

## FOCUS REVIEW

# Conjugated polymers applicable to colorimetric and fluorescent anion detection

Ryosuke Sakai

A reliable and practical method that allows simple and rapid anion detection has been in increasing demand because anions are recognized as important analytes in diverse fields. As a candidate to satisfy the above requirements, optical anion sensors have recently attracted much attention, and thus many efforts have been made to develop materials for sensor applications. This article reviews recent progress in the design and fabrication of conjugated polymer-based anion sensors. The validity of polymer-based anion sensors has been verified through the evaluation of colorimetric and fluorescent responses for a series of conjugated polymers with different binding sites and varied pendant structures. Through rational molecular design of the sensor polymers, certain structures have been found to possess desirable anion detection abilities, including enhanced binding affinity, strict size specificity and applicability to anions in an aqueous environment. Thus, the demonstration described in this focused review could provide useful insight not only for anion detection chemistry but also for polymer and supramolecular chemistry.

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## INTRODUCTION

Anions have an essential role in many biological processes including osmosis, ATP formation and DNA recognition.<sup>1</sup> They are widely used in many industrial processes such as electroplating. In agriculture, a large amount of fertilizers, which are composed of various anions involving phosphate, nitrate and sulfate, is necessary for efficient plant growth. Furthermore, anions are even present in commonly used household products. Despite the important contributions of anions, they can sometimes cause serious environmental problems. Hence, both qualitative and quantitative monitoring of anions in the environment is indispensable to building a sustainable society. Furthermore, anion analysis is also important in other diverse areas including the industrial, biological and medical fields.

Currently, practical anion analysis has been achieved by ion-exchange chromatography. Although it is well-accepted as a reliable technique, it has some drawbacks: it is time consuming and requires complicated sample preparation. Therefore, the development of more simple, rapid and practical methods for anion sensing is in increasing demand. Hence, much attention has focused on the fabrication of an optical anion sensor candidate that fully satisfies the present requirements of anion sensing.<sup>2–12</sup>

One of the important requirements in designing molecules for optical sensors is that the signaling unit must be capable of providing an optical response. Hence, a number of fluorescent and colorimetric probes for anions have already been designed and synthesized to detect fluorescence and colorimetric changes, fluorescence enhancement and fluorescence quenching techniques.<sup>13,14</sup> Another fundamental requirement for anion sensor fabrication is anion-binding capability.

However, the molecular design and synthesis of anion receptors are remarkably challenging tasks because of the diversity of the chemical and physical properties of anions, including their basicity, size and shape. Therefore, considerable effort has recently been devoted to exploring the rational design of receptor molecules for various target anions. For imparting sufficient anion-binding affinity to a receptor molecule, it is necessary to use a three-dimensional layout of multiple binding sites in which stiff and directional scaffolds, such as calixarene and the steroidal backbone, are used to fix the binding sites in an appropriate geometry.<sup>2–4</sup>

Considering the above requirements for anion sensory materials,  $\pi$ -conjugated polymers have emerged as leading candidates, primarily because they allow output of colorimetric and fluorescent responses via a molecular recognition event.<sup>15–19</sup> Another advantage of the conjugated polymer-based sensor is that the relatively stiff conjugated polymer backbone might act as a scaffold capable of arraying a number of receptors along the backbone, which is important for realizing enhanced anion recognition. Thus, incorporation of specific anion-binding sites into the polymer side chain of the conjugated polymer may make it possible to create a novel type of anion sensor.

This focused review presents recent advances in the molecular design, synthesis and optical response of conjugated polymers with anion-binding sites at the side chains. Specifically, the topics described in this paper include the following: (1) examination of the availability of the poly(phenylacetylene) backbone as a scaffold for anion reception; (2) fabrication of colorimetric anion sensors consisting of poly(phenylacetylene)s bearing various anion-binding sites; and (3) fluorescence turn-on detection of anions based on urea-functionalized

poly(phenylenebutadiynylene). Poly(phenylacetylene) was chosen as the main conjugated polymer because it was expected to produce sensing materials with the desired properties because of its unprecedented characteristics that allow for various molecular designs, immediate colorimetric response and three-dimensional organization of multiple pendant receptors, owing to its helical structure.<sup>16,18,19</sup> Poly(phenylenebutadiynylene) has emerged as a leading candidate for the fluorescent probe because of its ease of synthesis and promising fluorescent response.<sup>20,21</sup>

### POLYMERIC SCAFFOLD FOR ENHANCED ANION BINDING

Among the anion-binding units, the amide group is one of the most promising anion-binding sites, and it is widely used even in naturally occurring anion receptors,<sup>22,23</sup> such as phosphate- or sulfate-binding proteins; however, the isolated amide group has a very weak affinity toward anions.<sup>24,25</sup> Given that such anion-binding proteins acquire an improved affinity through the cooperated recognition of multiple spatially arranged amide groups, insight into the validity of the conjugated polymer backbone as a scaffold for the anion receptor would be provided by an evaluation of the anion recognition ability of an amide-functionalized conjugated polymer. Therefore, poly(phenylacetylene)-bearing amide receptors derived from L-leucine (Leu) (**1**) were synthesized, and its chiroptical response was examined on the addition of various anions (Figure 1a).<sup>26</sup>

The addition of the tetra-*n*-butylammonium salt of  $\text{CH}_3\text{CO}_2^-$  to the polymer solution in tetrahydrofuran produced a drastic change in the circular dichroism (CD) spectrum. An intense split-type Cotton effect developed in the range from 340 to 500 nm, though the polymer itself showed no significant Cotton effect (Figure 1b). This result indicates that a biased one-handed helical structure was induced in the polymer backbone of **1** by the  $\text{CH}_3\text{CO}_2^-$  addition. This conformational change in the polymer main chain was confirmed by a  $^1\text{H}$  NMR titration experiment as resulting from the complex formation between the amide receptor at the polymer side chain and the  $\text{CH}_3\text{CO}_2^-$ . Similarly, a change in the CD spectrum was also observed for  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{C}_6\text{H}_5\text{CO}_2^-$  and  $\text{N}_3^-$ . These results indicate that the polymer possesses a sufficient binding affinity toward these anions. In fact, the apparent anion-binding constant was significantly higher than that of the isolated amide group. This enhanced affinity is thought to result from the three-dimensional organization of multiple amide receptors along the polymer backbone. Hence, the results

clearly demonstrate the validity of the poly(phenylacetylene) backbone as a scaffold for arranging anion receptors even though a colorimetric response did not occur.

### POLYMERIC PROBE FOR COLORIMETRIC SENSING OF ANIONS

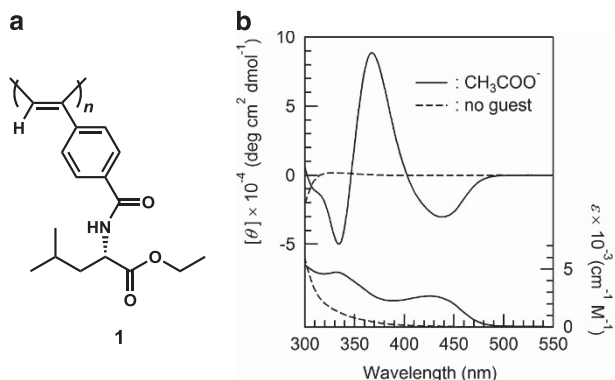
A number of polymer-based colorimetric probes for specific analytes have been designed and fabricated to produce reliable and practical analytical methods that can be applied to visual inspections.<sup>15–19</sup> This type of polymer sensor is generally realized by employing a conjugated polymer for which the colorimetric response is based on a change in the conjugation length of the polymer backbone. For instance, Marsella and Swager *et al.*<sup>27</sup> achieved colorimetric sensing of metal cations by using a  $\pi$ -conjugated polymer, that is, polythiophene consisting of bithiophene repeating units integrated into a crown ether. With the addition of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , the polymer exhibited clear bathochromic shifts depending on the cations, and the shift is considered to occur from the changes in the  $\pi$ -conjugation length via a twisting of the thiophene units triggered by the cation complexation event.

In another interesting example, Yashima *et al.*<sup>28,29</sup> revealed that poly(phenylacetylene) bearing  $\beta$ -cyclodextrin pendants exhibited a visible color change, as well as changes in the helical conformation in the main chain through a host–guest complexation. The polymer possessed a yellow–orange color resulting from the effective conjugation of the main chain and one-handed helical structure based on the chirality of the pendant  $\beta$ -cyclodextrin, which is a cyclic host molecule consisting of seven glucose units. When 1-adamantanol or (–)-borneol was added to the polymer solution, an immediate color change from yellow–orange to red was observed, which was accompanied by an inversion of the Cotton effect signs. This color change is thought to result from a structural change in the twist angle of the conjugated double bonds. In contrast, cyclooctanol and cyclohexanol produced neither a dramatic color change nor a CD inversion. Thus, both the color change and helix inversion events are suggested to be stimulated by the inclusion of guest molecules inside the cyclodextrin cavity.

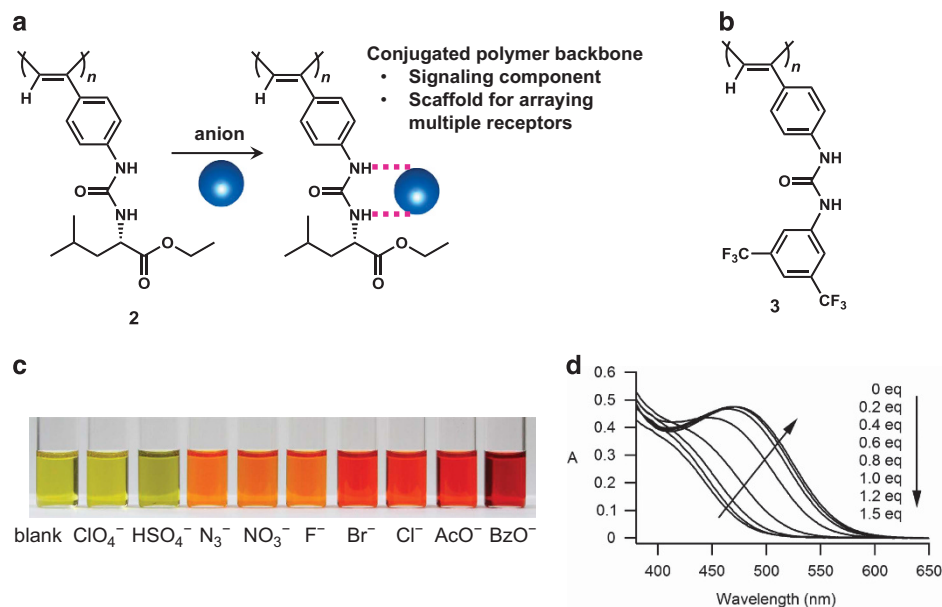
Despite the above sophisticated examples, a polymer-based colorimetric sensor for anions is still limited, probably because of a lack of progress in the field of anion recognition chemistry in comparison to other host–guest chemistries including that of cations.<sup>30–33</sup> To fabricate a polymer-based sensor for colorimetric anion detection, we synthesized poly(phenylacetylene)-bearing urea-binding sites derived from L-Leu (**2**) (Figure 2a).<sup>34</sup>

A tetrahydrofuran solution of the polymer exhibited a pale yellow color due to low absorption at  $\sim 400$  nm in the absorption spectrum. On the addition of the tetra-*n*-butylammonium salt of  $\text{CH}_3\text{CO}_2^-$ , the color of the polymer solution immediately turned red, indicating a colorimetric response capability of the polymer. In the ultraviolet–visible absorption spectrum, a significant bathochromic shift was observed in the absorption corresponding to the polymer backbone, and the wavelength of the maximum absorption ( $\lambda_{\text{max}}$ ) was almost 520 nm. Moreover, a large Cotton effect appeared in the CD spectrum along with the bathochromic shift. Hence, the observed color change is attributed to the extension of the main chain conjugation length, in which a conformational change in the polymer main chain triggered by the  $\text{CH}_3\text{CO}_2^-$  binding at the urea receptors is thought to have a crucial role.

As well as  $\text{CH}_3\text{CO}_2^-$ , other anions including  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{N}_3^-$  also produced distinctive changes in the absorption and CD spectra. It is important to note that the anion-triggered



**Figure 1** (a) The chemical structure of poly(phenylacetylene)s with amide receptors derived from L-leucine (**1**). (b) Circular dichroism (CD) and UV–vis absorption spectra of **1** in the absence and presence of  $\text{CH}_3\text{CO}_2^-$  in THF ([monomer units of **1**] = 3.5 mM, [anion]/[monomer units of **1**] = 10). THF, tetrahydrofuran; UV, ultraviolet; vis, visible.



**Figure 2** (a) A schematic illustration of anion recognition of poly(phenylacetylene)s with urea receptors derived from L-leucine (**2**). In this anion recognition event, the conjugated polymer backbone acts not only as a signaling component that allows a colorimetric response but also as a scaffold capable of arraying a number of receptor units along the backbone. (b) The chemical structure of poly(phenylacetylene) with urea-binding sites activated by two electron-withdrawing  $-\text{CF}_3$  substituents (**3**). (c) A photograph of the THF solutions of **3** in the presence of TBA salts of a series of anions ([monomer units of **3**] = 1.3 mM, [anion]/[monomer units of **3**] = 5.0). (d) Changes in the UV-vis absorption spectrum of **3** induced by the addition of  $\text{CH}_3\text{CO}_2^-$  in THF ([monomer units of **3**] = 130  $\mu\text{M}$ ). TBA, tetra-*n*-butylammonium; THF, tetrahydrofuran; UV, ultraviolet; vis, visible.

bathochromic shifts were highly dependent on the type of anion, thus enabling easy recognition of the anions, sometimes even visually. Although the complexation ability of an isolated urea receptor with an anionic species generally corresponds to the basicity of the anionic molecules,<sup>2</sup> the selectivity of the colorimetric response observed in this polymer is governed by the guest size, as well as the basicity, which is probably due to the spatial factor derived from the arrangement of multiple urea receptors along the polymer backbone.

To elucidate the importance of a three-dimensional organization of the urea groups, poly(phenylacetylene) hemi functionalized with urea-binding sites was synthesized by copolymerization; no color changes were observed with the addition of any of the anions. This indicated that a close arrangement of multiple urea receptors along with the polymer backbone was necessary for such a colorimetric response. Considering the observed brilliant colorimetric response dependent on the anion species and unique selectivity, the polymer clearly demonstrated the significance and value of fabricating a macromolecular receptor for colorimetric anion sensing.

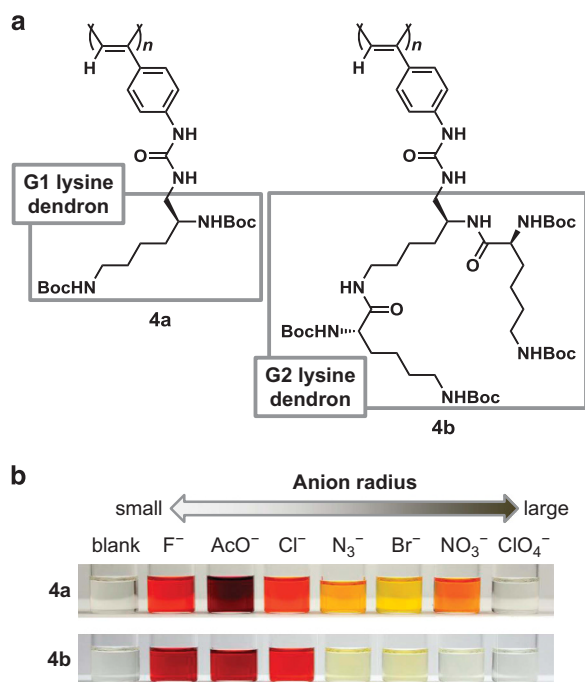
Similar to **2**, a series of poly(phenylacetylene) samples bearing urea functionalities derived from other amino acids, such as L-alanine (Ala), L-phenylalanine (Phe), L-isoleucine (Ile), L-glutamic acid (Glu) and L-aspartic acid (Asp), also exhibited CD and colorimetric responses to anions.<sup>35</sup> These results suggest that an anion-induced colorimetric response is universal for urea-functionalized poly(phenylacetylene)s. Although the color changes were nearly identical for all of the polymers, the CD spectral changes were strongly dependent on the amino acid structures at the pendant residues. For example, the signs of the first Cotton effect that appeared with the addition of  $\text{CH}_3\text{CO}_2^-$  were positive, positive, negative, positive, negative and negative for poly(phenylacetylene)s derived from L-Leu, L-Ala, L-Phe, L-Ile, L-Glu and L-Asp, respectively. Moreover, other anions produced different CD sign patterns, which may be a unique identifying characteristic. Thus, information about the color and CD

responses that are obtained from all of the above urea-functionalized poly(phenylacetylene)s could be applicable to a pattern recognition methodology that makes it possible to distinguish the anions.<sup>36–40</sup>

Although the above urea-functionalized poly(phenylacetylene)s are considered good candidates for use in colorimetric anion sensor applications, a more efficient and sensitive detection ability is required for practical use. To improve the anion-binding affinity, poly(phenylacetylene) polymers with [bis(trifluoromethyl)phenyl]urea pendants (**3**) were designed, and they have emerged as ideal candidates because the electron-withdrawing  $-\text{CF}_3$  substituents are expected to enhance the anion-binding abilities of the urea functionalities (Figure 2b).<sup>41</sup>

On the addition of  $\text{CH}_3\text{CO}_2^-$ ,  $\text{C}_6\text{H}_5\text{CO}_2^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{N}_3^-$  and  $\text{HSO}_4^-$ , **3** exhibited a color change depending on the type of anion, which is again visually recognizable (Figure 2c). To quantify the anion-binding ability of the polymer, an absorption titration experiment was conducted with varying amounts of anions (Figure 2d). The resulting titration curves displayed a sigmoidal curvature, particularly for  $\text{CH}_3\text{CO}_2^-$ ,  $\text{C}_6\text{H}_5\text{CO}_2^-$ ,  $\text{F}^-$  and  $\text{Cl}^-$ , indicative of a cooperative binding mode. Thus, this binding process was analyzed using the Hill equation, which is the optimal equation for determining both the binding constant and cooperativity in the case of a cooperative binding system. As a result, cooperative and positive homotropic allosteric binding was found to occur between the polymer and these four anions.<sup>42–46</sup> For this binding system, the partially formed urea/anion complex units in the polymer chain might produce a change in the entire main chain conformation that is favorable for further anion binding. Therefore, the incorporation of electron-withdrawing  $-\text{CF}_3$  groups results in significant enhancement of the binding ability without disturbing the color variation produced for different types of anions.

A rational design of the pendant structure also makes strict size selectivity possible. As already described, polymer **2** possessed a unique

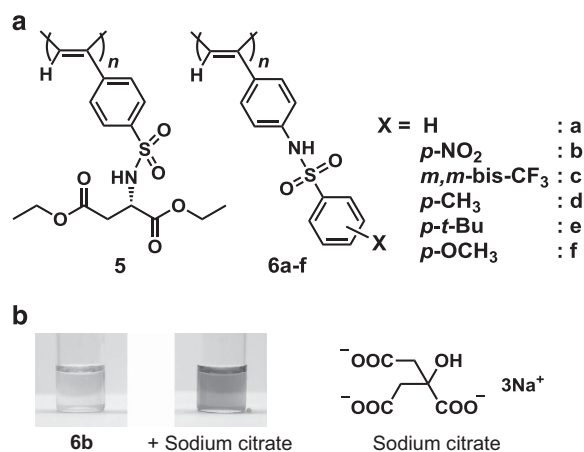


**Figure 3** (a) The chemical structures of poly(phenylacetylene)-bearing first (**4a**) and second (**4b**) generation lysine dendrons through the urea group. (b) Photographs of **4a** and **4b** in the presence of TBA salts of a series of anions in THF at 25 °C ([monomer units of **4a**] = [monomer units of **4b**] = 1.0 mM, [anion]/[monomer units of **4a**] = 10, [anion]/[monomer units of **4b**] = 20). TBA, tetra-*n*-butylammonium; THF, tetrahydrofuran.

selectivity in anion detection. Hence, the results inspired us to create a polymer-based anion sensor with stricter size specificity. For this purpose, we prepared poly(phenylacetylene)-bearing second-generation lysine dendrons through the urea groups (**4b**) in which the bulky G2 dendron was expected to influence the anion-binding event at the urea receptor unit (Figure 3a).<sup>47–56</sup>

The polymer showed an immediate colorimetric response with the addition of  $\text{CH}_3\text{CO}_2^-$ ,  $\text{F}^-$  and  $\text{Cl}^-$ , whereas the addition of  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{N}_3^-$  and  $\text{ClO}_4^-$  caused no essential color changes (Figure 3b).<sup>57</sup> This observed anion selectivity in the color change was different from the above urea-functionalized poly(phenylacetylene)s. Thus, we synthesized a control polymer with first-generation lysine dendrons (**4a**) to compare its anion detection ability to that of **4b**. As a consequence, the colorimetric response of **4a** was observed for  $\text{N}_3^-$ ,  $\text{NO}_3^-$  and  $\text{Br}^-$  as well as  $\text{CH}_3\text{CO}_2^-$ ,  $\text{F}^-$  and  $\text{Cl}^-$ . Given that the structural difference between **4a** and **4b** is only the generation of the lysine dendron, the selectivity of the colorimetric anion detection for these macromolecular receptors was demonstrated to be governed by the size of the pendant dendron. Presumably, for **4b**, the steric hindrance of the bulky G2 dendron might interrupt the interaction of the larger anions with the urea group and/or the complexation-triggered conformational change in the polymer chain, thus providing strict size specificity in the colorimetric anion detection.

As well as poly(phenylacetylene)-bearing urea receptors, sulfonamide-functionalized poly(phenylacetylene) (**5**) was useful for colorimetric anion sensing (Figure 4a).<sup>58</sup> The addition of  $\text{F}^-$  produced a significant bathochromic shift in the ultraviolet–visible absorption spectrum and also a color change from yellow to red. Similarly, a bathochromic shift was observed in the presence of  $\text{CH}_3\text{CO}_2^-$ , but the shift was lower than for  $\text{F}^-$ , thus producing an orange-colored



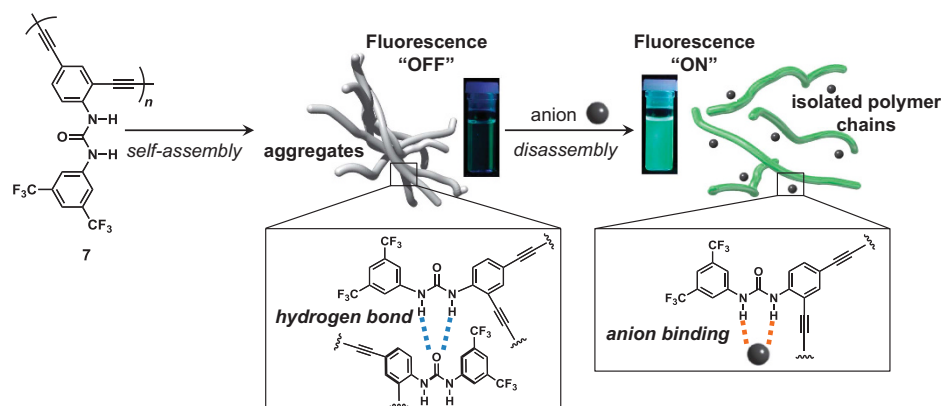
**Figure 4** (a) The chemical structures of sulfonamide-conjugated poly(phenylacetylene)s derived from L-aspartic acid (**5**) and with various electron-withdrawing and -donating substituents (**6a–f**). (b) Color changes in *N,N*-dimethylformamide (DMF)/ $\text{H}_2\text{O}$  (8/2, v/v) solutions of **6b** ( $1.0 \text{ mg ml}^{-1}$ ) obtained on the addition of 10 equiv. of sodium citrate. A full color version of this figure is available at *Polymer Journal* online.

solution. In contrast, other anions, including  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{N}_3^-$  and  $\text{ClO}_4^-$ , did not influence the absorption change. This selectivity in the colorimetric response is thought to be dictated by the basicity of the anions. Based on the NMR titration measurements, the deprotonation process is believed to have caused the sulfonamide–anion interaction, which is different from the binding mode between the urea receptor and the anion.<sup>59,60</sup> Other poly(phenylacetylene)s with sulfonamide receptors derived from various amino acids also showed similar colorimetric response abilities.<sup>61</sup>

Although the above polymers exhibited superior anion detection abilities for certain molecular designs, the colorimetric response is limited to organic solvents, which can be a problem. Generally, protic solvents, such as water, inhibit a hydrogen-bond interaction between the receptor and the anion. This is why direct sensing of anions in aqueous media is considered difficult.<sup>9</sup> However, we envisioned that employing a receptor unit that favors a deprotonation event rather than a hydrogen-bonding mechanism would overcome this setback. To develop a suitable probe that can operate in aqueous environments, we synthesized a series of sulfonamide-conjugated poly(phenylacetylene)s with various electron-withdrawing and -donating substituents (**6a–f**) (Figure 4a).<sup>62</sup> Among the sulfonamide-conjugated polymers, the poly(phenylacetylene) substituted with a nitro group (**6b**) exhibited obvious color changes in the presence of anions even in a solution containing up to 20% water, which even allowed the colorimetric detection of biologically important carboxylates, such as acetate, L-lactate, L-malate and citrate (Figure 4b).<sup>63</sup> In contrast, negative results were obtained for the rest of the polymers in the series. The positive results of **6b** can be attributed to the sample having the strongest electron-withdrawing nitro group, which enhanced the anion recognition ability.

#### POLYMERIC PROBE FOR FLUORESCENT SENSING OF ANIONS

One of the common goals in sensory materials is an increased sensitivity; therefore, much attention has focused on the development of a fluorescent chemosensor with increased sensitivity over a colorimetric one. Among a number of sophisticated designs for a fluorescent sensor, utilization of a conjugated polymer is a unique and rather practical approach for highly sensitive sensor fabrication.<sup>17</sup>



**Figure 5** Schematic illustration of fluorescence turn-on response of urea-functionalized poly(phenylenebutadiynylene) (**7**) triggered by anion recognition. The anion binding of the urea receptor produces disassembly of the polymer aggregate that was constructed by intermolecular hydrogen bonding between the urea units. Based on this disassembly process, the polymer recovers the original fluorescence emission that was quenched due to the aggregate formation.

This is because the conjugated polymer-based fluorescent sensor sometimes shows an amplified fluorescent response arising from the structural feature of the sensor polymer.<sup>64</sup> In this system, only a small fraction of complexed receptor sites is sufficient to cause a complete fluorescent response; this is in sharp contrast to a monomeric indicator in which every receptor must be occupied for a complete response. Therefore, this signal amplification phenomenon realized for fluorescent polymer sensors enables significantly enhanced sensitivity; for example, Swager *et al.*<sup>65,66</sup> reported that solid-state (thin film) fluorescent sensors made from a pentiptycene-derived phenyleneethynylene polymer caused fluorescence quenching on exposure to a trace amount of 2,4,6-trinitrotoluene vapor (10 p.p.b.).

To realize a simple and efficient anion-sensing approach,<sup>67–70</sup> we fabricated a fluorescent sensor based on urea-functionalized poly(phenylenebutadiynylene) (**7**). It consisted of a conjugated polymer backbone capable of bright fluorescence and multiple pendant urea-binding sites with strong anion-binding affinity activated by two -CF<sub>3</sub> substituents (Figure 5).<sup>71</sup> The polymer itself exhibited an extremely weak fluorescent emission, which was visually undetectable. In sharp contrast, a strong and red-shifted fluorescence was observed with the addition of F<sup>-</sup>, and the increase in intensity was >10-fold. Thus, the polymer possessed a fluorescence turn-on response to F<sup>-</sup>.<sup>72–75</sup>

To explain this fluorescence turn-on response, a dynamic light scattering measurement of the polymer was performed. In the absence of F<sup>-</sup>, polymer **7** formed aggregates through the intermolecular hydrogen bonds between urea units, while no aggregates were detected in the dynamic light scattering measurement of **7** after the addition of F<sup>-</sup>. This indicates that the F<sup>-</sup> addition triggered the collapse of the self-assembly of **7**, in which the binding mode at the urea functional sites probably changed from the intermolecular hydrogen-bonding interaction between the urea units to the urea/F<sup>-</sup> complex formation.<sup>76–78</sup>

To provide insight into the relationship between the disassembly of aggregates and the fluorescence turn-on phenomenon, a fluorescence decay measurement was performed using a time-correlated single-photon counting technique. Based on this result, the polymer was determined to emit almost no fluorescence before the addition of F<sup>-</sup> because the fluorescence quenching occurred due to the aggregate formation. Moreover, the isolated polymer chain resulted from the F<sup>-</sup>-induced disassembly of the aggregates was shown to recover the original fluorescence emission (Figure 5).

This fluorescence turn-on response was observed for other anions such as CH<sub>3</sub>CO<sub>2</sub><sup>-</sup>, C<sub>6</sub>H<sub>5</sub>CO<sub>2</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and N<sub>3</sub><sup>-</sup>. Because the color and brightness of the fluorescent emission depends on the type of anion, a rough discrimination of the anions might be visually possible. The detection limit of the polymer for F<sup>-</sup> was determined to be <5 μM. This detection sensitivity is 10 times greater than that of the colorimetric anion sensors that were previously mentioned. The improvement of the detection sensitivity could be due to the employment of the fluorescent conjugated polymer as a signaling unit. Because the mechanism of the fluorescence detection is based on a disassembly event of the polymer aggregates, the fluorescent response is not immediate. Although this is a weak argument for practical use, the demonstration would provide useful insight for the fabrication of more suitable fluorescence turn-on probes for anion detection with sufficient response speeds.

## CONCLUSIONS

This focused review has provided an overview of conjugated polymer-based anion sensors that we recently investigated. Both the colorimetric and fluorescent anion-sensing methods have been demonstrated by employing conjugated polymers functionalized with suitable anion-binding sites. The conjugated polymer backbone has been shown not only as a signaling component that allows a colorimetric and fluorescent response but also as a scaffold capable of arraying a number of receptor units along the backbone; this is important for enhancing the anion recognition abilities. Another important finding is that the binding affinity and specificity arising from polymeric structures have been observed, thus expanding the present limits in anion recognition chemistry. These results clearly show that a conjugated polymer-based sensor has some advantages not yet seen in small molecular systems. Thus, these demonstrations would provide useful insight into molecular design for the realization of more sophisticated and reliable optical anion sensors.

## CONFLICT OF INTEREST

The author declares no conflict of interest.

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Dr Ryosuke Sakai was born in Hokkaido, Japan in 1979. He received his PhD from Hokkaido University in 2006 under the supervision of Professor Toyoji Kakuchi. After he worked with Professor Craig J Hawker at the University of California, Santa Barbara as a JSPS postdoctoral fellow (2007–2008), he joined the Graduate School of Engineering, Hokkaido University in 2008 as an assistant professor. He is currently an associate professor of the Department of Materials Chemistry, the National Institute of Technology, Asahikawa College. He received the Inoue Research Award for Young Scientists from Inoue Foundation for Science (2007) and the Award for Encouragement of Research in Polymer Science from The Society of Polymer Science, Japan (2014).