Macromolecules
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Colorimetric Detection of Anions in Aqueous Solution Using Poly(phenylacetylene) with Sulfonamide Receptors Activated by Electron Withdrawing Group

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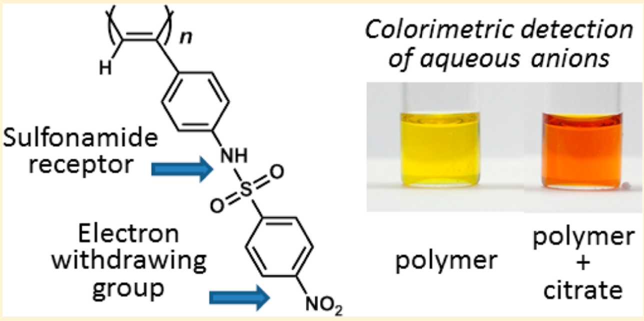
Supporting Information

ABSTRACT: A series of sulfonamide-conjugated poly(phenylacetylene)s with various electron withdrawing and donating substituents were designed and synthesized in order to develop a novel colorimetric probe for anions in water. The UV–vis absorption measurements, which were performed in an organic solvent to provide fundamental insights into the anion detection properties of these polymers, clarified that the colorimetric response ability is highly enhanced by the incorporation of strong electron withdrawing groups (EWG). Sulfonamide-conjugated poly(phenylacetylene) with nitro groups, the strongest EWG, was therefore used for the detection of anions in an aqueous environment. In a solution containing up to 20% water, the polymer exhibited obvious color changes to anions including the biologically important carboxylates. On the basis of the NMR titration analysis, such a colorimetric response was confirmed to be based on the deprotonation event of the sulfonamide binding site, which was suggested to be essential for the detection of aqueous anions.



INTRODUCTION

Anions are essential to life, since many biological processes including osmosis and ATP formation cannot be realized without them. They are also important for many industrial processes such as electroplating and are therefore often found as harmful pollutants in industrial waste. Consequently, the development of reliable, robust, and practical anion sensors applicable for use in complex media, such as serum, cells, soil, and environmental water, is highly desired.[1]

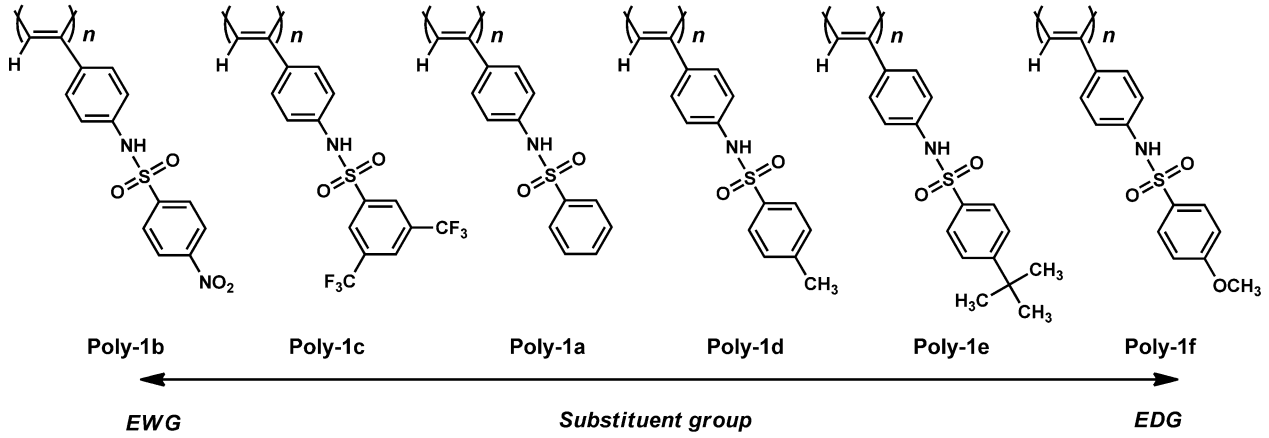
The fabrication of chemosensors for anion sensing based on supramolecular concepts naturally requires a means to output the sensory event in a quantifiable and measurable change.[2−14] One of the more appealing approaches involves the construction of colorimetric anion sensors, since visual detection without requiring any spectroscopic instrumentation immediately indicates qualitative information, while absorption spectroscopy provides quantitative information. Although considerable effort has therefore been devoted to the fabrication of colorimetric anion sensors, a direct sensing of anions in water is still recognized as a remarkably challenging task because of the difficulty in the anion recognition process in water due to the intrinsic properties of anions.[9] The most problematic aspect in the sensing of aqueous anions is that anions usually have higher free energies of solvation than cations with the same absolute charge and comparable size. Hence, in the anion binding process, the sensor molecule must compete with the solvent molecules especially in polar solvents such as water. To achieve anion sensing in aqueous solutions, a specific sensor design has recently been developed, which includes the spatial arrangement of multiple binding sites,[15−18] the construction of hydrophobic microenvironments on receptor moieties,[19−22] the incorporation of a metal complex receptor,[23−25] and employing highly acidic donor units as the binding sites.[26−28]

We have thoroughly investigated anion detection ability of conjugated polymers for the development of reliable and sophisticated anion sensor materials.[29−36] Based on such examinations, we discovered that the conjugated polymer-based sensors possessed characteristic anion sensing abilities that have never been observed for small molecule-based sensors, e.g., variable colorimetric response dependent on the types of anions,[29] highly size-specific anion detection,[35] and efficient anion detection based on the positive allosteric binding.[34] These unique and unprecedented anion sensing abilities, which are considered to be based on the characteristic feature of the conjugated polymer,[37−40] appear to overcome the present limitation in the development of a practical anion sensor. However, such superior anion detection abilities of these polymers are limited in organic solvents. The polymers hardly exhibit colorimetric responses to anions in a solvent containing even a small amount of water due to the inhibition of the polymer–anion interaction by the water molecules. In

Received: August 23, 2012
Revised: September 28, 2012
Published: October 11, 2012

dx.doi.org/10.1021/ma301767g | *Macromolecules* 2012, 45, 8221−8227

Chart 1. Structures of Sulfonamide-Functionalized Poly(phenylacetylene)s with Different Substituents



Scheme 1. Synthesis of a Series of Sulfonamide-Functionalized Poly(phenylacetylene)s

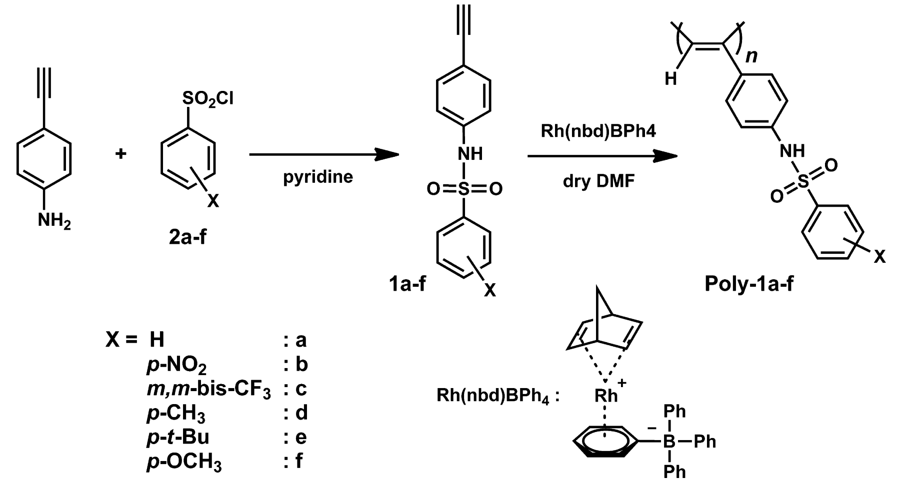


Table 1. Synthetic Results for a Series of Sulfonamide-Conjugated Poly(phenylacetylene)s[a]

polymer	yield[b] (%)	M_n[c] × 10^{-5}	M_w/M_n[c]	solubility[d]				
				DMF	DMSO	THF	DCM	Acetone
Poly-1a	86	0.90	1.97	++	—	—	—	—
Poly-1b	68	4.77	5.65	++	+	—	—	—
Poly-1c	84	2.44	3.54	++	++	++	—	++
Poly-1d	85	2.91	2.57	++	+	—	—	—
Poly-1e	81	1.20	3.33	++	+	—	—	—
Poly-1f	82	1.64	4.99	++	—	—	—	—

[a] Condition: [monomer] = 0.03 M; $[\text{monomer}]_0/[\text{Rh}]$ = 50; catalyst, Rh(nbd)BPh_4; solvent, dry DMF; temperature, 25 °C, time = 24 h. [b] Diethyl ether insoluble part, determined via gravimetry. [c] Determined by SEC in DMF containing LiCl (0.01 M) using polystyrene standards. [d] ++, soluble; +, partially soluble; —, insoluble at room temperature.

order to develop practical anion sensor materials, the realization of a conjugated polymer-based sensor capable of directly detecting aqueous anions is now very desirable.

We have designed poly(phenylacetylene)s with sulfonamide binding sites (**Poly-1a-f**), which emerge as ideal candidates because of the expectation that the highly acidic sulfonamide will operate as an anion receptor even in an aqueous solution (Chart 1).[41−43] A series of substituent groups with varying electron withdrawing (EWG) and donating (EDG) properties was incorporated to explore the optimized receptor design. First, in order to provide a fundamental insight into the anion detection ability of the synthesized polymers, the colorimetric response to anions was examined in organic solvent. Moreover, a ^{1}H NMR measurement was carried out to elucidate the anion-binding mechanism of the sulfonamide receptors. After determining the most suitable candidate, we finally applied this polymeric receptor in the detection of anions in aqueous media.

■ RESULTS AND DISCUSSION

Polymer Synthesis. The desired polymers were synthesized via a two-step synthetic route as illustrated in Scheme 1. The coupling reactions between ethynylaniline and a series of substituted bezenesulfonyl chlorides (**2a**−**f**) proceeded in high yields to produce the various sulfonamide-conjugated novel monomers (**1a**−**f**). To provide an extended π-conjugated system for anion signaling, the prepared monomers were polymerized using Rh(nbd)BPh_4 as the catalyst to produce the corresponding polymers (**Poly-1a**−**f**) in good yields (Table 1). In all cases, the respective SEC profiles showed monodisperse polymers with high molecular weights. All of the obtained polymers were soluble in *N*,*N*-dimethylformamide (DMF), but partially soluble or insoluble in dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane (DCM), and acetone. Figure 1 depicts the assigned ^{1}H NMR spectrum of **Poly-1a** as a representative example. The ^{1}H NMR spectrum showed a characteristic signal due to the main chain proton at 5.60 ppm, indicative of the *cis*-configuration in the polyacetylene main chain.[44] Similar results were also obtained for other polymers. Thus, based on the SEC and ^{1}H NMR results, a series of poly(phenylacetylene)s with the various sulfonamide groups were found to be synthesized via a facile two-step synthetic process.

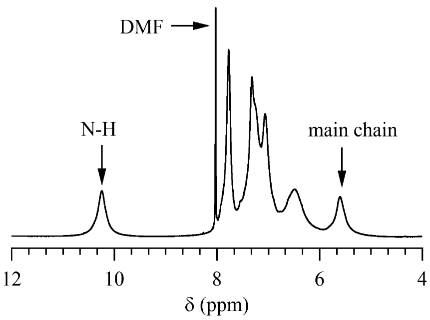


Figure 1. ^{1}H NMR spectrum of **Poly-1a** in DMF-d_7 at ambient temperature.

Anion Detection Properties of Sulfonamide-Conjugated Poly(phenylacetylene)s. To provide fundamental insights into the suitability of the sulfonamide-conjugated scaffolds as optical anion detectors, the anion recognition properties of the synthesized polymers were first investigated by monitoring the UV−vis spectral changes in the respective polymer solutions upon the addition of different anions. As a typical example, Figure 2 displays the absorption spectral changes of **Poly-1a** in DMF in the presence of various anions, which were introduced as their tetra-*n*-butylammonium (TBA) salts. **Poly-1a** showed a characteristic absorption peak in the absorption wavelength ranging from 370 to 550 nm where the π-conjugation of the polymer backbone typically appears. The obvious spectral changes including a distinct red shift in the absorption local maxima were seen upon the addition of fluoride (F^-) to the solution of **Poly-1a** in DMF. This absorption spectral change is considered to be the direct consequence of the change in the main-chain conformation induced by the interaction between the sulfonamide receptor in **Poly-1a** and F^-.[30] Furthermore, similar bathochromic shifts were obtained upon the addition of acetate (AcO^-), benzoate (BzO^-) and dihydrogen phosphate ($H_2PO_4^-$) anions, whereas no essential changes were observed for the azide (N_3^-), chloride (Cl^-), bromide (Br^-), iodide (I^-), nitrate (NO_3^-), hydrogen sulfate (HSO_4^-), and perchlorate (ClO_4^-) anions. As well as **Poly-1a**, all the synthesized polymers responded to the anion addition with clear red shifts. The detailed spectral changes are summarized in Figure S1 in Supporting Information. Important to note is that the observed distinct spectral changes produced specific colorimetric changes that were easy to visually recognize. Figure 3 shows a typical example of such a colorimetric change. These results demonstrated that the simple sulfonamide-conjugated poly(phenylacetylene)s are quite suitable as an optical chemosensor capable of detecting anion species.

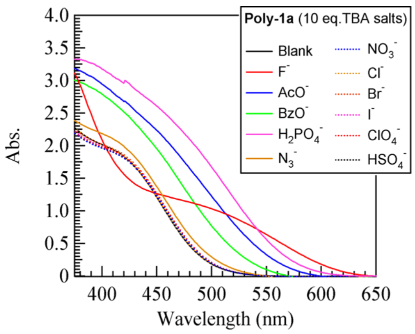


Figure 2. UV−vis absorption spectra of DMF solutions of **Poly-1a** obtained upon the addition of a series of anions ([**Poly-1a**] = 0.2 mg mL^{-1}; [anion]/[monomeric units in **Poly-1a**] = 10).

Figure 3. Color changes in DMF solutions of **Poly-1b** (1.0 mg mL^{-1}) obtained upon the addition of 10 equiv of tetra-*n*-butylammonium salts of a series of anions (from left to right: blank, F^-, AcO^-, BzO^-, $H_2PO_4^-$, N_3^-, Cl^-, Br^-, I^-, NO_3^-, HSO_4^-, ClO_4^-).

To accurately quantify the anion detection properties of the synthesized polymers, we carried out UV−vis titration experiments. For the **Poly-1b**/F^- system, the polymer was found to detect fluoride anions at concentrations as low as 1.3×10^{-4} M (Figure S2, Supporting Information). Similar results were obtained for other detectable anions, thus demonstrating that the polymers can detect a wide range of anions at a sufficient sensitivity.

The observed anion-induced spectral and colorimetric changes in the polymers were dependent on the types of both the polymers and anions. In order to clarify the mechanism of such a selectivity, we next tried to establish a correlation between the sulfonamide receptor and anion. A summary of the spectroscopic and colorimetric responses of the polymers is presented in Table 2 in conjunction with the Hammett constants of the substituent groups in the polymers.[45] As already established elsewhere, the anion binding affinity of the urea or thiourea receptors generally correlates to the basicity of the target anions.[2,46] Similar to such receptors, the examined sulfonamide-functionalized polymers showed a colorimetric change in accordance with the basicity indices of the introduced anion species. Therefore, a sufficient basicity of the anions is necessary for this colorimetric detection. Although all the polymers could response to anions with a relatively high basicity, such as F^-, AcO^-, BzO^-, and $H_2PO_4^-$, a clear substituent effect of the polymers was observed in the colorimetric detection of N_3^-.[41] The polymers decorated with a nitro group of a strong EWG (**Poly-1b**) and two trifluoromethyl group of a weak EWG (**Poly-1c**) are able to even detect a mildly basic azide anion, while polymers with EDGs hardly detect the azide anion. Strong EWGs would

Table 2. Summary of the Anion Detection by Various Poly(phenylacetylene)s[a]

		anion detection					
polymer	Hammett constants[b]	F^-	AcO^-	BzO^-	$H_2PO_4^-$	N_3^-	NO_3^-, Cl^-, Br^-, I^-, ClO_4^-, HSO_4^-
Poly-1b	0.78	○	○	○	○	○	×
Poly-1c	0.46[c]	○	○	○	○	○	×
Poly-1a	0.00	○	○	○	○	×	×
Poly-1d	−0.14	○	○	○	○	×	×
Poly-1e	−0.15	○	○	○	○	×	×
Poly-1f	−0.28	○	○	○	○	×	×

[a] Based on the bathochromic shift observed in the absorption spectrum shown in Figures 2 and S1, Supporting Information. Key: ○, detected; × , not detected. [b] Para-substituted parameters, σ_p. [c] Meta-substituted parameter, σ_m.

decrease the electron density at the receptor nitrogen atom and hence increase the strength of the receptor–anion interaction, which results in enhanced anion detection properties. In contrast, the EDGs increase the electron density on the receptor nitrogen atom, therefore reducing the ability of receptor–anion interactions by the detector molecules. We believe that this is the first instance for a polymeric anion–detector scaffold in which the anion detection properties were enhanced by manipulation of the substituent groups.

After establishing the effect of EDG versus EWG groups on the anion detection properties of the series of sulfonamide-conjugated poly(phenylacetylene)s, we next tried to clarify the mechanism of anion recognition. Recent work by Fabbrizzi and co-workers revealed that host-anion interactions are classified into two general types, i.e., hydrogen bonding and deprotonation.[47] For determining the exact mechanism of the host-anion interactions, ^{1}H NMR titration has been known as an insightful method, since the shifting or broadening of specific peaks in the spectra are specific to different interaction mechanisms. To this end, the ^{1}H NMR titration experiments were carried out by the progressive addition of aliquots of fluoride anion to a solution of the monomer in DMF-d_7. It should be noted here that the monomer was used as a model compound of the polymer because the highly broadened signals in the ^{1}H NMR spectrum of the polymer were expected to provide no useful information. The results for **1b** are shown in Figure 4 as a representative example. We traced the aromatic protons adjacent to the sulfonamide. With the increasing addition of fluoride, an upfield shift was observed in the signals due to all the aromatic protons of **1b**. This upfield shift reflects the generation of the deprotonated species. The proposed deprotonation mechanism and the resulting formation of the deprotonated species are presented in Scheme 2. The sulfonamide proton is considered to be more acidic than the corresponding amide and urea protons.[41,43] This is precisely why the neat deprotonation of the sulfonamide-based anion receptor is possible. Thus, the ^{1}H NMR titration results indicated that the colorimetric response of a series of sulfonamide-conjugated poly(phenylacetylene)s is the direct consequence of the anion-induced deprotonation process of the sulfonamide receptor.

We next investigated the effect of EWG versus EDG on this deprotonation process. Since Hammett and others have clarified, the acidity values of simple aromatic Brønsted acids, such as benzoic acid and sulfonic acid, are significantly influenced by substituent groups, it is logically expected that the acidity, i.e., the anion recognition properties, of substituted benzenesulfonamides studied herein can be manipulated by the inherent substituent effect. To clarify this, we compared the ^{1}H NMR titration of **1b** with the nitro groups of EWG and **1f** with the methoxy groups of EDG. Furthermore, to extract meaningful results, the azide anion that has a moderate basicity was employed for the titration experiments (Figure S3 and S4, Supporting Information). The result of the titration of **1b** with the azide anion was essentially the same as the result for fluoride anion as discussed above. In contrast, the result of the **1f**/azide system showed that the deprotonation event did not occur. As a point of note, these results exactly match the colorimetric responses of **Poly-1b** and **Poly-1f** toward the azide anion. Thus, this simply adds more proof that the anion recognition properties of the polymers can be rationally and deliberately manipulated to the target anions by simply selecting the appropriate functional group as a substitute of benzenesulfonamide.

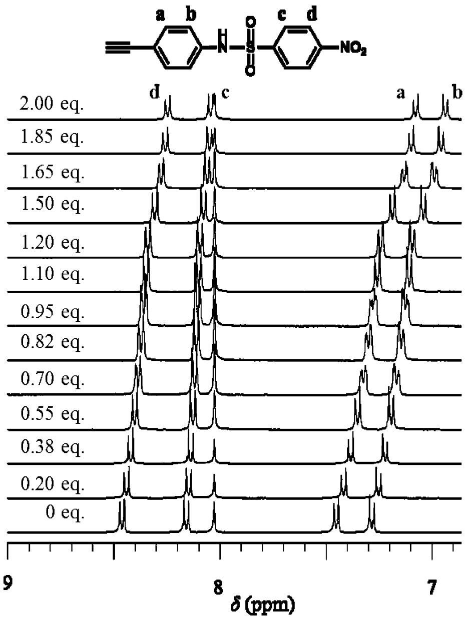
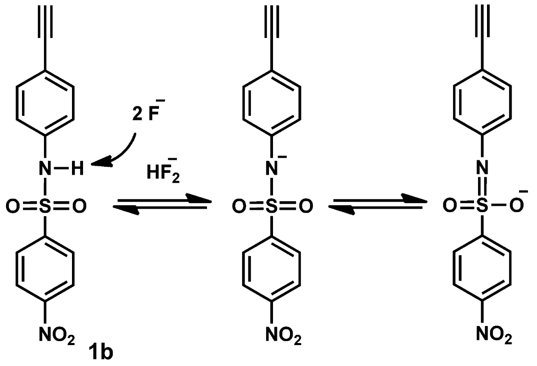


Figure 4. ^{1}H NMR spectra of **1b** with various equivalents of tetra-*n*-butyl ammonium fluoride (TBAF) in DMF-d_7.

Scheme 2. Mechanism of Deprotonation of 1b by the Addition of F^-



Colorimetric Detection of Anions in Aqueous Environments. Generally, protic solvents such as water compete with anions for the host binding sites thereby impeding the interaction between the host and guest.[9] This is the reason why the direct sensing of anions in aqueous media has been recognized to be quite difficult. However, on the basis of the demonstrated enhanced anion recognition ability of the sulfonamide-conjugated polymers, we envisioned that this setback could be overcome by employing a receptor molecule that leverages a deprotonation event rather than a hydrogen-bonding mechanism. Hence, we explored the potential of **Poly-1b**, which has the strongest electron withdrawing nitro group, as a simple and novel colorimetric sensor for anions in aqueous environments.

We first analyzed the effect of increasing the water content on the detection of the fluoride anion, as show in Figure 5.

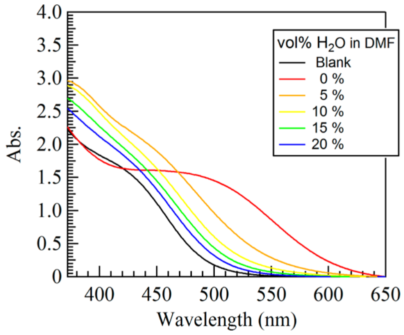
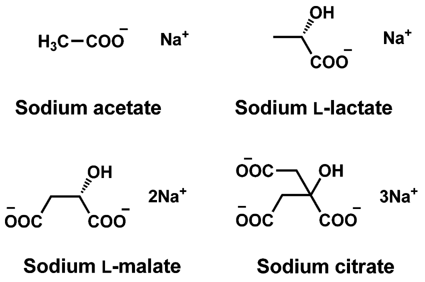


Figure 5. UV–vis absorption spectra of **Poly-1b** with F^- in DMF/H_2O mixed solvents ([**Poly-1b**] = 0.67 mM; [F^-] = 6.7 mM).

Interestingly, the **Poly-1b**/F^- system showed an obvious red shift even in a mixed solvent containing up to 20% water, though the spectroscopic response decreased with the increasing water content. These spectral changes also provided colorimetric changes from yellow to orange that can be visually recognized. Therefore, this investigation indicated that the polymer is applicable for a practical colorimetric sensor capable of detecting anions in aqueous media. On the contrary, we obtained negative results when we tested the rest of the polymers in the library. This can be attributed to the fact that **Poly-1b** has the strongest electron withdrawing nitro group, which would impart an exceptional anion recognition ability to the polymer.

To further expand this interesting property, we then examined whether **Poly-1b** is applicable for the colorimetric sensing of biologically important carboxylates, such as acetate, L-lactate, L-malate, and citrate (Chart 2). These four carboxylates are simple, basic, and particularly known, thus providing meaningful insights into the applicability of **Poly-1b** as a colorimetric probe for various biologically important carboxylates in an aqueous solution.[48] For this demonstration, carboxylates were employed as sodium salts that are the general form in nature. Figure 6 shows the UV–vis spectra of **Poly-1b** in the presence of a series of carboxylates in a DMF/H_2O (9/1, v/v) mixed solvent. Obvious spectral changes were observed for all the carboxylates in spite of the presence of a considerable amount of water in the solutions. Moreover, **Poly-1b** was found to output this information as a visible color change, even though 20% of the water exists in the system (Figure 7).

Chart 2. Structures of Employed Sodium Carboxylates



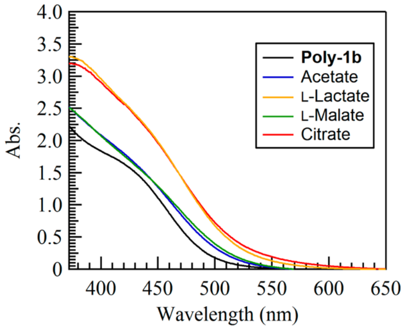


Figure 6. UV–vis absorption spectra of DMF/H_2O (9/1, v/v) solutions of **Poly-1b** obtained upon the addition of various sodium salts of carboxylates ([**Poly-1b**] = 0.67 mM; [sodium carboxylate] = 6.7 mM).

Figure 7. Color changes in DMF/H_2O (8/2, v/v) solutions of **Poly-1b** (1.0 mg mL^{-1}) obtained upon the addition of 10 equiv. of various sodium carboxylates (from left to right: blank, sodium acetate, sodium L-lactate, sodium L-malate, sodium citrate).

Furthermore, the UV–vis titration results of **Poly-1b** with citrate showed that a clear red shift in the spectra was observed upon the addition of only 0.2 equivalents of citrate (Figure S5, Supporting Information). This result clarified that **Poly-1b** is a potent probe that can detect anions including biologically important ones in aqueous media even at low anion concentrations.

To elucidate the anion binding mechanism of **Poly-1b** in aqueous media, ^1H NMR titration experiments were carried out by the progressive addition of aliquots of sodium acetate to a solution of **1b** in DMF-d_7/D_2O (9/1, v/v). Similar to the case of **1b** in DMF-d_7, the ^1H NMR titration results showed a characteristic upfield shift in the aromatic peaks, indicative of the direct deprotonation of **1b** even in the presence of water (Figure S6, Supporting Information). Therefore, the deprotonation reaction was concluded to play a crucial role in the colorimetric changes observed for **Poly-1b** in the presence of the anions in an aqueous environment. Given the difficulty in detecting aqueous anions by the previously prepared polymeric receptors with a hydrogen bonding-based anion recognition property, the deprotonation mechanism may be necessary for such an efficient sensing of anions in aqueous media. In addition, based on the screening of all the sulfonamide-conjugated poly(phenylacetylene)s synthesized here, the strong EWG as well as the deprotonatable sulfonamide binding site was confirmed to be essential for the detection of aqueous anions.

■ CONCLUSIONS

We synthesized a series of novel poly(phenylacetylene)s with various sulfonamide groups to evaluate an efficient colorimetric anion probe that can even operate in aqueous media. All the prepared polymers showed visible colorimetric responses upon the addition of anions to an organic solution, which was clarified to be due to the deprotonation event of sulfonamide receptors by a ^{1}H NMR titration experiment. Among the polymers, poly(phenylacetylene)s with sulfonamide receptors activated by a strong EWG (nitro group) exhibited an enhanced anion recognition property, thus being applicable to the colorimetric detection of anions in an aqueous environment. Considering that the detection of aqueous anions by colorimetric means is still a highly difficult task, this demonstration would be valuable in anion recognition chemistry. Important to note is that the anion sensing ability was suggested to be simply and straightforwardly tunable with a substituent group that is located adjacent to the sulfonamide receptor. Therefore, we believe that this investigation provided useful insights into molecular design for the realization of a practical sensor for aqueous anions including biologically and environmentally important ones.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and Figures S1−S6 (UV-vis spectra and absorption and NMR titration). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported in part by a Grant-in-Aid for Scientific Research (B), a Grant-in-Aid for Young Scientists (B), and the Global COE Program (Catalysis as the Basis for Innovation in Materials Science) from the Ministry of Education, Culture, Sports, Science, and Technology (MEXT), Japan.

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