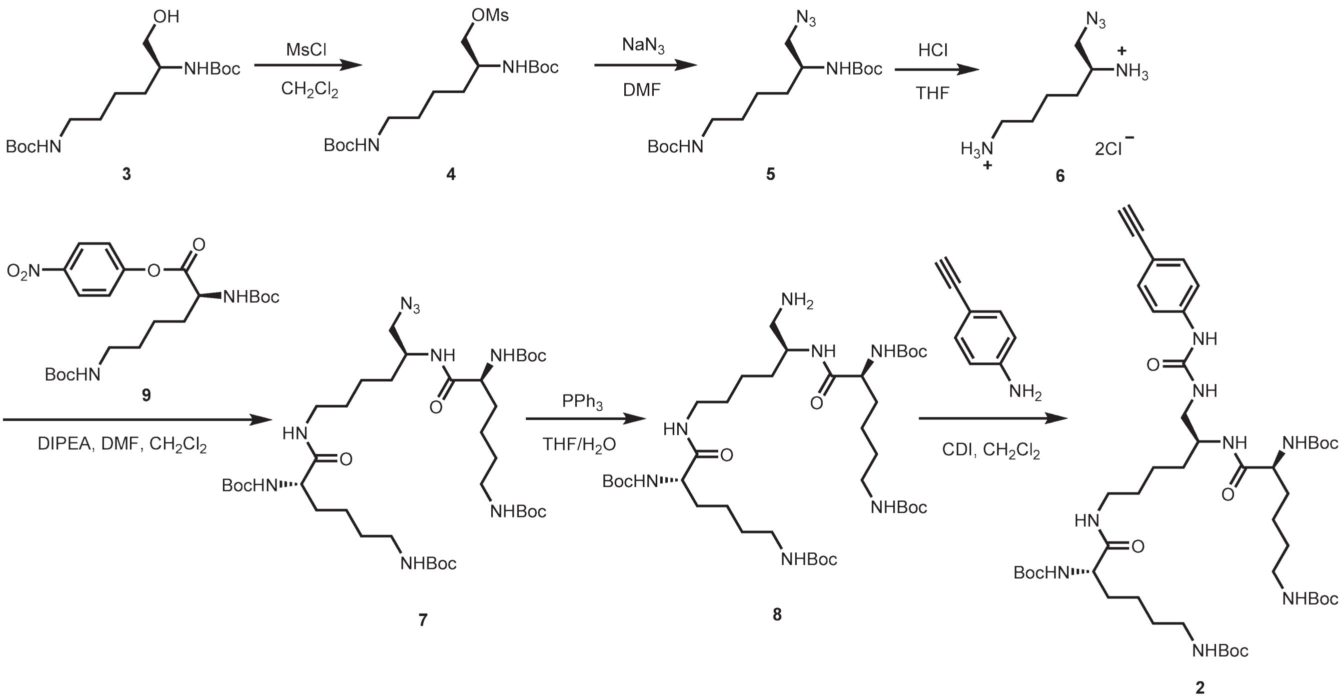
Polymerization of 1. The polymerization of **1** was carried out in a dry Schlenk flask under an argon atmosphere. Rh(nbd)BPh_4 (6.3 mg, 12 μmol) was added to a Schlenk flask with a stirring bar and was evacuated for 15 min. Monomer **1** (294 mg, 619 μmol) was placed in another flask and dissolved in dry THF (21.0 mL). The monomer solution was sparged with argon for 10 min and then transferred via a cannula to the Schlenk flask loaded with Rh(I) catalyst. The reaction mixture was stirred at room temperature for 24 h. PPh_3 (19.9 mg, 75.8 μmol) was then added to the reaction mixture to terminate the polymerization reaction. The solution was concentrated and then poured into a large amount of diethyl ether. The precipitate was purified by reprecipitation with THF/diethyl ether and was then dried under reduced pressure to give poly-**1** as a green powder. Yield: 263 mg (89.4%). M_n = 2.0 × 10^5, M_w/M_n = 3.4.

Polymerization of 2. The same procedure as that for the polymerization of **1** was applied to the polymerization of **2**, in which Rh(nbd)BPh_4 (5.6 mg, 11 μmol), **2** (500 mg, 530 μmol), dry THF (18.0 mL), and PPh_3 (18.0 mg, 67.0 μmol) were used to give poly-**2** as a brown solid. Yield: 470 mg (93.0%). M_n = 2.5 × 10^5, M_w/M_n = 9.0.

Polymerization of 11. The same procedure as that for the polymerization of **1** was applied to the polymerization of **11**, in which Rh(nbd)BPh_4 (2.3 mg, 4.47 μmol), **11** (103 mg, 224 μmol), dry THF (7.2 mL), and PPh_3 (6.9 mg, 26.3 μmol) were used to give poly-**11** as a yellow solid. Yield: 92.5 mg (89.8%). M_n = 7.4 × 10^4, M_w/M_n = 3.1.

Typical Experimental Procedure for CD and Absorption Measurements. All CD and UV−vis absorption measurements were performed in dry THF. The concentrations of poly-**1**, poly-**2**, and poly-**11**, which were calculated on the basis of the monomer units, were 1.0 mM for all measurements. A typical experimental procedure is

Scheme 2. Synthesis of Phenylacetylene Monomer Featuring G2 Lysine Dendron and Urea Receptor (2)



described as follows: Stock solutions of poly-**2** (2.0 mM) and tetra-*n*-butylammonium acetate (TBAA) (50 mM) in THF were prepared in flasks equipped with stopcocks. The poly-**2** solution (1 mL) and the TBAA solution (0.8 mL) were transferred to a vial, and the resulting mixture was then diluted with dry THF (0.2 mL) to give the sample solution, in which the [monomer units of poly-**2**] and [TBAA]/[monomer units of poly-**2**] were adjusted to 1.0 mM and 20, respectively. The CD and UV−vis absorption spectra of the resulting sample solution were measured in a quartz cell with a 1.0 mm path length at 25 °C.

■ RESULTS AND DISCUSSION

Synthesis of Poly(phenylacetylene) Bearing Lysine-Based Dendron. The synthetic procedure for the phenylacetylene monomer with a second generation lysine dendron and a urea group (**2**) is illustrated in Scheme 2. Boc-protected lysinol (**3**) was treated with MsCl, followed by the substitution reaction with NaN_3 to afford core unit (**5**). The deprotection of **5** using 25% HCl(aq) in THF provided the corresponding HCl salt (**6**). Compound **6** was reacted with Boc-Lys(Boc)-ONp (**9**) to produce azide-functionalized second generation lysine dendron (**7**), which was further converted to the corresponding amine (**8**) through a Staudinger reaction with PPh_3. Finally, the precursor **8** was reacted with 4-ethynylaniline and CDI to yield target G2 monomer (**2**).

The polymerization of **2** was carried out using $Rh(nbd)BPh_4$ in dry THF at ambient temperature for 24 h to produce dendronized poly(phenylacetylene) (poly-**2**) in 93% yield (Scheme 1). By the size exclusion chromatography (SEC) measurement, the number-average molecular weight ($M_{n,SEC}$) and molecular weight distribution (M_w/M_n) of poly-**2** were determined to be 2.5 × 10^5 and 9.0, respectively. The ^1H NMR spectrum of poly-**2** displayed the signals due to the dendron protons of poly-**2**, while no signal was observed at 3.26 ppm where the acetylene proton appeared for that of monomer **2** (Figure 1). It is important to note that signals corresponding to the main chain and aromatic protons were extremely broadened under any analysis conditions. This phenomenon is ascribable to the low mobility of the polymer backbone probably due to the dendronized structure. Given the tendency that poly(phenylacetylene) brushes show no main chain signals in their ^1H NMR spectra,[80−84] the G2 dendron on poly-**2** is bulky enough to provide significant influence on the whole polymer structure and conformation of poly-**2**.

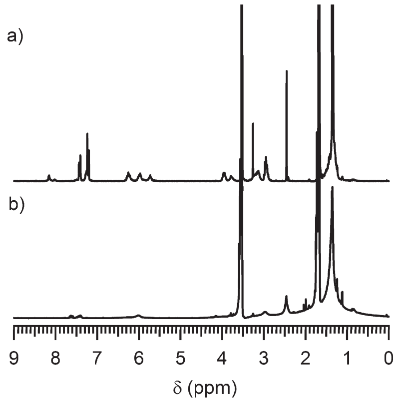


Figure 1. ^1H NMR spectra of (a) **2** and (b) poly-**2** in THF-d_8 at ambient temperature.

In order to further provide information on the morphology of poly-**2** in solution, the absolute molecular weight ($M_{w,MALLS}$) and viscosity were determined by SEC equipped with a multiangle laser light scattering (MALLS) detector and viscosity detector. The resulting $M_{w,MALLS}$ value was 1.6 × 10^6, which

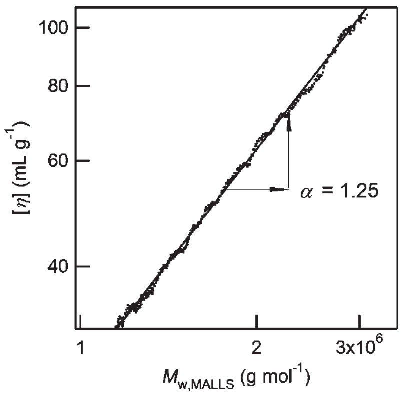


Figure 2. Mark−Houwink plots of poly-**2** in THF.

was much higher than that determined by the above SEC measurement. In addition, the inherent viscosity ([η]) was estimated to be 50 mL g^{-1}. These values are the averaged value of the entire polymer chain of poly-**2**. Because the detectors are connected to the SEC in this instrument, the dependences of the $M_{w,MALLS}$ and [η] values of each polymer chain could also be obtained, which allows a more detailed discussion of the morphology of poly-**2**.

The relationship between the intrinsic viscosity and the molecular weight is described by the Mark−Houwink−Sakurada equation as follows:

$$[\eta] = KM^{\alpha}$$

where K and α are the Mark−Houwink constant and exponent, respectively. Based on the results of the light scattering and viscosity measurements, the Mark−Hauwink plots, double-logarithmic plots of [η] versus $M_{w,MALLS}$ of poly-**2**, were prepared (Figure 2). The plots displayed linearity with a slope of 1.25, which is identical with the α value of poly-**2**. The α value is a particularly important value, which is known to be closely related to the polymer morphology in solution. In general, conventional linear polymers with a random coil conformation possess α values ranging from 0.5 to 0.8. On the other hand, α values larger than 1.0 are obtained for elongated rod polymers. Therefore, the observed large α value of 1.25 strongly suggests that poly-**2** possesses an elongated rodlike conformation in THF, which should be ascribed to the huge G2 dendron pendants. Comprehensively considering the morphology of poly-**2** in THF, the elongated poly(phenylacetylene) backbone is certain to be densely covered with a number of the bulky lysine dendrons. Note that the urea functionalities in poly-**2** as the anion receptor units are also located medial to the whole polymer chain, leading to a unique size specificity in anion recognition.

Colorimetric Anion Detection. To evaluate the anion-sensing ability of poly-**2**, circular dichroism (CD) and UV−vis measurements were performed in the presence of tetra-*n*-butylammonium (TBA) salts of a series of anions in THF, as shown in Figure 3. Although poly-**2** possesses a π-conjugated system in the main chain structure, no absorption was observed in the visible range, leading to a colorless solution. Considering the brown color of poly-**2** in the solid state, the conjugation length of the main chain, which is susceptible to the polymer conformation, should be very short in solution probably due to the bulkiness of the G2 dendron and intramolecular hydrogen bonding between the urea groups.[85] In the CD spectrum of poly-**2**, a negative Cotton effect was observed at a wavelength shorter than 300 nm, whereas it should be due to the chirality of the lysine dendron itself. Although the very small positive Cotton effect at 330 nm might be due to the main chain chirality, poly-**2** was not found to form a one-handed helical structure regardless of the side chain chirality derived from the lysine dendron.[86]

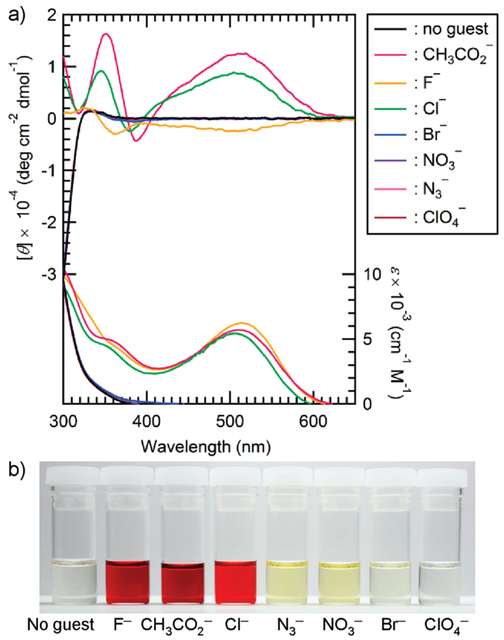
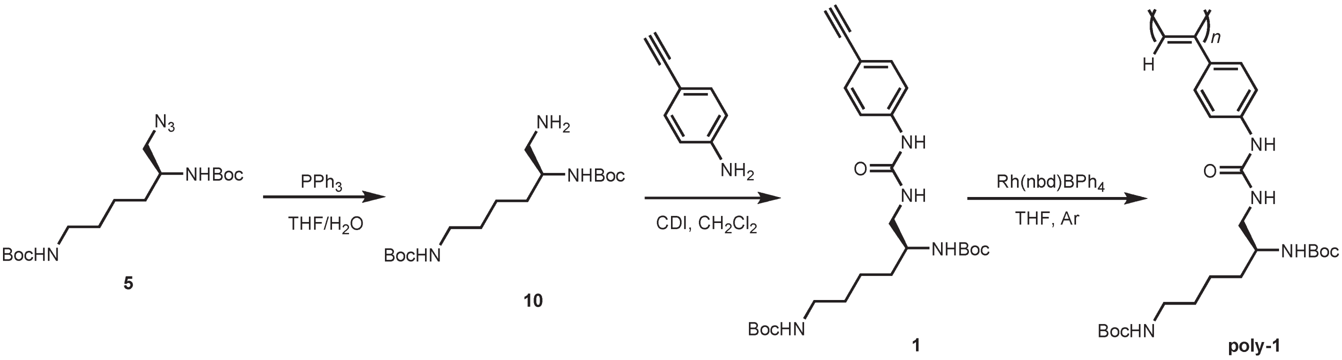


Figure 3. (a) CD (upper) and absorption (lower) spectra and (b) photograph of poly-**2** in the presence of TBA salts of a series of anions in THF at 25 °C ([monomer units of poly-**2**] = 1.0 mM, [anion]/[monomer units of poly-**2**] = 20).

Upon the addition of $CH_3CO_2^-$, the colorless polymer solution immediately turned to a red solution, indicating an acetate recognition property of poly-**2**. As shown in Figure 3a, a new absorbance with a maximum at 512 nm was developed by the $CH_3CO_2^-$ addition.[87] On the other hand, the CD spectrum of the poly-**2**/$CH_3CO_2^-$ system showed an intense split-type Cotton effect in the range from 340 to 630 nm, indicating that a biased one-handed helical structure was induced in the backbone of poly-**2** by the $CH_3CO_2^-$ addition. Given that the absorption change was accompanied by a drastic CD change, the observed color change was found to be attributable to the extension of the main chain conjugation length based on the conformation change in the polymer main chain.

Large bathochromic shifts similar to the case with $CH_3CO_2^-$ were observed for the addition of F^- and Cl^-, thus providing red solutions (Figure 3).[87] The accompanying CD change indicated that the colorimetric response is based on the conformational change in poly-**2**. However, the CD spectrum of poly-**2** in the presence of F^- exhibited a weak negative Cotton effect at 500 nm, which was different from those observed with $CH_3CO_2^-$ and Cl^-. The F^- recognition of poly-**2** may produce a different helical conformation from those driven by $CH_3CO_2^-$ and Cl^-. In contrast to the above three anions, Br^-, NO_3^-, N_3^-, and ClO_4^- apparently caused no essential changes in both their CD and absorption spectra, though slightly pale yellow solutions were obtained in the cases with NO_3^- and N_3^-. These results suggested that poly-**2** possesses a strict selectivity in the colorimetric anion detection.

Scheme 3. Synthesis of Poly(phenylacetylene) Bearing G1 Lysine Dendrons (Poly-1)



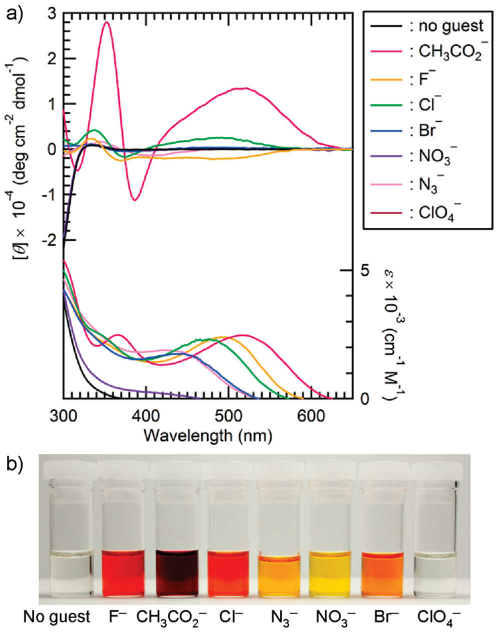


Figure 4. (a) CD (upper) and absorption (lower) spectra and (b) photograph of poly-**1** in the presence of TBA salts of a series of anions in THF at 25 °C ([monomer units of poly-**1**] = 1.0 mM, [anion]/[monomer units of poly-**1**] = 10).

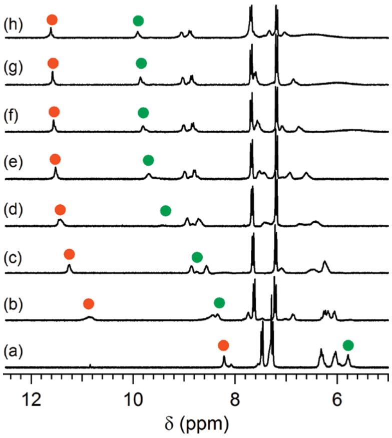
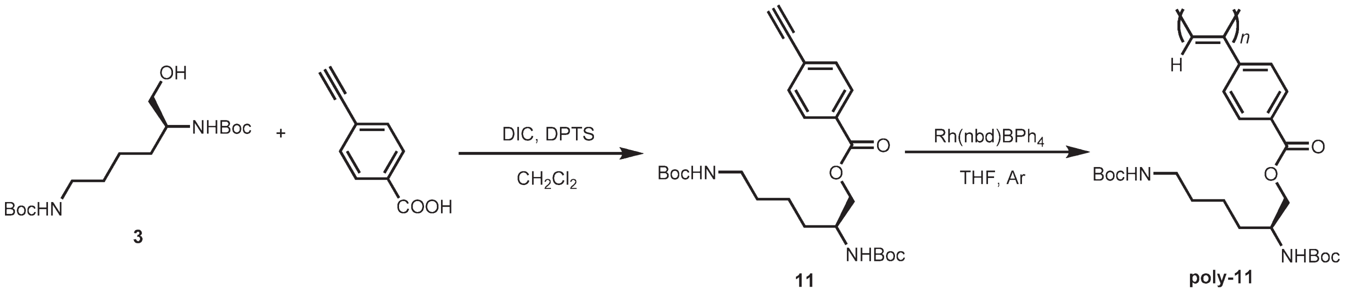


Figure 5. ^{1}H NMR spectra of **2** in the presence of (a) 0, (b) 0.5, (c) 1.0, (d) 2.0, (e) 3.0, (f) 4.0, (g) 5.0, and (h) 10 equiv of TBAA in THF-d_8. Closed circles show the signals due to the urea protons.

Although a number of urea-based receptor molecules have been clarified to possess an anion-responsive property, the observed anion selectivity in the color change was unprecedented.[18,88] Considering that the most characteristic feature of poly-**2** is a dendronized structure, such unusual selectivity in the colorimetric response might be caused by the bulky dendron side groups. Thus, we synthesized a control polymer with first generation lysine dendrons (poly-**1**) to compare its anion detection ability with that of poly-**2**. According to the synthetic procedure summarized in Scheme 3, poly-**1** was successfully prepared. The CD and UV–vis measurements of poly-**1** were then conducted in the presence of TBA salts of a series of anions in THF (Figure 4). Poly-**1** itself afforded an almost colorless solution similar to the case of poly-**2**. Upon the addition of anions except for ClO_4^-, the colorless solution immediately turned to colored solutions dependent on the anions. These anions brought about clear changes in both CD and UV–vis spectra, indicating that the observed colorimetric response was basically due to the conformational change in the polymer main chain of poly-**1**.[87] In sharp contrast to poly-**2**, poly-**1** exhibited obvious colorimetric responses to N_3^-, NO_3^-, and Br^-. Given that the structural difference between poly-**1** and poly-**2** is only the generation of the lysine dendron, the size of the pendant dendron might play an important role in governing the selectivity in the colorimetric anion detection for these macromolecular receptors.

In order to provide further insight into the selectivity in the colorimetric anion detection, we next focused on the clarification of the detailed mechanism of the anion recognition event. In anion recognition 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.[88−91] To elucidate the anion recognition mode of poly-**2**, we performed a ^{1}H NMR titration experiment on monomer **2** with $CH_3CO_2^-$, in which **2** was used as a model compound of poly-**2** because the highly broadened signals in the ^{1}H NMR spectrum of poly-**2** were expected to provide no useful information. With the addition of $CH_3CO_2^-$, a downfield shift was observed in the signals due to the urea protons of **2** (Figure 5). This downfield shift of the urea protons indicates the establishment of a hydrogen bond interaction between urea groups and $CH_3CO_2^-$.[92] Furthermore, as well as urea protons, those of the amide and carbamate of **2** in the range from 8.3 to 5.7 ppm also shifted to the downfield region with the $CH_3CO_2^-$ addition. These results indicate that

Scheme 4. Synthesis of Urea-Deficient Poly(phenylacetylene) Bearing G1 Lysine Dendrons (Poly-11)



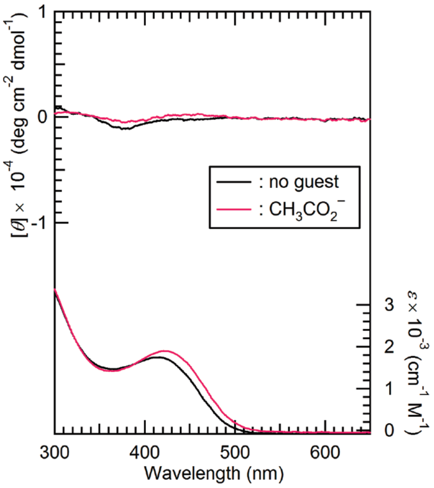


Figure 6. CD (upper) and absorption (lower) spectra of poly-**11** in the presence and absence of tetra-*n*-butylammonium acetate (TBAA) in THF at 25 °C ([monomer units of poly-**11**] = 1.0 mM, [TBAA]/[monomer units of poly-**11**] = 20).

all the urea, amide, and carbamate groups on poly-**2** participate in the anion binding.

Here a question arises. Is the urea group unnecessary for the colorimetric anion detection? To exclude this possibility, a urea-deficient polymer, poly(phenylacetylene) bearing first generation dendrons through ester linkages (poly-**11**), was prepared as a suitable model compound for clarifying the importance of the urea receptor unit in the colorimetric anion detection (Scheme 4). The CD and UV−vis measurements of poly-**11** were carried out in the presence of $CH_3CO_2^-$ in THF (Figure 6). In sharp contrast to poly-**1** and poly-**2**, no essential change was observed in the spectra of poly-**11**. On the basis of these observations, the complex formation between the urea group and the anion is clarified to play a crucial role in the colorimetric anion detection of poly-**1** and poly-**2**. Although the amide and carbamate groups on the polymers might facilitate the anion binding event, such interactions do not contribute to the color change of the polymers.

We finally focused on the elucidation of the selectivity in the colorimetric response of poly-**1** and poly-**2**. For anion recognition based on urea receptors, the color change is generally dictated by the basicity of the anions,[18,88] which increases in the order of $ClO_4^- < Br^- \approx NO_3^- < Cl^- < N_3^- < CH_3CO_2^- < F^-$.[93] However, neither poly-**1** nor poly-**2** showed a colorimetric response well correlated with the basicity of the anions. Therefore, other

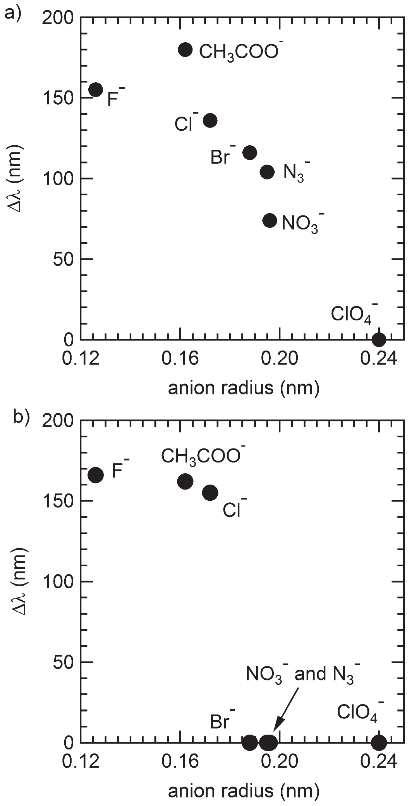


Figure 7. Relationship between the ionic radius of the employed anion and the apparent red shift (Δλ) observed in the UV−vis absorption spectra of (a) poly-**1** and (b) poly-**2**.

factors should be involved in the anion detection events of both poly-**1** and poly-**2**.

Figure 7 shows the relationship between the ionic radius[94,95] of the employed anion and the apparent red shift (Δλ) observed in the UV−vis absorption spectra of poly-**1** and poly-**2**.[96] The plots for poly-**1** indicated a tendency for a smaller anion to provide a larger red shift in the absorption spectrum. In addition, a more clear-cut effect of the anion size on the colorimetric response was observed in the plots for poly-**2**. Therefore, it is no wonder that the steric factor of the pendant dendron participates in this colorimetric response as one of the prime elements dictating the selectivity of the anion detection. Particularly for poly-**2**, the steric hindrance of the bulky G2 dendron would highly restrict the interaction itself of the larger anions with the urea group and/or the complexation-triggered conformational change in the polymer chain, thus realizing the unprecedentedly strict size-specific anion detection. Although some effective methods for size-specific anion detection have already been established, such strict size specificity has never been achieved.

■ CONCLUSIONS

We demonstrated the size-selective colorimetric anion sensing based on poly(phenylacetylene) bearing second generation lysine dendrons through a urea group. On the basis of various experiments and instrumental analyses, the conjugation of the bulky G2 dendrons in the vicinity of the urea receptors was clarified to impart the strict size selectivity to the dendronized polymer. Although there are several ways to enhance selectivity in anion recognition, the present approach that leverages a macromolecular receptor densely covered with variable sizes of pendants is a novel method for realizing highly specific anion recognition. It is important to note that the practical colorimetric anion detection was also accomplished in this system, in which the adoption of poly(phenylacetylene) enabled the imparting of the optical output ability. Given the novelty and significant performance in this examination, we believe that the demonstrated size-specific anion detection based on the dendronized poly(phenylacetylene) receptor will contribute to the future design of reliable and sophisticated anion sensor materials.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** CD and absorption spectra of poly-**1** and poly-**2** in the presence of increasing amounts of anions and the resulting titration curves. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel +81 11 706 6602; Fax +81 11 706 6602; e-mail kakuchi@poly-bm.eng.hokudai.ac.jp.

Present Addresses

§Department of Materials Chemistry, Asahikawa National College of Technology, Asahikawa 071-8142, Japan.

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(85) A similar hypsochromic effect probably due to intramolecular hydrogen bonding was also observed for previously reported poly(phenylacetylene)s with urea pendants, though a colorless solution has never been obtained. See refs 37−39.

(86) Similar polymers also showed no obvious Cotton effect probably due to the structural feature including urea functionalities. See refs 37 and 38.

(87) The spectral changes in CD and absorption in the presence of increasing amounts of anions and the resulting titration curves are shown in the Supporting Information.

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(93) The acid−base equilibrium constants in DMSO were used as an alternative.

(94) We used the thermochemical radii for anionic guests because the anions, except for halide, did not possess ionic radii.

(95) Bianchi, A.; Bowman-James, K.; Garcia-Espana, E. *Supramolecular Chemistry of Anions*; Wiley-VCH: New York, 1997.

(96) Because a maximum absorption wavelength could not be determined for poly-**1** and poly-**2**, the $\Delta\lambda$ value was defined as a red shift from 340 nm for poly-**1** and 350 nm for poly-**2**. Although the estimated $\Delta\lambda$ value does not mean an exact red shift, it is sufficient to discuss the colorimetric response.