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Novel Polyphenylenes Containing Phenol-Substituted Oxadiazole Moieties as Fluorescent Chemosensors for Fluoride Ion

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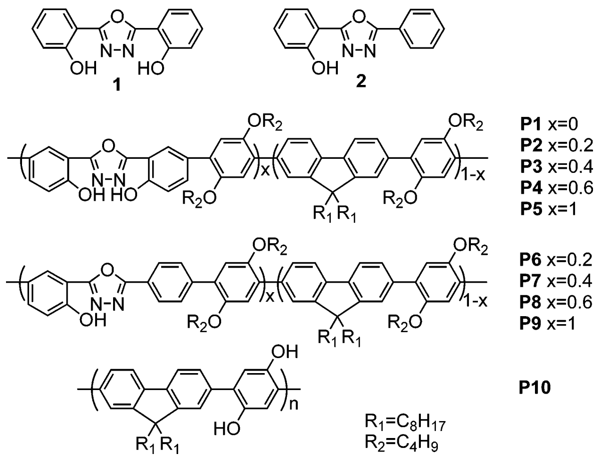
ABSTRACT: Novel phenyl-based conjugated polymers with different content of 2,5-bis(2-hydroxyphenyl)-1,3,4-oxadiazole (**1**) or 2-(2-hydroxyphenyl)-5-phenyl-1,3,4-oxadiazole (**2**) units in the main chain were synthesized through Suzuki coupling. The measurements of sensing behavior to various anions, i.e., F^-, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, and $H_2PO_4^-$, reveal that the polymers are highly sensitive and selective F^- sensory materials, and the sensitivity is much higher than that of small molecules **1** and **2**. The best performance was observed with polymer **P3** containing 40 mol % oxadiazole unit **1**. A 380-fold fluorescence quenching occurred upon adding F^- into **P3** chloroform solution, with only 6-fold reduction of emission by using $H_2PO_4^-$ instead. Addition of other anions caused almost no change in emission spectra. The sensitivity of the polymers to F^- decreases with increasing solvent polarity. Like molecules **1** and **2**, these polymers can also be used as colorimetric sensors for F^- and $H_2PO_4^-$.

Introduction

Fluorescent conjugated polymers (CPs) have been widely explored as highly sensitive chemosensors.[1−3] A key advantage of sensors based on CPs over those using small molecules[4−7] is that the former ones exhibit transport collective properties and are very sensitive to minor perturbations. In CP-based sensors, only fractional binding of analyte can cause an amplified signal due to delocalization of exciton along the conjugated chain. Poly(*p*-phenylene)s,[8] poly(*p*-phenylene ethynylene)s,[9] poly(*p*-phenylene vinylene)s,[10] polythiophenes,[11] polyfluorenes[12] with receptor groups, e.g., crown ethers,[13] pyridine derivatives,[14] and ionic groups[15] in the side chain or main chain have been successfully used for sensing ions and biological species. Anion sensing is one of current research interest in chemosensors because of their importance in biological monitoring and environmental assays. However, while many fluorescent conjugated polymers for sensing metal ions were demonstrated,[16−19] few examples have been reported for sensing anions.[8,20] Among all anion sensors, those for fluoride ion are of particular importance in revealing a number of biological processes, disease states, and environmental pollutions.[21] Several approaches have been developed based on small molecules for sensing fluoride ion.[22−28] Recently, we reported two organic small molecules, **1** and **2** (Chart 1), as fluorescent chemosensors for phosphate and fluoride ions based on hydrogen-bonding and electrostatic interactions between receptors and analytes.[29] Both **1** and **2** show high phosphate/chloride and fluoride/chloride selectivity. In particular, compound **1** can even distinguish phosphate from fluoride. Herein, we designed and synthesized novel conjugated polymers with **1** or **2** units in the main chain for combining their selectivity with high sensitivity of polymeric systems.

Chart 1



Results and Discussion

Synthesis and Structure Characterization. Structures of polymers in current work are depicted in Chart 1. They were synthesized following Scheme 1. Monomers **3** and **4**, which include one and two methoxyl groups, respectively, were synthesized from commercially available starting materials. Their copolymerization with 1,4-diborate-2,5-dibutoxybenzene and 2,7-dibromo-9,9-dioctylfluorene through Suzuki coupling[30] followed with demethylation[31] afforded target polymers **P1−P10**. The feed ratio of comonomers was adjusted to control the content of oxadiazole moieties in the polymers. The structures of polymers were verified with ^1H NMR, FTIR, GPC, and elemental analysis. The actual content of the oxadiazole moiety was calculated from the integration of the peaks at $\delta = 8.30$ and 3.88−4.01 ppm in ^1H NMR spectra of the polymers, which are attributed to the *o*-phenyl proton at the oxadiazole unit and the methylene proton close to the oxygen atom in the dibutoxybenzene unit, respectively. As seen in Table 1, the actual composition of the copolymers is almost consistent with the feed ratio. Molecular weight and polydispersity of polymers before demethylation are listed in Table 1. The complete demethylation of the polymers was confirmed by the appearance of a ^1H NMR signal at 10.2 ppm and an IR peak at 3259 cm^{-1}, characteristics of a phenol group, and the disappearance

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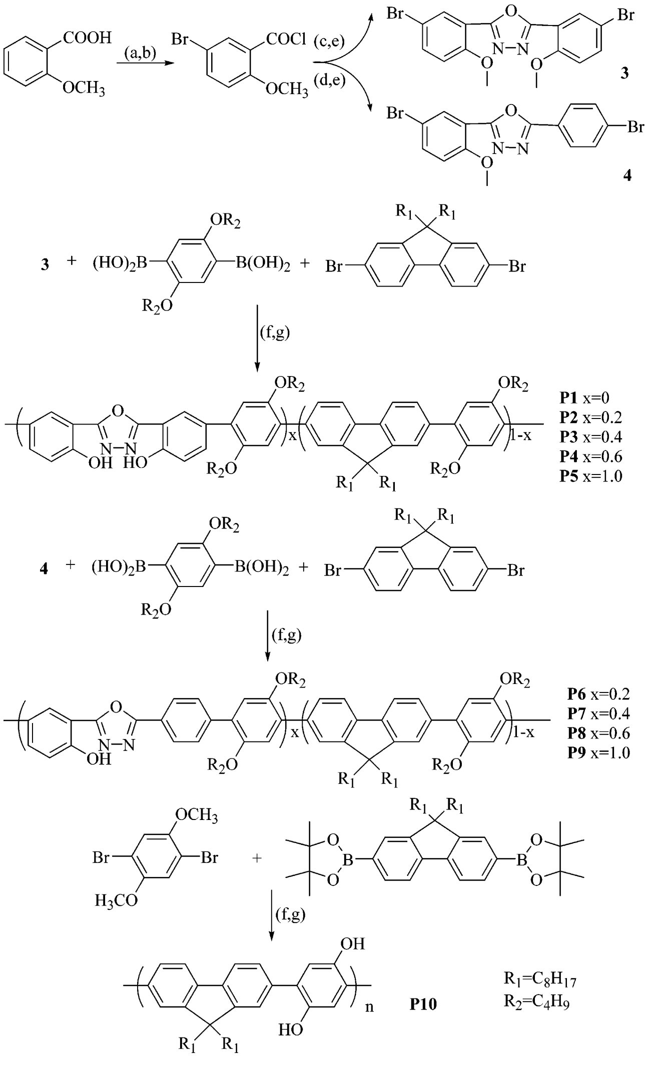
Scheme 1. Synthesis of Polymers P1−P10[a]



[a] (a) Br_2, CH_3COOH, dark, 0 °C, 10 h; (b) $SOCl_2$, 60 °C, 4 h; (c) NH_2NH_2HCl, Et_3N, $CHCl_3$, 70 °C, 12 h; (d) *p*-BrPh-$COONHNH_2$, Et_3N, $CHCl_3$, 70 °C, 12 h; (e) $POCl_3$, 80 °C, 5 h; (f) $Pd(PPh_3)_4$, K_2CO_3, THF/H_2O, 80 °C, 72 h; (g) CH_2Cl_2, BBr_3, −78 °C, 24 h.

Table 1. Weight-Average Molecular Weight (M_w), Polydispersity (PDI), UV−Vis Absorption/Fluorescence Maximum, and Photoluminescence Quantum Yield in Chloroform Solution with Concentration of 5×10^{-6} M (Repeat Unit)

polymer	X_f[a]	X_c[b]	M_w[c]	PDI[c]	$\lambda_{max,abs}$ (nm)	$\lambda_{max,PL}$ (nm)	Φ_{PL}[d]
P1	0.00	0.00	34 010	1.51	372	416, 440 (sh[e])	0.74
P2	0.20	0.20	40 823	1.76	300, 355	417	0.44
P3	0.40	0.39	43 521	1.93	298, 353	398, 422 (sh[e])	0.23
P4	0.60	0.58	8 502	1.37	296, 349	440	0.09
P5	1.00	1.00	13 100	1.42	294	423	0.01
P6	0.20	0.21	41 198	1.56	299, 356	417	0.37
P7	0.40	0.39	35 281	1.53	296, 351	434	0.20
P8	0.60	0.55	11 569	1.73	295, 350	427	0.05
P9	1.00	1.00	13 480	1.58	295	425	0.01
P10			15 521	1.37	356	418, 436 (sh[e])	0.17

[a] The feed ratio of oxadiazole units. [b] The content of oxadiazole units as calculated from ^{1}H NMR spectra. [c] The values measured before demethylation with GPC using polystyrene as standard. [d] Solution fluorescence quantum yield measured relative to 9,10-diphenylanthracene (10^{-5} M).[32] [e] Shoulder peak.

Table 2. Stern−Volmer Constants (K_{sv}) Value of Polymers for Different Anions[a]

polymer	$K_{sv}[F^-]$[a]	$K_{sv}[H_2PO_4^-]$	$K_{sv}[Cl^-]$
P2	4.25×10^5	3.71×10^4	$<1 \times 10^3$
P3	7.11×10^5	9.58×10^4	$<1 \times 10^3$
P4	1.78×10^5	9.97×10^3	$<1 \times 10^3$
P6	2.49×10^5	7.61×10^4	$<1 \times 10^3$
P7	3.57×10^5	1.71×10^5	$<1 \times 10^3$
P8	6.25×10^4	1.74×10^4	$<1 \times 10^3$

[a] All errors are ±15%. Anions used in this assay were in the form of their tetrabutylammonium salts.

of the proton signal of methoxyl groups in ^{1}H NMR spectra at 4.1 ppm. All polymers have good solubility in common organic solvents, such as chloroform ($CHCl_3$) and tetrahydrofuran (THF).

Optical Properties. Absorption and fluorescence spectra of all polymers have the similar features with maximum various in the range of 349−356 and 398−440 nm, respectively, depending on the content of oxadiazole moieties (as seen in the Supporting Information). In contrast to model compounds **1** and **2** in which long wavelength emission attributed to excited-state intramolecular proton transfer (ESIPT) was observed,[29] all polymers exhibit a featureless emission band independent of excitation wavelength from conjugated backbone, The absence of ESIPT emission in polymers is probably due to different excited-state structure of polymers from those of compounds **1** and **2**. The photoluminescence quantum yield is greatly affected by the content of oxadiazole moieties and decreases from 0.74 for **P1** to 0.01 for **P5** and **P9** (Table 1). The decreased quantum yield with the increasing oxadiazole content is probably due to low photoluminescence quantum yield of **1** and **2**, as reported by Doroshenko et al.[33] Moreover, the photoluminescence quantum yield of the polymers is weakly solvent dependent; for example, that of **P3** in methylene chloride, chloroform, ethyl acetate, THF, and DMF is 0.28, 0.23, 0.20, 0.19, and 0.13, respectively. The measurements of sensing properties were concentrated on **P2**−**P4** and **P6**−**P8** in the following sections because of very low photoluminescence quantum yield of **P5** and **P9** and the absence of oxadiazole moieties in **P1**.

Sensing Properties. The sensing capability of **P2**−**P4** and **P6**−**P8** to different anions was characterized in 5 μM chloroform solutions. The Stern−Volmer constants (K_{sv}) for F^-, $H_2PO_4^-$, and Cl^- are listed in Table 2. All polymers show the lowest K_{sv} for Cl^- owing to their weak hydrogen-bond-forming ability. In contrast to compounds **1** and **2**,[29] all these polymers show higher K_{sv} for F^- than that for $H_2PO_4^-$. Furthermore, polymers **P2**−**P4** with units **1** have higher K_{sv} for F^- and lower K_{sv} for $H_2PO_4^-$, respectively, compared with **P6**−**P8**. The K_{sv} value for both F^- and $H_2PO_4^-$ increased from **P2** and **P6** to **P3** and **P7** and then decreased with further increasing oxadiazole moieties. The increased sensitivity at low content of oxadiazole moieties is due to the increased number of binding site.[34] The decreased sensitivity at high content of oxadiazole moieties is probably attributed to the lower quantum yield of the polymers along with their lower molecular weight.

Figure 1 reveals fluorescence emission response profiles of polymers **P2**−**P4** and **P6**−**P8** upon addition of different anions with the concentration of 10^{-3} M. While almost no emission quenching is observed upon addition of Cl^-, Br^-, I^-, BF_4^-, and PF_6^-, all these polymers are active to F^- and $H_2PO_4^-$ and have the highest sensitivity to F^-. Polymers **P2**−**P4**, which have two phenol groups in each oxadiazole unit, exhibit higher sensitivity to F^- and lower sensitivity to $H_2PO_4^-$, respectively,

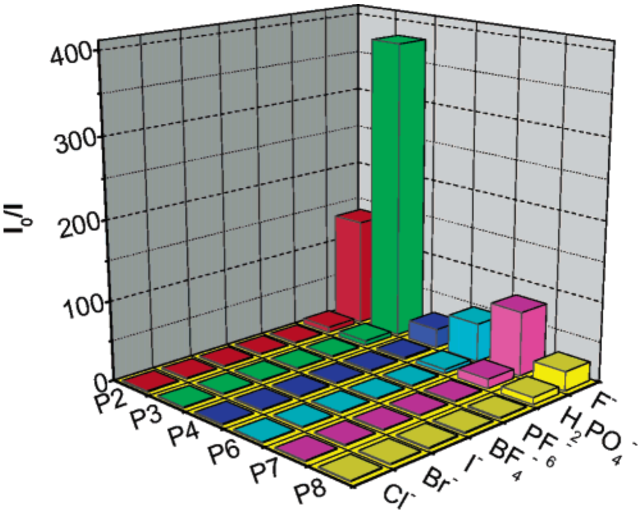


Figure 1. Fluorescence emission response profiles of polymers **P2**−**P4** and **P6**−**P8** upon addition of various anions.

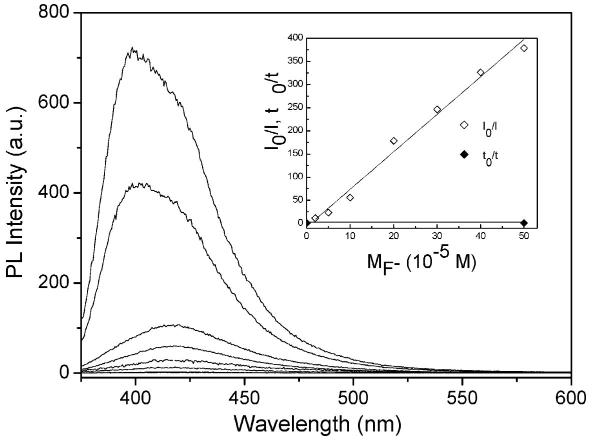


Figure 2. Fluorescence spectra of **P3** (5 μM) in chloroform upon titration with F^-. The Stern−Volmer plots are shown as inset, and the plots show τ_0/τ independent of F^- concentration.

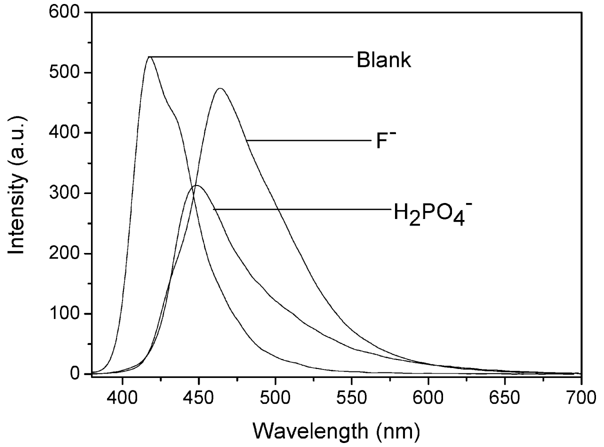


Figure 3. Fluorescence spectra of **P10** upon addition of F^- and $H_2PO_4^-$.

compared with **P6**−**P8** with one phenol group in each oxadiazole unit. The best performance was observed with **P3** containing 40 mol % oxadiazole unit. In particular, the strongest emission quenching with addition of F^- accompanied by low sensitivity to $H_2PO_4^-$ indicates **P3** is a highly sensitive and selective F^- sensory material. The dependence of quenching effect on the content of oxadiazole moieties is in the same trend with that of K_{sv}.

Figure 2 displays the fluorescence spectra upon titration of polymer **P3** (5 μM in $CHCl_3$) with F^-. Upon addition of F^-, emission intensity decreased dramatically with an emission red shift up to 15 nm and fluorescence quenching up to 380-fold. In contrast, only around 3-fold reduction of emission intensity was observed for compound **1**.[29] The much higher sensitivity of **P3** than that of compound **1** is consistent with amplification effect of conjugated polymers. As shown in the inset of Figure 2, polymer **P3** displays a linear Stern−Volmer relationship with the addition of F^-. Additionally, the lifetime of **P3** is almost independent of F^- concentrations. With F^- concentration of 0, 10^{-5}, and 10^{-3} M, it is 0.16, 0.14, and 0.15 ns, respectively. The association constant K_a determined to be 6.09×10^5 M^{-1} is close to K_{sv} (7.11×10^5). These indicate that a static quenching process instead of a dynamic quenching process is dominant in this polymer chemosensor.[35,36] Titration of **P3** with other halide ions and BF_4^-, PF_6^- did not cause obvious change of fluorescence spectra, and the addition of $H_2PO_4^-$ only led to a 6-fold reduction in emission intensity, indicating that **P3** has very high selectivity and sensitivity to F^- over other anions. The fact that **P3** shows the most efficient fluorescence quenching and highest binding affinity to fluoride ion than other anions is actually not surprising because of the smaller size, higher charge density, and higher electron affinity of F^-,[37] which enables it to be a strong hydrogen-bonding acceptor and be able to easily interact with phenolic group, OH.[38]

The anion-binding properties of **P7** in $CHCl_3$ are similar to those of **P3**. An over 80-fold quenching is observed upon addition of 10^{-3} M F^- while other halide brings almost no change of the emission intensity. The significantly different sensitivity between **P3** and **P7** for F^- is due to the different number of receptor in each repeat unit. Notably, it demonstrated a selective 11-fold quenching upon addition of excess $H_2PO_4^-$, exhibiting different behavior from polymer **P3**.

From above discussion, unlike compounds **1** and **2**, which have higher selectivity to phosphate ion, polymers **P2**−**P4** and **P6**−**P8** have much higher selectivity to fluoride ion over phosphate ion. This difference can be explained as follows: It is well-known that polymer chain can form a coil in solution depending on the surrounding environment.[39] Consequently, it will be much more difficult for large anions such as $H_2PO_4^-$ to access the hydroxyl group than a smaller anion F^- because of steric hindrance. For small molecules like **1** and **2**, this concept is not applicable, and both F^- and $H_2PO_4^-$ ions can access the hydroxyl group easily. On the other hand, from a previous report, compound **1** can form a stable dimer with $H_2PO_4^-$ through two hydrogen bonds to efficiently quench the emission.[29] Therefore, polymers **P6**−**P8** have a higher sensitivity to phosphate ion than **P2**−**P4**, as revealed in Table 2 and Figure 1.

The hydrogen-bonding ability of both receptor and analyte molecules is one of the main factors affecting sensing behavior of materials.[24−27,40] To evaluate the importance of oxadiazole group, we also synthesized **P10** without oxadiazole moieties for comparison. Below 1-fold fluorescence quenching along with 50−70 nm red shift for both F^- and $H_2PO_4^-$ was observed (Figure 3). It is believed that electron-withdrawing effects will render the phenolic proton more acidic and lead to higher anion binding affinities.[27] This indicates that oxadiazole moi-

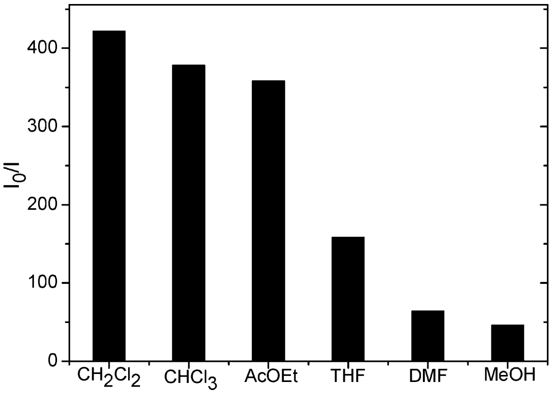


Figure 4. Fluorescence emission response profiles of **P3** in different solvents.

eties are crucial in current system for achieving high sensitivity.

It is well-known that intramolecular charge transfer (ICT) can cause a bathochromic shift of the emission with increasing solvent polarity.[41] The presence of ICT in current polymers is confirmed by the red-shifted photoluminescence with increasing solvent polarity, as seen in the Supporting Information. Our studies also show that solvent properties can greatly change the nature of the quenching effects.[42] In the current system, the sensitivity of the polymers to F^- decreases with increased solvent polarity. As an example shown in Figure 4, polymer **P3** exhibits the highest sensitivity to F^- in methylene chloride. Upon addition of F^- with the concentration of 10^{-3} M, a 430-fold emission quenching was observed in methylene chloride, while the emission in methanol was only quenched 50 times. This difference should be attributed to the different conformations of polymer chains in different solvents and the solvent polarity related charge-transfer interaction.[40] Moreover, in protonic solvents, hydrogen-bonding interactions between binding site and analyte are greatly influenced by the competition between the solvent molecules and fluoride ion.[26] The aggregation of the polymer in DMF and methanol is probably another factor to reduce the sensitivity, as revealed by the low photoluminescence quantum yield of **P3** in DMF (0.13) and its poor solubility in methanol. The sensitivity of **P3** to $H_2PO_4^-$ slightly decreased with increasing solvent polarity. A 3.3-fold emission quenching was observed in DMF, corresponding to 6.8-fold quenching in methylene chloride.

Similar to model compounds **1** and **2**, polymers **P2**–**P4** and **P6**–**P8** can also be used as colorimetric chemosensors.[6] Figure 5 shows a photograph of chloroform solutions of polymer **P3** (5 μM) containing excess amount (10^{-3} M) of certain anions (Cl^-, Br^-, I^-, BF_4^-, PF_6^-, $H_2PO_4^-$, and F^-). The solutions remain colorless upon addition of all the above anions, except for F^- and $H_2PO_4^-$, whereby the solutions turn dark-brown and yellowish, respectively. These color changes are caused by the changes of absorption spectra as revealed in Figure 6. Addition of Cl^- into the solution of **P3** caused almost no changes of absorption spectra. While F^- and $H_2PO_4^-$ were added, a long-wavelength absorption band around 462 nm appeared along with a reduction of the main absorption band around 375 nm. These absorption changes indicate the appearance of the hydrogen-bonding complex[26] and originated from that enhanced electron cloud density on phenol oxygen, which strengthens the intramolecular charge transfer (ICT) effect between the 1,3,4-oxadiazole electron-withdrawing group and the OH electron-donating group.[26,38,43,44]

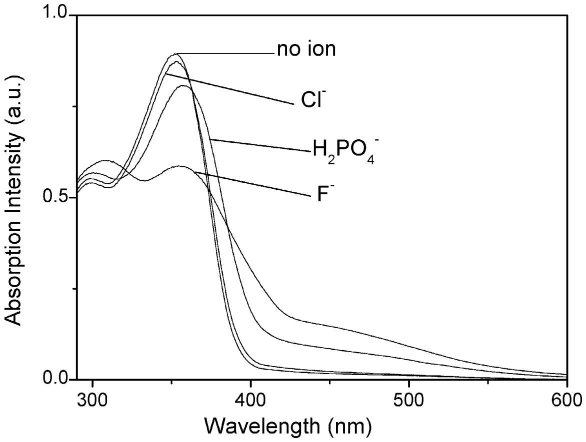


Figure 6. Absorption spectra of **P3** (5 μM) in chloroform upon addition of anions with the concentration of 10^{-4} M.

Conclusion

Novel conjugated polymers with oxadiazole units carrying phenol groups in the main chain as both colorimetric and fluorescent chemosensors for fluoride ion have been designed and synthesized. Key observations are recapitulated as follows:

(1) All polymers are active to F^- and $H_2PO_4^-$ with much higher sensitivity to F^-, while almost no change of emission upon adding anions Cl^-, Br^-, I^-, BF_4^-, and PF_6^- is observed. Polymers containing oxadiazole units

Figure 5. Color changes of **P3** (5 μM) in chloroform upon addition of no anion, Cl^-, Br^-, I^-, BF_4^-, PF_6^-, $H_2PO_4^-$, and F^- (from left to right) with the concentration of 10^{-4} M.

with two phenol groups, i.e., **P2**−**P4**, have higher sensitivity to F^- and lower sensitivity to $H_2PO_4^-$, respectively, than **P6**−**P8**, which contain oxadiazole units with only one phenol group.

(2) The polymer with optimized content of 2,5-bis(2-hydroxyphenyl)-1,3,4-oxadiazole (**1**), i.e., **P3** with 40 mol % oxadiazole unit, exhibits the best performance as a fluoride ion sensor. A 380-fold fluorescence quenching occurred upon adding F^- into **P3** chloroform solution while $H_2PO_4^-$ could only cause 6-fold reduction.

(3) The sensitivity of the polymers to F^- decreases with increasing solvent polarity. The polymer **P3** shows the highest sensitivity in methylene chloride and lowest sensitivity in methanol with 430-fold and 50-fold fluorescence quenching, respectively.

(4) The polymers can also be used as colorimetric sensors to F^- and $H_2PO_4^-$ without response to other anions.

Experimental Section

Material Synthesis. All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to standard procedures. All chemical reactions were carried out under an inert atmosphere. Intermediates 2,7-dibromo-9,9-dioctyl-9*H*-fluorene and 1,4-diborate-2,5-dibutoxybenzene were synthesized as previously described.[30]

4-Bromo-2-methoxybenzoic Acid. Into a solution of 2-methoxybenzoic acid (15.2 g, 0.10 mol) in 100 mL of acetic acid was slowly added bromine (24 g, 0.15 mol) in 50 mL of acetic acid. After 10 h, the mixture was poured into 300 mL of water. The precipitate was filtered and recrystallized from ethanol to give the product as a white crystal (21.2 g, 92%). ^1H NMR ($CDCl_3$) δ (ppm): 11.29 (s, 1H), 8.30 (s, 1H), 7.91 (d, 1H), 6.99 (d, 1H), 4.09 (s, 3H).

5-Bromo-2-methoxybenzoyl Chloride. A mixture of 4-bromo-2-methoxybenzoic acid (23 g, 0.10 mol) and thionyl chloride (100 mL) was refluxed for 5 h. Excess thionyl chloride was removed by distillation under vacuum. The residue was recrystallized from hexane to give the product as a white needlelike crystal (18.8 g, 76%). ^1H NMR ($CDCl_3$) δ (ppm): 8.17 (s, 1H), 7.66 (d, 1H), 6.90 (d, 1H), 3.92 (s, 3H).

1,2-Bis(5-bromo-2-methoxy)benzoylhydrazine. Into a mixture of hydrazine hydrochloride (3.4 g, 0.49 mol), triethylamine (20 mL), and chloroform (80 mL) was slowly added 5-bromo-2-methoxybenzoyl chloride (12.4 g, 0.10 mol) in 50 mL of chloroform. The mixture had been refluxed for 10 h before filtration. The solid was washed with methanol three times and recrystallized from ethanol to afford the product (5.6 g, 53%). ^1H NMR ($CDCl_3$) δ (ppm): 8.15 (s, 2H), 7.61 (d, 2H), 6.99 (d, 1H), 3.95 (s, 6H).

1-(5-Bromo-2-methoxy)benzoyl-2-(4-bromobenzoyl)hydrazine. Into a solution of 4-bromobenzoic acid hydrazide (10.7 g, 0.05 mol), triethylamine (20 mL), and chloroform (80 mL) was slowly added 5-bromo-2-methoxybenzoyl chloride (6.2 g, 0.05 mol) in 50 mL of chloroform. The mixture had been refluxed for 10 h before filtration. The solid was washed with methanol three times and recrystallized from ethanol to afford the product (7.0 g, 61%). ^1H NMR ($CDCl_3$) δ (ppm): 8.14 (s, 1H), 8.00 (d, 2H), 7.81 (d, 2H), 7.71 (d, 1H), 6.99 (d, 1H), 3.94 (s, 3H).

2,5-Bis(5-bromo-2-methoxyphenyl)-[1,3,4]oxadiazole (3). A mixture of 1,2-bis(5-bromo-2-methoxy)benzoylhydrazine (9.2 g, 0.02 mol) and 30 mL of phosphorus oxychloride was refluxed for 6 h. Excess phosphorus oxychloride was removed, and the residue was recrystallized from ethanol/chloroform to give pure product as a white crystal (6.4 g, 74%). ^1H NMR ($CDCl_3$) δ (ppm): 8.13 (s, 2H), 7.61 (d, 2H), 6.97 (d, 2H), 4.00 (s, 6H).

2-(5-Bromo-2-methoxyphenyl)-5-(4-bromophenyl)-[1,3,4]-oxadiazole (4). A mixture of 1-(5-bromo-2-methoxy)benzoyl-2-(4-bromobenzoyl)hydrazine (8.6 g, 0.02 mol) and 30 mL of phosphorus oxychloride was refluxed for 6 h. Excess phosphorus oxychloride was removed, and the residue was recrystallized from ethanol/chloroform to give pure product as white crystal (5.6, 68%). ^1H NMR ($CDCl_3$) δ (ppm): 8.11 (s, 1H), 7.96 (d, 2H), 7.79 (d, 2H), 7.61 (d, 1H), 7.02 (d, 1H), 3.96 (s, 3H).

General Procedure of Polymerization with P3 as an Example. To a flask containing 2,7-dibromo-9,9-dioctylfluorene (0.164 g, 0.300 mmol), 1,4-diborate-2,5-dibutoxybenzene (0.155 g, 0.500 mmol), 2,5-bis(5-bromo-2-methoxyphenyl)-[1,3,4]oxadiazole (0.0881 g, 0.200 mmol), and tetrakis(triphenylphosphine)palladium(0) (20 mg) was added 3 mL of 2 M aqueous potassium carbonate and 4 mL of tetrahydrofuran under argon. The mixture was stirred at 80 °C for 72 h. The mixture was then poured into methanol. The precipitate was collected by filtration, dried, and then dissolved in dichloromethane. The solution was washed with water and dried over anhydrous Na_2SO_4. After removing most of the solvent, the residue was poured into methanol to give fiberlike polymer. The polymer was further purified by a Soxhlet extraction in acetone for 24 h. The reprecipitation procedure in dichloromethane/methanol was then repeated for several times. The final product, a light-yellow fiber, was obtained after drying in a vacuum with a yield of 0.136 g (48%). ^1H NMR ($CDCl_3$) δ (ppm): 8.31−3.93 (m, Ar−H), 4.15 (s, OCH_3), 4.05−3.97 (m, OCH_2), 2.03−1.10 (m, CH_2), 0.99−0.79 (m, CH_3). IR (CaF_2), cm^{-1}: 2957 (sh), 2928 (s), 2856 (m), 1612 (w), 1511 (w), 1463 (s), 1379 (m), 1259 (sh), 1205 (m), 1069 (m), 1027 (m), 979 (w), 869 (w), 822 (w), 757 (w). Anal. Calcd for $C_{189}H_{246}N_4O_{16}$: C, 80.25; H, 8.70; N, 1.98. Found: C, 80.50; H, 8.39; N, 1.53.

General Procedure of Demethylation with P3 as an Example. Into a mixture of 0.101 g of polymer and 30 mL of dichloromethane was dropwise added boron tribromide at −78 °C. The mixture was allowed to warm to room temperature and stirred for one more day and then poured into 100 mL of water. The mixture was extracted with dichloromethane (3 × 100 mL). The dichloromethane extracts were combined, washed with brine, and dried over anhydrous Na_2SO_4. After the solvent was evaporated to around 5 mL, the residue was poured into hexane to give the product (0.0413 g, 40%) as an orange powder. ^1H NMR ($CDCl_3$) δ (ppm): 10.01 (s, OH), 8.31−3.93 (m, Ar−H), 4.05−3.97 (m, OCH_2), 2.03−1.10 (m, CH_2), 0.99−0.79 (m, CH_3). IR (CaF_2), cm^{-1}: 3560 (w), 3259 (br), 2957 (m), 2928 (s), 1628 (w), 1591 (w), 1540 (w), 1495 (w), 1464 (s), 1270 (m), 1233 (m), 1199 (m), 1065 (w), 1025 (w), 823 (w), 734 (w). Anal. Calcd for $C_{185}H_{238}N_4O_{16}$: C, 80.14; H, 8.59; N, 2.02. Found: C, 80.47; H, 8.43; N, 1.61.

Characterizations and Measurements. ^1H NMR spectra were collected using Varian HG-300 (300 MHz) or HG-400 (400 MHz) spectrometer with chloroform-*d* as solvent and tetramethylsilane as the internal standard. The elemental analysis was performed on a Bio-Rad elemental analysis system. Gel permeation chromatography (GPC) analysis was conducted on a Waters 510 system using polystyrene as standard and THF as eluent. IR spectra were obtained on Bio-Rad FTS 135 spectrometer by dispersing samples in KBr matrix. Fluorescence spectra were obtained on a Perkin-Elmer LS 50B luminescence spectrometer with xenon discharge lamp excitation. UV/vis measurements were carried out on a Perkin-Elmer Lambda 35 UV/vis spectrophotometer. Fluorescence lifetimes were obtained on FL920 fluorescence lifetime spectrometer with a nF900 flash lamp (Edinburgh Instruments).

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Supporting Information Available: Detailed UV−vis absorption and photoluminescence spectra in dilute solution upon titration. This material is available free of charge via the Internet at http://pubs.acs.org.

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