

UREA-BASED POLYACETYLENES AS AN OPTICAL SENSOR FOR FLUORIDE IONS*

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Abstract Novel acetylenes carrying urea groups, 1-(4-ethynylphenyl)-3-(4-nitrophenyl) urea (**1**), 1-(4-propargyl)-3-(4-nitrophenyl) urea (**2**), were synthesized and polymerized with rhodium catalyst. Polymers [poly(**1**) and poly(**2**)] with moderate molecular weights were obtained in good yields. The anion sensing ability of poly(**1**) and poly(**2**) was estimated using the tetra-*n*-butylammonium (TBA) salts of a series of anions in DMF. Upon the addition of F[−], the color of the DMF solution of poly(**1**) and poly(**2**) immediately turned to a different color, while the color of solution changed slightly upon addition of Cl[−], HSO₄[−], Br[−], and NO₃[−], indicating the F[−] sensing ability of poly(**1**) and poly(**2**). The ¹H-NMR titrations of poly(**1**) revealed that the colorimetric response of poly(**1**) was triggered by the urea/F[−] interaction through the hydrogen bonding and/or deprotonation process. The absorption spectra titration and Hill plot analysis were carried out to measure the F[−] binding ability, and the Hill coefficient in the poly(**1**)/F[−] complexation was found to be 5.8. This result clearly indicated that this binding mode between poly(**1**) and F[−] was based on a positive homotropic allosterism.

Keyword: Polyacetylenes; Urea; Fluoride ion; Ion recognition.

INTRODUCTION

The sensitive and selective detection of fluoride ions has attracted much attention, due to its role in preventing dental *caries* and in the treatment of osteoporosis^[1–3], and fluoride's unique properties compared to its congeners as a result of relative size and electronegativity. Recently, considerable efforts have been made to develop colorimetric and fluorescent molecular sensors for the recognition of fluoride ions, because of their “naked eye” detection of target species and offering qualitative and quantitative information using inexpensive instrumentation^[4–6]. One approach to reach colorimetric fluoride ions sensors involves a π -conjugated material with very favorable optoelectronic properties containing urea^[7–9], thiourea^[10, 11], amide^[12], boranes^[13–15] and phenol groups^[16–18].

Over past years, π -conjugated polyacetylenes have attracted much attention due to electro- and photoluminescent properties, gas permeability, and ability to form helical structures^[19–21]. Tang and coworkers have synthesized a series of functional polyphenylacetylenes which showed different emission colors such as violet, blue and green with high photoluminescence (PL) efficiency, and reported that the photoluminescence (PL) efficiency could be externally modulated by ion^[22]. Yashima and coworkers reported that the solution of polyphenylacetylenes carrying β -cyclodextrin (CyD) residues in side chains showed an immediate color change

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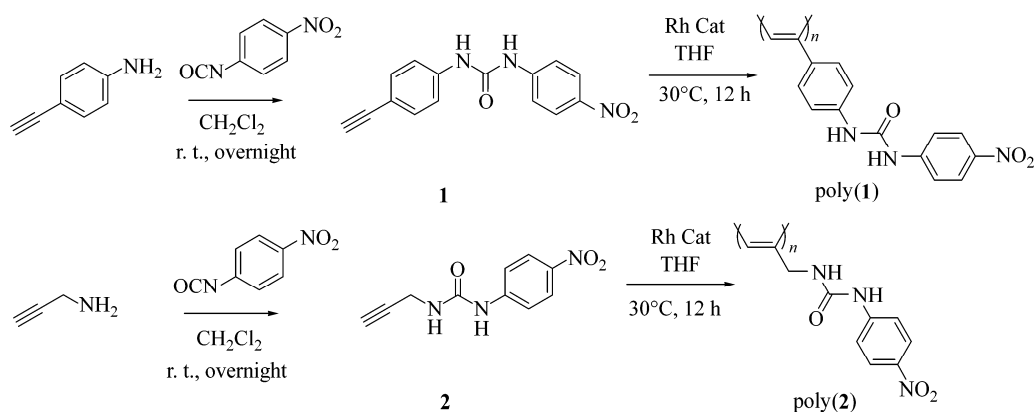
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from yellow-orange to red, accompanying by the inversion of the Cotton effect signs, when 1-adamantanol or (-)-borneol was added to the solution^[23]. Kachuchi and coworkers have synthesized various of polyphenylacetylenes containing urea^[24–26], amide^[27] and sulfonamide^[28] pendants, which exhibited a drastic anion-induced colorimetric and/or CD signal response depending on the employed anion. This finding implied that polyacetylenes could act as chromogenic anion sensing systems.

In this article, we design two acetylenes containing urea groups, 1-(4'-ethynylphenyl)-3-(4'-nitro-phenyl) urea (**1**) and 1-(4'-propargyl)-3-(4'-nitro-phenyl) urea (**2**), and polymerize them in THF using rhodium complex as catalyst to yield the polyacetylenes containing urea moieties[poly(**1**) and poly(**2**)] (Scheme 1). We also investigate the colorimetric detection of fluoride ions by using the obtained polymers.



Scheme 1 Synthesis and polymerization of acetylene monomers containing urea moieties

EXPERIMENTAL

Measurements

¹H- (400 MHz) and ¹³C- (100 MHz) NMR spectra were recorded on a Bruker Avance/DMX 400-MHz NMR spectrometer with DMSO-d₆ as solvent and tetramethylsilane as an internal reference. IR spectra were measured using a Shimadzu FTIR-8100 spectrophotometer. Melting points (mp) were measured on a digital melting point apparatus (WRS-1B). Elemental analysis was carried out at the Sun Yat-Sen University Elemental Analysis Center. The number- and weight-average molecular weights (*M_n* and *M_w*) of polymers were determined by gel permeation chromatography (GPC) on a P230 system (PU-980, CO-965 and RI-210) equipped with polystyrene gel columns (Shodex columns KF805) using tetrahydrofuran (THF) as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. UV-Vis spectra were recorded in a quartz cell (thickness: 1 cm) at room temperature using a Shimadzu UV-2450 spectropolarimeter.

Materials

[(nbd)RhCl]₂, 4-nitro phenyl isocyanate, propargylamine, tetra-*n*-butylammonium nitrate (TBAN), tetra-*n*-butylammonium fluoride (TBAF), tetra-*n*-butylammonium bromide (TBABr), tetra-*n*-butylammonium benzoate (TBAB) and tetra-*n*-butylammonium acetate (TBAA) were purchased from Sigma-Aldrich Chemical Co., Inc. and used as received. 4-Ethynylaniline, tetra-*n*-butylammonium chloride (TBACl) and tetra-*n*-butylammonium hydrogen sulfate (TBAHSO₄) were purchased from Tokyo Kasei Kogyo Co., Ltd. (TCI, Tokyo, Japan), and used without further purification. (nbd)Rh⁺[η^6 -C₆H₅B⁻(C₆H₅)₃] was prepared as reported^[29].

Monomer Synthesis

1-(4-Ethynylphenyl)-3-(4-nitrophenyl) urea (**1**)

A 100 mL flask was equipped with a three-way stopcock and a magnetic stirring bar, and charged with dry nitrogen. A solution of 4-nitro phenyl isocyanate (2.46 g, 15 mmol) in dry CH₂Cl₂ (15 mL) was added into a solution of 4-ethynylaniline (1.76 g, 15 mmol) in dry CH₂Cl₂ (15 mL) at room temperature. The reaction mixture

was stirred overnight. The resulting solution was washed with 1 mol/L HCl, saturated NaHCO₃ aqueous solution and brine. The organic layer was dried over anhydrous MgSO₄ and evaporated to dryness. The residue was purified by silica gel column chromatography eluted with hexane/ethyl acetate = 4:1 (volume ratio) to provide **1** as a yellow solid in 86% yield. Mp 122–123 °C. ¹H-NMR (400 MHz, DMSO-d₆): δ 9.48 (s, 1H, NH), 9.12 (s, 1H, NH), 8.20 (s, 2H, Ar), 7.71 (s, 2H, Ar), 7.46–7.52 (d, 4H, Ar), 4.05 (s, 1H, CH); ¹³C-NMR (100 MHz, DMSO-d₆): δ 79.5, 83.6, 115.2, 117.5, 118.5, 125.0, 132.5, 139.7, 141.1, 146.0, 151.7; IR (cm⁻¹, KBr): 3261, 3088, 2357, 2108, 1648, 1587, 1544, 1405, 1340, 1229, 1109, 970, 841, 744, 694. Anal. Calcd for C₁₅H₁₁N₃O₃, %: C, 64.05; H, 3.94; N, 14.94; O, 17.07. Found, %: C, 64.10; H, 3.92; N, 14.99; O, 16.99.

1-(4-Nitrophenyl)-3-(propargyl)urea (2)

The title compound was synthesized from propargylamine and 4-nitro phenyl isocyanate in a manner similar to **1**. Yield 92% (white solid). Mp 107–108.5 °C. ¹H-NMR (400 MHz, DMSO-d₆): δ 9.41 (s, 1H, NH), 8.16 (s, 2H, Ar), 7.64 (s, 2H, Ar), 6.81 (s, 1H, NH), 3.92 (s, 2H, CH₂), 3.14 (s, 1H, CH); ¹³C-NMR (100 MHz, DMSO-d₆): δ 28.8, 73.0, 81.6, 117.0, 125.1, 140.6, 146.8, 154.0; IR (cm⁻¹, KBr): 3279, 3076, 2361, 2109, 1658, 1605, 1561, 1498, 1422, 1331, 1236, 1178, 1109, 911, 856, 758, 692. Anal. Calcd for C₁₀H₉N₃O₃, %: C, 54.79; H, 4.14; N, 19.17; O, 21.90. Found, %: C, 54.77; H, 4.20; N, 19.19; O, 21.84.

Polymerization

All the polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under dry nitrogen. A typical experimental procedure for the polymerization of **1** by [Rh(nbd)Cl]₂ is given below.

56.4 mg (2 mmol) of **1** was added into a baked 20 mL Schlenk tube with a stopcock in the side arm. The tube was evacuated under vacuum and then flushed with dry nitrogen three times through the side arm. Freshly distilled THF (1 mL) was injected into the tube to dissolve the monomer. The catalyst solution was prepared in another tube by dissolving [Rh(nbd)Cl]₂ (0.004 mmol) in 1 mL of THF with one drop of Et₃N, which was transferred to the monomer solution using a hypodermic syringe. The solution was kept at 30 °C for 12 h. The polymerization mixture was then diluted with 2 mL of THF and poured into a large amount of diethyl ether to precipitate a polymer. The precipitate was collected by filtration and dried under vacuum at room temperature to a constant weight. The polymeric product was isolated as solid in a 71% yield.

Spectroscopic Data of the Polymers

Poly(**1**): ¹H-NMR (400 MHz, DMSO-d₆): δ 6.18 (s, 1H, CH), 7.71–8.20 (m, 8H, Ar), 9.06 (s, 1H, NH), 9.74 (s, 1H, NH). IR (cm⁻¹, KBr): 3298, 3075, 2360, 1717, 1655, 1594, 1498, 1410, 1330, 1268, 1108, 898, 848, 7481.

Poly(**2**): ¹H-NMR (400 MHz, DMSO-d₆): δ 3.84 (s, 2H, CH₂), 6.17–6.45 (m, 2H, CH, NH), 7.52 (s, 2H, Ar), 7.74 (s, 2H, Ar), 9.06 (s, 1H, NH). IR (cm⁻¹, KBr): 3361, 3084, 2361, 1667, 1605, 1553, 1503, 1412, 1333, 1228, 1180, 1112, 850, 750, 690.

Typical Experimental Procedure for UV-Vis Absorption Measurements

All UV-Vis absorption measurements were performed in dry solvent. A typical experimental procedure for UV-Vis absorption measurements of poly(**1**) is given below.

The concentration of poly(**1**) solution, which was calculated on the basis of the monomeric units, was 100 μmol/L for all the measurements. A typical experimental procedure is described as follows: Stock solutions of poly(**1**) (9.3 mg/10 mL) and tetra-*n*-butylammonium fluoride (TBAF) (1.0 mmol/L) in DMF were prepared in flasks equipped with stopcocks, respectively. The poly(**1**) solution (0.3 mL) and the TBAF solution (0.1 mL) were transferred to a vial, and then the resulting mixture was diluted to 10 mL with dry DMF to give the sample solution, of which [monomeric units of poly(**1**)] and [TBAF]/[monomeric units of poly(**1**)] were adjusted to be 100 μmol/L and 10, respectively. The UV-Vis absorption spectrum of the resulting sample solution was measured in a quartz cell with a 10 mm path length at 25 °C.

Absorption Titrations and Hill Plots

Sample solutions with varying anion amount were prepared in a manner similar to the above procedure, and the UV-Vis absorption was measured to determine the change. The titration curve was obtained by plotting the

absorbance at the proper wavelength versus the [anion]/[monomeric units of poly(**1**)] ratio. The binding data were further analyzed using the Hill equation: $\lg[Y/(1 - Y)] = n \lg[\text{anion}] + n \lg K_a$, where Y , K_a , and n represent the fractional saturation of the host, the apparent binding constant and the Hill coefficient, respectively. The Y value was calculated by the following equation: $Y = \Delta A_{\text{obs}} / \Delta A_{\text{max}} = (A_{\text{obs}} - A_0) / (A_{\text{max}} - A_0)$, 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**).

RESULTS AND DISCUSSIONS

Monomer Preparations and Polymerization

Acetylene monomers **1** and **2** were synthesized by reaction of 4-ethynyl aniline or propargylamine with 4-nitro phenyl isocyanate in dry dichloromethane. The products were isolated in high yields (86% or 92%) after purifications by silica gel chromatography. The monomers were characterized by spectroscopic methods and satisfactory analysis data corresponding to their molecular structures were obtained (Fig. 1).

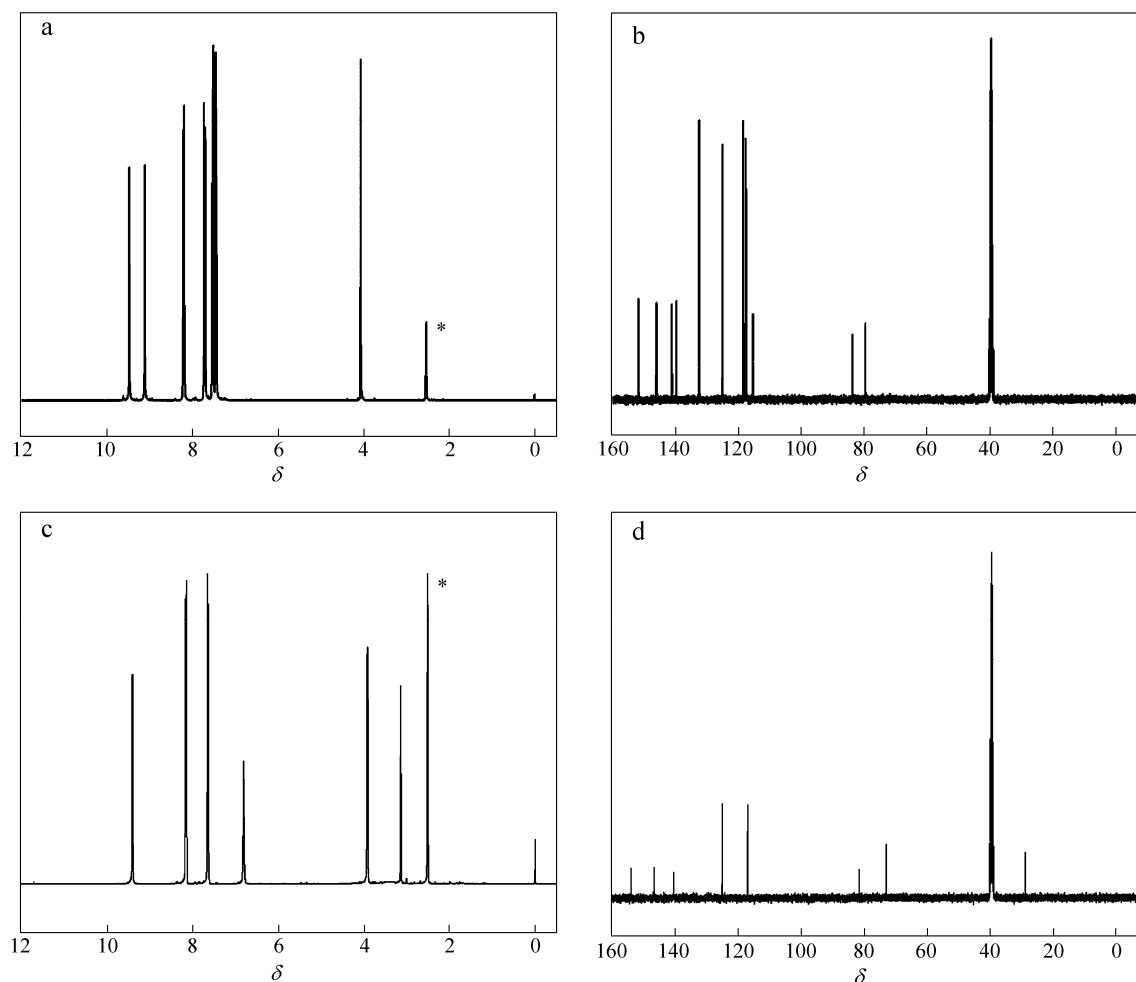


Fig. 1 (a) ^1H -NMR of **1**, (b) ^{13}C -NMR of **1**, (c) ^1H -NMR of **2**, and (d) ^{13}C -NMR of **2**
* The peaks due to the DMSO

To prepare the polyacetylenes carrying urea moieties, we attempted to polymerize **1** and **2** using Rh complex. We first attempted to polymerize **1** using $\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$, a good catalyst for polymerization of *N*-propargylamides^[30, 31]. As can be seen from Table 1, the polymerization of **1** catalyzed by $\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ in THF affords polymer with moderate molecular weight ($M_n = 4400$). Then, we check the polymerization with $[\text{Rh}(\text{nbd})\text{Cl}]_2$. $[\text{Rh}(\text{nbd})\text{Cl}]_2$ works well for the acetylene polymerization in THF/ Et_3N , furnishing polymer with M_n up to 8300 in over 78% yields. We also attempted to polymerize **2** using $[\text{Rh}(\text{nbd})\text{Cl}]_2$ or $\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$. $\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$ works well for the **2** polymerization in THF, furnishing poly(**2**) with M_n up to 5700 in 77% yields.

Table 1. Polymerization of **1** and **2**^a

Run	Momomer	Catalyst	Yield ^b (%)	M_n^c	M_w/M_n^c
1	1	$\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$	67	4400	1.42
2	1	$[\text{Rh}(\text{nbd})\text{Cl}]_2$	78	8300	1.53
3	2	$\text{Rh}^+(\text{nbd})[\eta^6\text{-C}_6\text{H}_5\text{B}^-(\text{C}_6\text{H}_5)_3]$	77	5700	1.54
4	2	$[\text{Rh}(\text{nbd})\text{Cl}]_2$	63	3100	1.63

^a Conditions: $[\mathbf{1}]_0 = 0.1$ mol/L, $[\mathbf{1}]_0/[\text{Rh}]_0 = 50$, at 30 °C for 24 h;

^b Diethylether-insoluble part;

^c Determined by GPC eluted with THF calibrated by polystyrene standards

Structural Characterizations by Spectroscopic Methods

The obtained polymers were characterized by spectroscopic methods, and the polymers [poly(**1**) and poly(**2**)] gave satisfactory analysis data corresponding to expected molecular structures. Figure 1 shows the NMR spectra of monomer **1** and **2** in DMSO-d_6 . The protons of the acetylene triple bond of **1** and **2** resonate at $\delta = 4.05$ and 3.14, respectively, which disappear in the spectra of poly(**1**) and poly(**2**), as shown in Fig. 2. The results clearly indicate that the acetylene polymerization took place to form polymers containing alternating single and double bonds along the main chain.

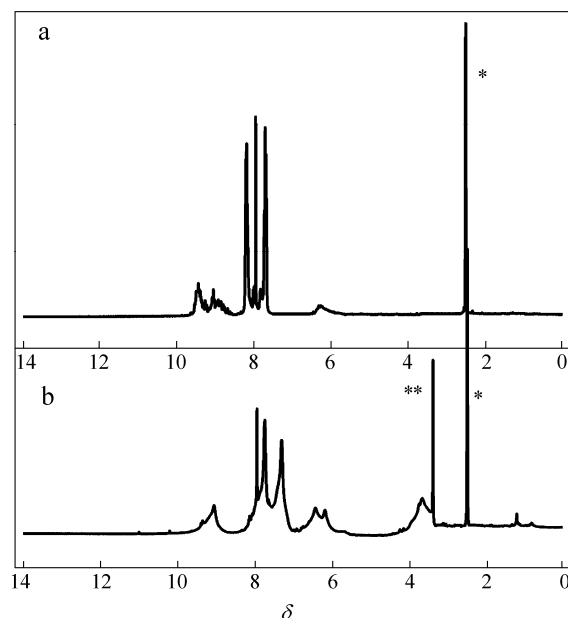


Fig. 2 (a) ^1H -NMR of poly(**1**) and (b) ^1H -NMR of poly(**2**)

* The peaks due to the DMSO; ** The peaks due to the H_2O

Anion-recognition Properties

To examine the anion recognition properties of the urea carrying polyacetylenes [poly(**1**) and poly(**2**)], a series of tetra-*n*-butylammonium (TBA) salts were added to the solution of poly(**1**) and poly(**2**) in DMF. As shown in

Fig. 3(a) and Fig. 4(a), the solution of poly(**1**) exhibits a yellow color, while the solution of poly(**2**) is colorless. A complete color change from yellow or colorless to red, respectively, was observed after the addition of fluoride ions. On the other hand, exposure to $\text{C}_6\text{H}_5\text{COO}^-$, CH_3COO^- , Cl^- , Br^- , I^- , NO_3^- and HSO_4^- (as their tetrabutylammonium salts) did not lead to any obvious change in color of the solution of poly(**1**) and poly(**2**) in DMF. This dramatic chromogenic response capability allows a rough discrimination of the fluoride ion by the naked eye.

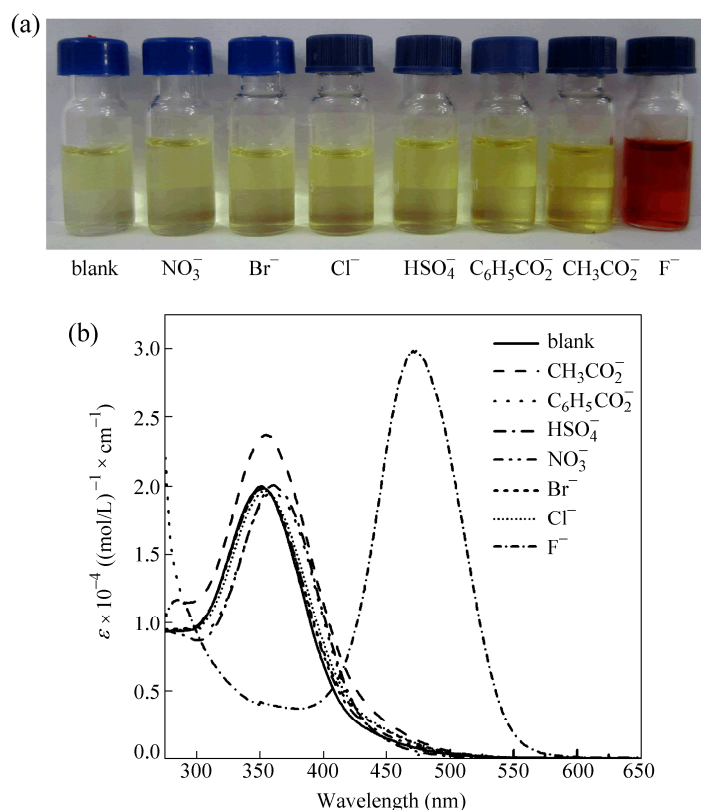


Fig. 3 (a) Photograph of DMF solutions and (b) absorption spectra of poly(**1**) in the presence of TBA salts of a series of anions ([monomeric units of poly(**1**)] = 1.0 mmol/L in photograph and 100 $\mu\text{mol/L}$ in absorption spectra, [anion]/[monomeric units of poly(**1**)] = 10.)

The anion binding properties of poly(**1**) and poly(**2**) have been also investigated using UV-Vis spectroscopy. As shown in Figs. 3(b) and 4(b), a red shift was observed in the absorption spectrum of poly(**1**) and poly(**2**) upon addition of F^- , while the absorption spectrum changes slightly upon addition of $\text{C}_6\text{H}_5\text{COO}^-$, CH_3COO^- , Cl^- , Br^- , I^- , NO_3^- and HSO_4^- . Thus, the system caused a distinct host-guest interaction only for F^- . The selectivity of urea moieties relates to the size, basicity and configuration of the anions. Fluoride anion is a sphere anion with minimum size and highest basicity. It seems that fluoride anion prefer to interacting with polymers.

To provide an insight into the colorimetric response of poly(**1**), we carried out $^1\text{H-NMR}$ titrations of poly(**1**) in the presence of F^- (Fig. 5). The addition of fluoride ions to the poly(**1**) solution induces a distinct downfield shift of the urea protons peaks, which means the establishment of a hydrogen bond interaction with F^- . It seems that the colorimetric response of poly(**1**) was considered to be the direct consequence of the supramolecular complex formation between the urea functionality and F^- . These results strongly supported the fact that the drastic color changes were triggered by the urea/ F^- interaction through the hydrogen bonding^[32, 33].

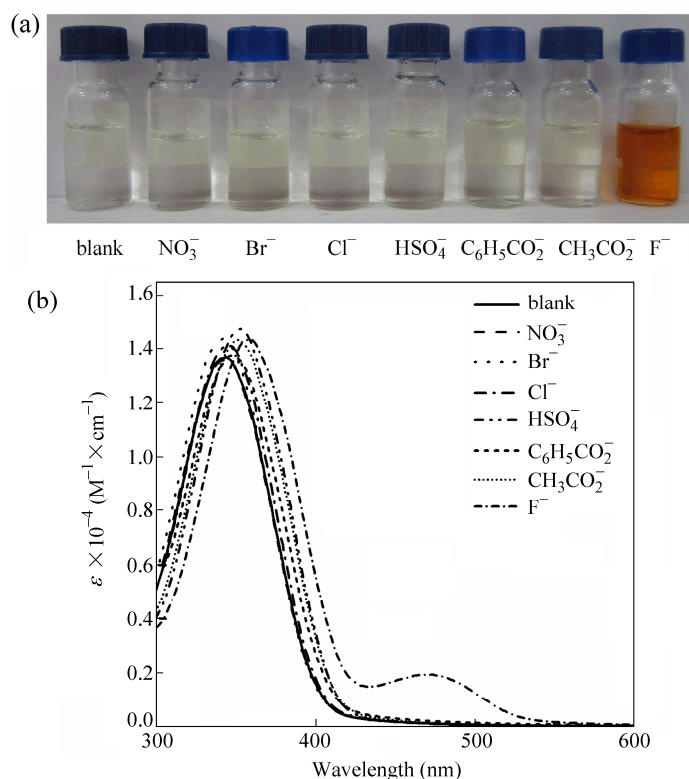


Fig. 4 (a) Photograph of DMF solutions and (b) absorption spectra of poly(**2**) in the presence of TBA salts of a series of anions ([monomeric units of poly(**2**)] = 1.0 mmol/L in photograph and 100 μ mol/L in absorption spectra, [anion]/[monomeric units of poly(**2**)] = 10)

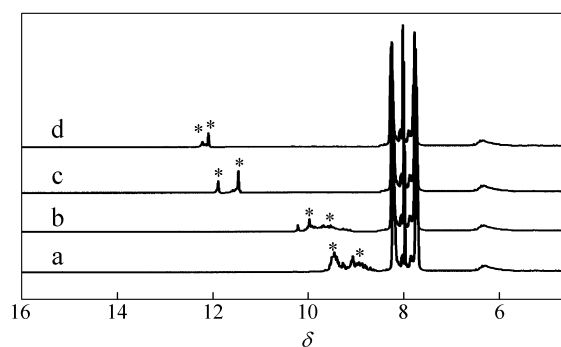


Fig. 5 ^1H -NMR spectra of poly(**1**) in the presence of (a) 0, (b) 0.5, (c) 1.0, and (d) 2.0 equiv. of TBAF in DMSO-d_6

* The peaks due to the urea protons

We also measured the IR of poly(**2**) in solution upon addition of F^- or Br^- to investigate the chromogenic response of poly(**2**). Figure 6 depicts the partial IR spectra of poly(**2**) in presence of TBAF or TBABr in DMF. In the solution state, poly(**2**) exhibited the urea $\nu_{\text{C=O}}$ at 1667 cm^{-1} . The peak of C=O stretching of the urea moiety of poly(**2**) in the presence of TBAF was observed 13 cm^{-1} higher than its original state. But urea $\nu_{\text{C=O}}$ of poly(**2**) kept stable upon addition of TBABr. The addition of fluoride ions to the poly(**2**) solution induced a distinct high wavenumber shift in the urea $\nu_{\text{C=O}}$, which meant the establishment of a hydrogen bond interaction with F^- . These results indicated that the colorimetric response of poly(**2**) was considered to be the direct consequence of the supramolecular complex formation between the urea functionality and F^- .

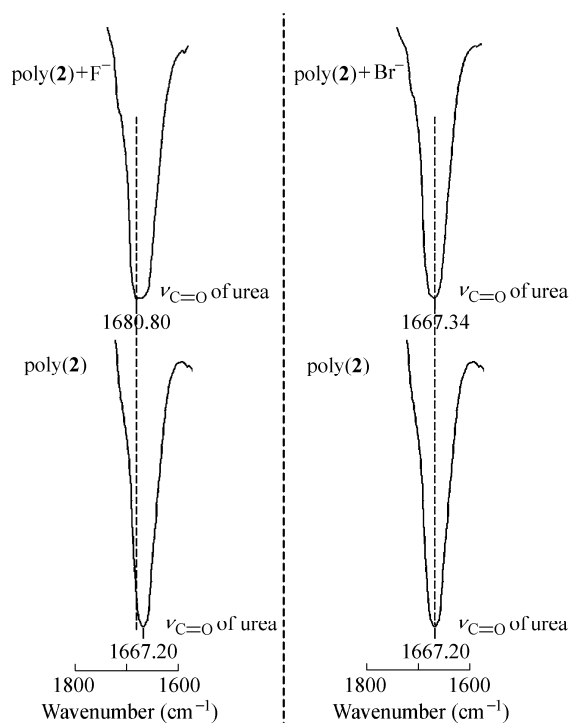


Fig. 6 The IR spectra in solution of poly(**2**) with TBAF and TBABr in DMF ([monomeric units of poly(**2**)] = 20 $\mu\text{mol/L}$, $[\text{F}^-]/[\text{monomeric units of poly(2)}] = 10$, $[\text{Br}^-]/[\text{monomeric units of poly(2)}] = 10$)

The changes observed when poly(**1**) was treated with increasing quantities of TBAF in DMF were also recorded (Fig. 7). On gradual addition of TBAF to a solution of poly(**1**) (100 $\mu\text{mol/L}$, DMF), the absorbance at 350 nm first red shift to 375 nm, then underwent gradual decrease in its intensity with concomitant increase at 475 nm (Fig. 7a). The absorbance intensity of poly(**1**) was saturated with 40 equiv. of F^- . It seems that the higher limit of poly(**1**) detection to F^- is 2.0 mmol/L, and the lower limit detection reaches 0.8 mmol/L. This red shift by 100 nm points to the significant stabilization of the intramolecular charge transfer achieved through interaction of poly(**1**) with fluoride anion. As shown in Fig. 7(b), the titration curve displayed a sigmoidal curvature, which means that binding mode is a cooperative binding mode^[34, 35].

Then, the binding constant (K_a) and coefficient (n) were determined using the Hill equation, which is a suitable equation for determining the cooperativity in the case of a cooperative binding system. Poly(**1**) exhibited binding affinities to F^- , of which the binding constant (K_a) is 758 $(\text{mol/L})^{-1}$. An exceptional n value was observed up to 5.8 in this binding system. It seems that the cooperative and positive allosteric binding occurs between poly(**1**) and F^- . The n value greater than 1 is obtained in the case of positive allosteric binding mode, in which the partially formed urea/ F^- complex units in the polymer chain should change the main chain conformation to facilitate further F^- binding. Therefore, the binding ability of poly(**1**) nonlinearly increases with the increasing amount of F^- bound to poly(**1**).

We further examined the effect of π -conjugated systems on the anion binding affinity by comparison to that of polyacetylenes featuring urea receptors [poly(**2**)]. The change in the absorption spectrum with the addition of F^- and the resulting titration curve are shown in Fig. 8. From Fig. 8, the lower limit of poly(**2**) detection to F^- is 1 mmol/L, and the higher limit detection is 5 mmol/L. Poly(**2**) exhibited a bathochromic shift similar to poly(**1**) upon the addition of F^- . On the basis of the Hill analysis, the K_a and n values of this binding system were found to be 500 $(\text{mol/L})^{-1}$ and 2.3, 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 F^- .

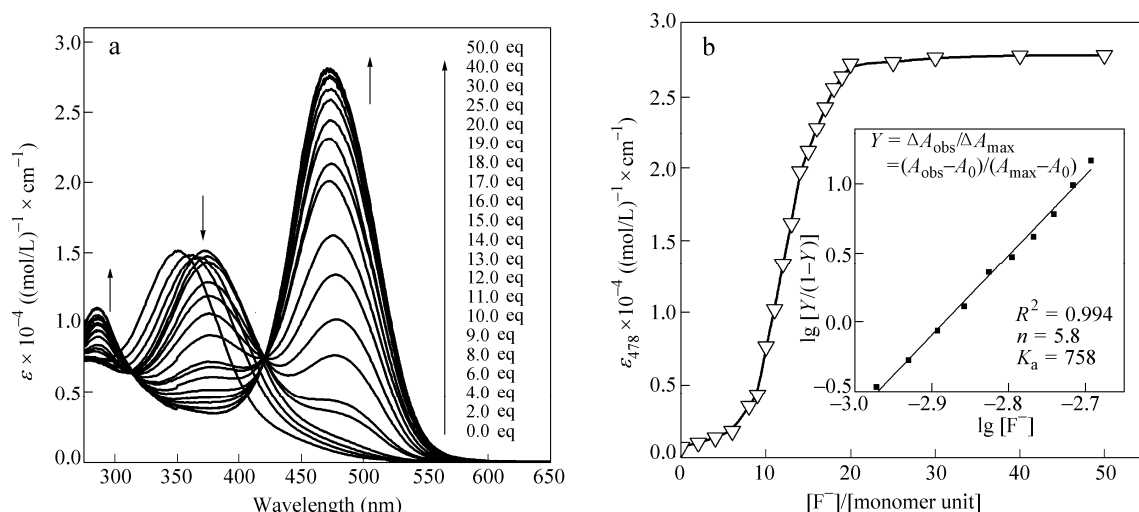


Fig. 7 (a) UV-Vis absorption titration and (b) the resulting titration curve of poly(**1**) with F^- in DMF ([monomeric units of poly(**1**)] = 100 $\mu\text{mol/L}$, $[F^-]/[\text{monomeric units of poly(**1**)}] = 0\text{--}50$) Inset shows the Hill plot analysis of this complexation.

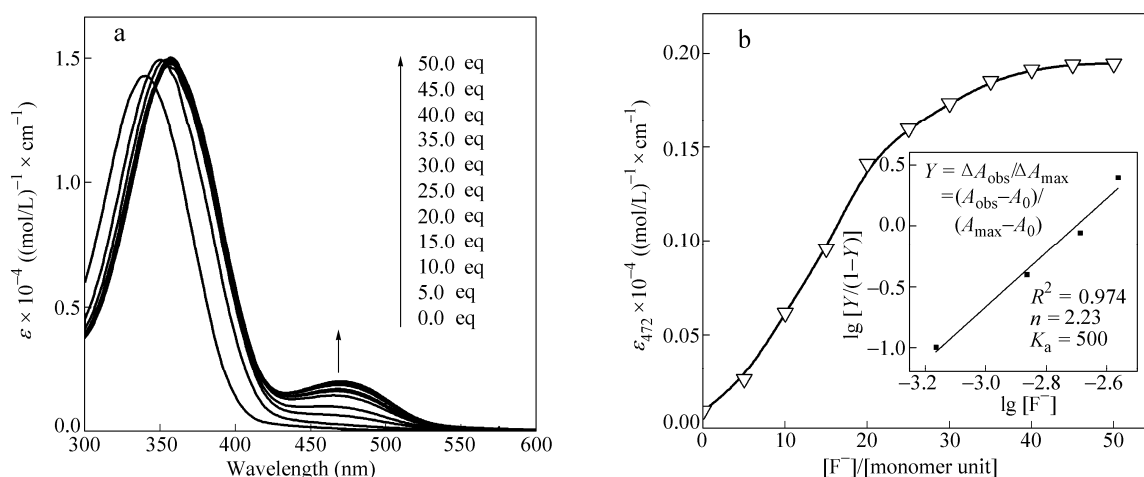


Fig. 8 (a) UV-Vis absorption titration and (b) the resulting titration curve of poly(**2**) with F^- in DMF ([monomeric units of poly(**2**)] = 100 $\mu\text{mol/L}$, $[F^-]/[\text{monomeric units of poly(**2**)}] = 0\text{--}50$) Inset shows the Hill plot analysis of this complexation.

The most reasonable explanation in the improvement of the binding ability of poly(**1**) is the π -conjugated systems. π -Conjugated systems probably endow the urea receptor with a more robust and efficient hydrogen bonding ability, thus enabling the improved anion binding affinity.

CONCLUSIONS

Urea containing novel acetylenes, 1-(4-ethynylphenyl)-3-(4-nitrophenyl) urea (**1**), 1-(4-propargyl)-3-(4-nitrophenyl) urea (**2**), were synthesized and polymerized with rhodium catalyst. Polymers [poly(**1**) and poly(**2**)] with moderate molecular weights were obtained in good yields. The anion sensing ability of poly(**1**) and poly(**2**) was estimated using the tetra-*n*-butylammonium (TBA) salts of a series of anions in DMF. Upon the addition of F^- , the color of the DMF solutions of poly(**1**) and poly(**2**) immediately turned to a different color, while the color of solution changed slightly upon addition of Cl^- , HSO_4^- , Br^- , and NO_3^- indicating the F^- -sensing ability of poly(**1**) and poly(**2**). The $^1\text{H-NMR}$ titrations of poly(**1**) revealed that the colorimetric response of poly(**1**) was

triggered by the urea/ F^- interaction through the hydrogen bonding and/or deprotonation process. The absorption spectra titration and Hill plot analysis were carried out to measure the F^- binding ability, and found that the Hill coefficient in the complexation between poly(**1**) and F^- was high up to 5.8. This result clearly indicated that this binding mode was based on a positive homotropic allosterism, in which the partially formed urea/ F^- complex units in the polymer chain should produce a change in the whole main chain conformation, facilitating further anion binding.

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