Perylenebisimide-Based Colorimetric and Fluorescent Sensors for Selective Detection of Anions

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Abstract: A new type of perylenebisimide-based imidazolium chemosensor was synthesized for selective recognition of anions. Imidazolium-anchored receptor PBI-**1** showed high binding affinity to F^- due to the role of the phenolic hydroxyl group as an additional binding site. The hydroxyl-protected receptor PBI-**2** could serve as highly selective and sensitive colorimetric and fluorometric sensor for $H_2PO_4^-$. The study indicated that the C_2-H of the imidazolium ring played an essential role in the anion recognition *via* synergistic effects of multiple hydrogen-bonding and electrostatic interactions. In addition, it was noteworthy that the phenolic hydroxy of the receptor was not indispensable for binding $H_2PO_4^-$, but very pivotal for binding F^-.

Keywords: Anion recognition, colorimetric and fluorometric detection, hydrogen bonds, imidazolium chemosensor, perylenebisimide, phenolic hydroxyl.

INTRODUCTION

The development of synthetic receptors capable of recognizing anions has gained extensive interest in the past few decades due to their practical importance in many chemical, biological, medical, and environmental processes [1]. It is well known that the positively charged imidazolium group is a good binding subunit for anions through synergistic effects of unconventional hydrogen bonds and cation–anion interactions [2]. As a new class of promising building blocks to create supramolecular systems, imidazolium group has been utilized for the design and synthesis of receptors for anion recognition by forming $(C–H)^+\cdots X^-$ hydrogen bonds between the imidazolium ring and the guest anion [3]. Lots of X-Ray data and NMR study results have also unequivocally proved the existence of the unconventional $(C–H)^+\cdots X^-$ type hydrogen bonds [4]. Among imidazolium-based sensors reported for anion recognition, the selective chemosensors for $H_2PO_4^-$ or F^- have attracted more interests [3,5]. Even though great achievement in the field of anion chemosensors has been obtained, there is still a demand to develop new indicators with improved properties, especially colorimetric and fluorescent sensors with specific selectivity toward F^- or $H_2PO_4^-$ over other competitive anions. However, to the best of our knowledge, there were only a few examples using imidazolium-based colorimetric sensors for F^- or $H_2PO_4^-$ [6]. Therefore, the design and construction of colorimetric and fluorescent sensors based on imidazolium for highly selective recognizing F^- or $H_2PO_4^-$ is very significant.

Colorimetric methods can be convenient in practical applications without the aid of any advanced instruments. Recently, considerable efforts have been made to develop colorimetric probes for the recognition of anions [7]. Perylene-3,4:9,10-tetracarboxylic acid bisimide (PBI) is a particularly promising class of organic dyes that exhibit unique photophysical and photochemical properties [8]. Because their fluorescence spectra between 500~650 nm are very suitable for both colorimetric and fluorimetric detection [9], PBI-based chemosensors have been designed and widely applied for the optical detection of anions, cations and biological molecules in recent years [10]. However, there are no PBI-attached chemosensors by incorporating the imidazolium units designed for the anion recognition so far. On the basis of the above considerations and in continuation of our ongoing interest in the development of imidazolium-based supramolecular chemistry [11], we herein present the synthesis of PBI-based imidazolium chemosensors PBI-**1** and PBI-**2** and the spectroscopic investigations toward different anions. To further illustrate the importance of the phenolic hydroxy of the receptor for binding F^-, an analogue without imidazolium group PBI-**3** was synthesized for the comparative experiment.

RESULTS AND DISCUSSION

Perylenebisimide compounds PBI-**1** and PBI-**2** functionalized with imidazolium units were successfully synthesized by a two-step reaction using *N*-octadecyl-1,6,7,12-tetra(4-tert-butylphenoxy) perylene-3,4:9,10-tetracarboxylic-3,4-anhydride-9,10-imide (**7**) as starting material. As demonstrated in Scheme **1**, **7** reacted with 2,6-bis(imidazolylmethyl)-4-aminophenol (**2**) and 3,5-bis(imidazolylmethyl)-4-methoxyaniline (**6**) in toluene afforded PBI-based intermediates **8** and **9**, respectively. Quaternization reactions of **8** and **9** with MeI were easy to accomplish in solvent-free conditions, and then followed by anion exchange of I^- with PF_6^- affording the corresponding imidazolium receptors PBI-**1** and PBI-**2**. PBI-**3** was synthesized by a straightforward reaction of **7** with 4-aminophenol.

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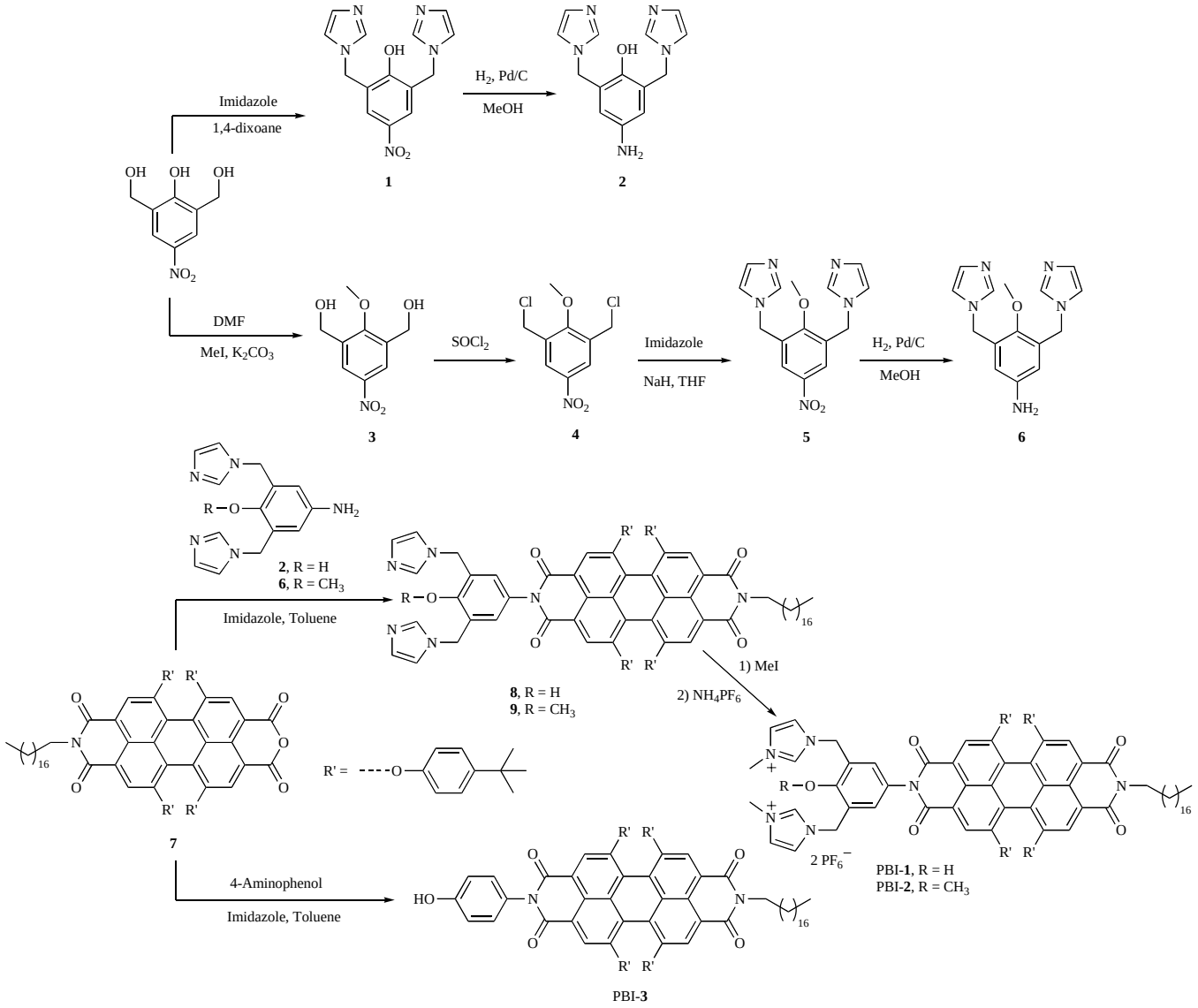

Scheme 1. Synthesis of perylenebisimide-based receptors PBI-**1**, PBI-**2** and PBI-**3**.

The fluorescence response of PBI-**1** to anions was investigated in CH_3CN. As displayed in Fig. (**1**), the fluorescence emission spectra of PBI-**1** consist of a strong band at 604 nm upon excitated at 568 nm. Among the anions selected for fluorescence experiments, F^- and $H_2PO_4^-$ resulted in almost complete quenching of fluorescence, AcO^- quenched nearly 50 percent fluorescent intensity, but no significant changes of fluorescence signal were observed upon addition of Cl^-, Br^-, I^-, ClO_4^- and HSO_4^- anions. In investigating the fluorescent spectra of PBI-**1**, we observed that anions could induce visible color changes of PBI-**1** (Fig. **S1** in Supplementary Material). Addition of 2 equiv of tetrabutylammonium salts of F^- or $H_2PO_4^-$ resulted in a perceived color changes from red to purple, which indicated that the receptor PBI-**1** could serve as a colorimetric and fluorescent sensor for selective detection of F^- and $H_2PO_4^-$ in acetonitrile. We speculated that imidazolium units and phenolic hydroxy of the receptor could serve as the hydrogen bond donor and played an important role in recognition process, respectively. The fluorescence quenching might be due to the photoinduced electron transfer (PET) and/or intramolecular electron transfer (IET). Imidazolium ring is the electron-deficient unit, which is usually less quenching effect on the fluorophore. However, the formation of $(C–H)^+\cdots X^-$ hydrogen bonds between the C-2 hydrogen atom of the imidazolium ring and the guest anion resulted in an increase in electron density of the ring, which could give rise to quenching effect on the perylene-fluorophore [12]. Furthermore, phenolic hydroxy was electron rich in itself, and the formation of $O–H\cdots X^-$ hydrogen bond between the phenolic hydroxy and the guest anion could strengthen the quenching effect by an IET principle.

To evaluate the essential role of the C-2 hydrogen atom of the imidazolium ring in the anion recognition, the ^1H NMR spectroscopic study of PBI-**1** was undertaken in $CDCl_3$. As shown in Fig. (**2**), before and after F^- or $H_2PO_4^-$ were added, significant ^1H NMR spectral changes of C_2-H of the imidazolium rings were observed, indicating that one of interactions between receptor and guest happened through the hydrogen bonds between the C_2-H and guest anions.

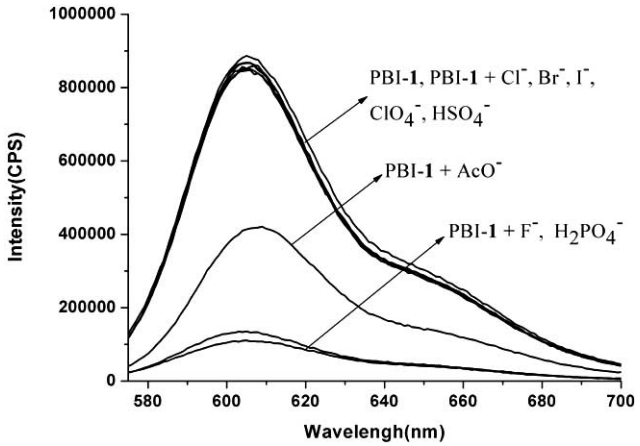

Fig. (1). Changes in fluorescence intensity of PBI-**1** (10 μM) (λ_{ex} = 568 nm, slit = 1.5 nm) upon addition of 2 equiv of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^- in CH_3CN.

Upon addition of an equimolar amount of F^- into the $CDCl_3$ solution of PBI-**1**, the imidazolium C_2-H peaks underwent downfield shifts by 0.67 ppm (from 8.51 to 9.18). In contrast, $H_2PO_4^-$ resulted in a larger downfield shifts by 0.78 ppm (from 8.51 to 9.29), which indicated that the hydrogen bonding interaction between the C_2-H and $H_2PO_4^-$ was stronger than that between the C_2-H and F^-. In addition, almost all protons of the aromatic rings, including the protons of perylene-scaffold also gave rise to slight upfield shifts. The reason might be an increase in electron density of the aromatic rings *via* the interaction of hydrogen bonds between the host and guest molecules, which rendered an increasing shielding effect.

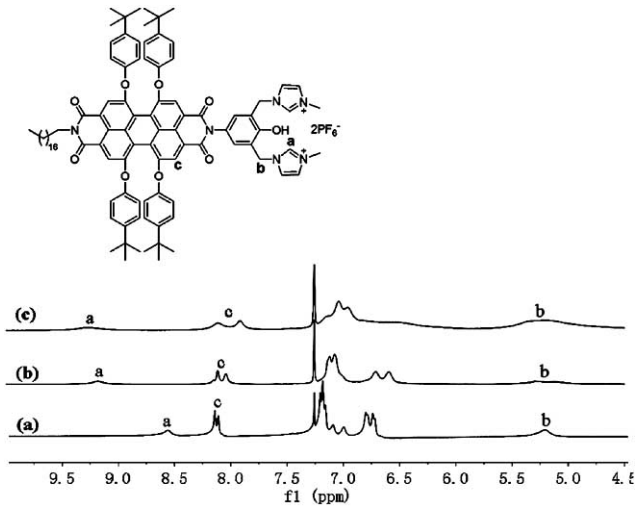

Fig. (2). Partial ^{1}H NMR spectra of PBI-**1** (**a**), PBI-**1** + 1.0 equiv of F^- (**b**) and PBI-**1** + 1.0 equiv of $H_2PO_4^-$ (**c**) at 25 ºC in $CDCl_3$.

We wondered whether the phenolic hydroxyl group of the receptor was necessary for anions recognition. Thus, the imidazolium-anchored receptor PBI-**2**, of which the phenolic hydroxyl group was protected by methyl group was designed and synthesized for comparative experiments. The responses of PBI-**2** to various anions were investigated under the same condition as PBI-**1**. We were delighted to find that only $H_2PO_4^-$ resulted in dramatic color change of PBI-**2** from red to blue purple among a series of individual anions (Fig. **S2** in Supplementary Material). We further investigated the fluorescent spectra of PBI-**2** in the presence of various anions. As shown in Fig. (**3**), $H_2PO_4^-$ quenched nearly 90 percent fluorescent intensity of PBI-**2**, while other anions did not induce any obvious changes of emission intensities. The high selectivity and sensitivity of PBI-**2** to $H_2PO_4^-$ could be potentially applicable in physiological and environmental studies. From the above experimental results, we could also draw a possible conclusion that the phenolic hydroxy of the receptor was very pivotal for binding F^-, but not indispensable for binding $H_2PO_4^-$.

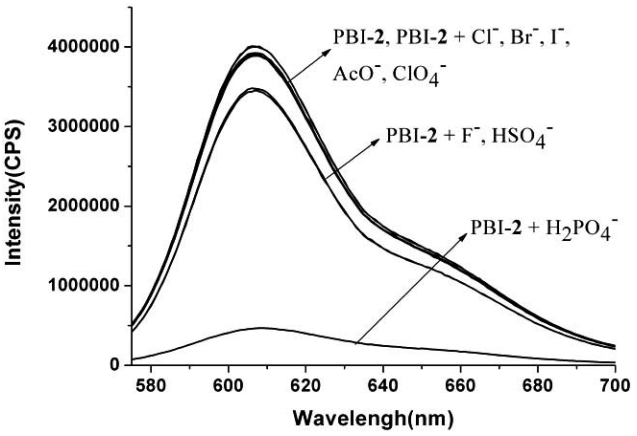

Fig. (3). Changes in fluorescence intensity of PBI-**2** (10 μM) (λ_{ex} = 568 nm, slit = 1.5 nm) upon addition of 2 equiv of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^- in CH_3CN.

The fluorescence titration experiments of PBI-**1** and PBI-**2** were carried out with various anions including F^-, Cl^-, Br^-, I^-, ACO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^- as shown in Fig. (**4**) and Figs. (**S3-S10**). Taking F^- anion as a representative example, the fluorescence emission intensity of PBI-**1** at 604 nm gradually decreased with concentration increase of F^- from 0 to 5 equiv (Fig. **4**). Job's plot analysis for the complexation of PBI-**1** and F^- corroborated the 1:1 binding stoichiometry (Fig. **4**, Inset). The association constants of the supramolecular complexes were calculated by using nonlinear curve fitting. The association constant *K* values of PBI-**1** and PBI-**2** for F^- were calculated to be 4.74×10^5 and 1.72×10^4, respectively (Table **1**). The data provided a clear indication that PBI-**1** bound F^- with approximately 28-fold stronger affinity than PBI-**2**, which further revealed the importance of the phenolic hydroxyl group for binding F^- anion. However, the two receptors PBI-**1** and PBI-**2** showed an approximate association constant toward $H_2PO_4^-$ anion, suggesting that the effect of phenolic hydroxyl group of the receptor for binding $H_2PO_4^-$ was negligible.

In addition, the receptor PBI-**3** without imidazolium group was synthesized to further shed light on the importance of the phenolic hydroxy for binding F^- anion. Chloroform was selected as the solvent due to the poor solubility of PBI-**3** in CH_3CN. Fig. (**5**) showed the changes in fluorescence intensity of PBI-**3** upon addition of F^-, Cl^-,

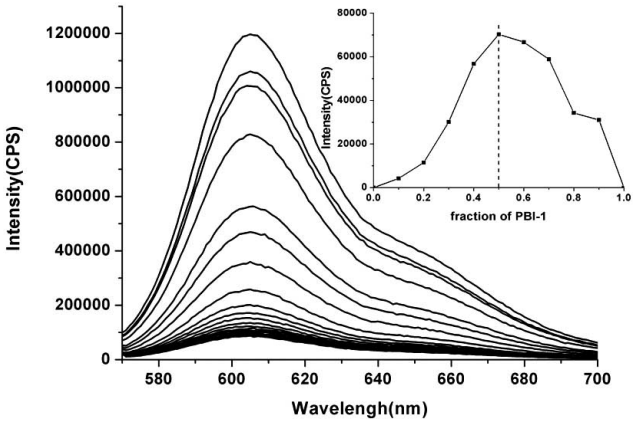

Fig. (4). Fluorescent titrations of PBI-**1** (10 μM) with tetrabutylammonium fluoride (0-5 equiv) in CH_3CN (λ_{ex} = 568 nm, slit = 1.5 nm). Inset: the Job's plot.

Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^- anions in $CHCl_3$. Only the F^- anion could modulate the fluorescence of PBI-**3**, while other anions did not show obvious fluorescence response. However, it was worth noting that F^- anion only quenched nearly 50 percent fluorescent intensity of PBI-**3** even though 50 equiv of F^- anion was added, which provided directed evidence that the phenolic hydroxy of PBI-**1** acted as an auxiliary binding site for F^- anion.

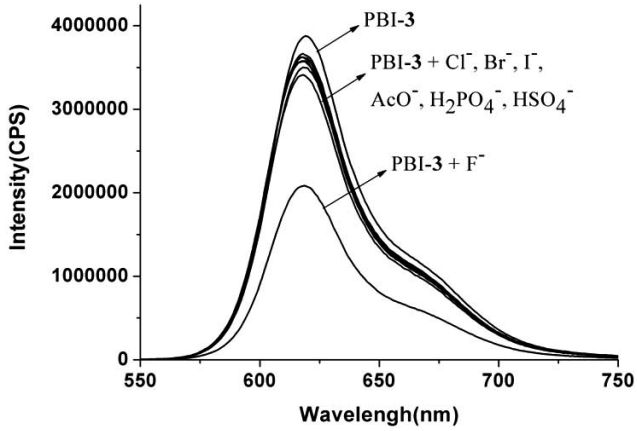

Fig. (5). Changes in fluorescence intensity of PBI-**3** (10 μM) (λ_{ex} = 570 nm, slit = 1.5 nm) upon addition of 50 equiv of tetrabutylammonium salts of F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, ClO_4^- and HSO_4^- in $CHCl_3$.

In conclusion, perylenebisimide-based imidazolium receptors were synthesized and served as colorimetric and fluorescent sensors for selective binding of F^- or $H_2PO_4^-$ in acetonitrile. The receptor PBI-**1** exhibited higher binding affinity to F^- than other anions. For the phenolic hydroxyl group protected receptor PBI-**2**, only $H_2PO_4^-$ resulted in a dramatic color change from red to blue purple. These results highlighted that imidazolium units were very important to recognize both F^- and $H_2PO_4^-$ anions, and the phenolic hydroxyl group acted as an additional binding site for F^- anion. We believed that these results and the design strategy were helpful to the development novel anion sensors.

EEXPERIMENTAL SECTIONS

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 (^1H: 400 MHz; ^{13}C: 100 MHz) or a Varian INOVA-400 (^1H: 400 MHz; ^{13}C: 100 MHz). ^1H NMR experiments were measured relative to the signals for residual solvent signal at 7.26, 2.50, and 3.31 ppm for $CDCl_3$, DMSO-d_6, and CD_3OD, respectively. ^{13}C NMR experiments were measured relative to the signals for residual solvent signal at 77.2, 39.5, and 49.0 ppm for $CDCl_3$, DMSO-d_6, and CD_3OD, respectively. Mass spectra (MS) were obtained on a Waters Quattro Premier XE Mass Spectrometer. High-resolution mass spectra (HR-MS) were obtained by ESI-TOF (Waters-Q-TOF-Premier). Melting points were determined with XRC-1 and were uncorrected. Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. All of the solvents were either HPLC or spectroscopic grade in the optical spectroscopic studies. The stock solutions of fluorophores and anions were freshly prepared and used for each measurement. Each time a 3 mL of solution of receptor was filled in a quartz cell of 1 cm of optical path length, and the stock solution of anion was added into a quartz cell dropwise using a micro-syringe. The volume of anion stock solution added was less than 100 μL to remain the concentration of receptor unchanged. Fluorescent emission spectra were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer.

Table 1. Association Constants K^a (M^{-1}) for the Complexes of PBI-1 and PBI-2 with Various Anions[b] in CH_3CN at 25 °C

Receptor	K (F^-)	K ($H_2PO_4^-$)	K (Cl^-)	K (Br^-)	K (HSO_4^-)
PBI-**1**	4.74×10^5	3.03×10^5	418	806	-
PBI-**2**	1.72×10^4	2.27×10^5	-	-	4.76×10^3

[a]Errors were estimated to be <15%. [b]All anions were used as tetrabutylammonium salts, and the correlation coefficient (R) of nonlinear curve fitting is over 0.99.

Experimental Procedure for 1

2,6-Bis(hydroxymethyl)-4-nitrophenol (0.63 g, 3.2 mmol), imidazole (0.81 g, 12.0 mmol) were added to 1, 4-dioxane (10 mL) and stirred under reflux for 2 hours. After the solvent was evaporated, the reaction was continued at 130-140 °C for 5 hours. After cooling, the agglomerating mixture was dissolved in ethanol, then water was added, filtered and the solid was recrystallized in ethanol, afforded product as a yellow solid (0.67 g, yield 71%). mp: 168-170 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 5.06 (s, 4H), 7.17 (s, 2H), 7.43 (s, 2H), 7.88 (s, 2H), 8.33 (s, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 47.1, 120.9, 124.3, 124.8, 126.5, 128.8, 136.7, 173.8; MS (ESI): calcd for $C_{14}H_{12}N_5O_3$ $[M-H]^-$ 298.09, found 298.02.

Experimental Procedure for 2

Pd/C (5%, 52 mg) and **1** (0.5 g, 1.7 mmol) were added to methanol (30 mL), and stirred under H_2 (0.7 Mpa) at 55 °C for 3.5 h. After cooling, Pd/C was filtered off and solvent was removed under the reduced pressure. The solid was recrystallized in ethanol, afforded product as a pale solid (0.3 g, yield 66%). mp > 150 °C (decomposition); ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.07 (s, 4H), 6.16 (s, 2H), 6.88 (s, 2H), 7.10 (s, 2H), 7.65 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 45.3, 114.1, 119.7, 127.1, 128.3, 137.5, 142.0, 142.4; MS (ESI): calcd for $C_{14}H_{14}N_5O$ [M-H]$^-$ 268.12, found 268.04.

Experimental Procedure for 3

A mixture of 2,6-Bis(hydroxymethyl)-4-nitrophenol (2 g, 10 mmol), MeI (0.51 mL, 10 mmol), K_2CO_3 (1.38g, 10 mmol) and DMF (4 mL) was stirred at room temperature for 20 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as the eluent, afforded product as a faint yellow solid (0.54 g, yield 25%). mp: 137.5-138.5 °C; ^{1}H NMR (400 MHz, CD_3OD): δ 3.86 (s, 3H), 4.72 (s, 4H), 8.27 (s, 2H) ppm; ^{13}C NMR (100 MHz, CD_3OD): δ 59.3, 62.5, 123.6, 137.7, 145.5, 161.3; MS (ESI): calcd for $C_9H_{11}NO_5$ [M-H]$^-$ 212.06, found 212.02.

Experimental Procedure for 4

A mixture of **3** (1.1 g, 5.16 mmol) and $SOCl_2$ (4 mL) was stirred at room temperature for 12 h. Then $SOCl_2$ was removed and the residue was purified by column chromatography on silica gel using ethyl acetate/petroleum ether as the eluent, afforded product as a faint yellow solid (0.67 g, yield 52%). mp: 32-34 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 3H), 4.67 (s, 4H), 8.29 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 39.7, 63.5, 126.7, 133.1, 144.0, 161.5; MS (ESI): calcd for $C_9H_9Cl_2NO_3$ [M+Cl]$^-$ 283.96, found 283.21.

Experimental Procedure for 5

Imidazole (0.53 g, 7.79 mmol), sodium hydride (0.19 g, 7.91 mmol) in THF (15 mL) were stirred at RT for 15 min and solution of **4** (0.67 g, 2.68 mmol) in THF (1 mL) was added drop wise. The mixture was stirred at room temparature for 12 h. The solution was filtered and evaporated to dryness, residue was purified by column chromatography on silica gel using methanol/dichloro-methane/ethyl acetate as the eluent, afforded product as a yellow solid (0.17 g, yield 20%). mp: 218-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.70 (s, 3H), 5.23 (s, 4H), 6.93 (s, 2H), 7.13 (s, 2H), 7.59 (s, 2H), 7.89 (s, 2H); ^{13}C NMR (100 MHz, CD_3OD): δ 46.3, 62.8, 121.1, 125.5, 129.7, 134.1, 139.1, 145.8, 162.2; MS (ESI): calcd for $C_{15}H_{15}N_5O_3$ [M+H]$^+$ 314.12, found 314.11.

Experimental Procedure for 6

Pd/C (5%, 58 mg) and **5** (0.5 g, 1.60 mmol) were added to methanol (15 mL), and stirred under H_2 (0.7 Mpa) at 55 °C for 3.5 h. After cooling, Pd/C was filtered and solvent was removed under the reduced pressure. The solid were recrystallized in ethanol, afforded product as a white solid. (0.29 g, yield 64%). mp > 190 °C (decomposition); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.61 (s, 3H), 3.97 (s, 2H), 4.96 (s, 2H), 5.10 (s, 4H), 6.08 (s, 2H), 6.91 (s, 2H), 7.11 (s, 2H), 7.68 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 44.7, 61.5, 113.1, 119.8, 128.5, 131.0, 137.7, 145.2, 145.5; MS (ESI): calcd for $C_{15}H_{17}N_5O$ [M-H]$^-$ 282.14, found 282.19.

Experimental Procedure for 7

7 was prepared according to the referrence [13]. mp: 238-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8.0 Hz, 3H), 1.22-1.29 (m, 66H), 1.62-1.69 (m, 2H), 4.09 (t, J = 8.0 Hz, 2H), 6.81-6.84 (m, 8H), 7.23-7.26 (m, 8H), 8.22 (s, 2H), 8.21 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.2, 28.2, 29.4, 29.5, 29.6, 29.8, 31.6, 32.0, 34.5, 40.9, 118.1, 119.4, 119.5, 119.8, 121.7, 121.8, 122.3, 123.2, 126.8, 126.9, 133.1, 133.4, 147.7, 147.8, 152.7, 155.9, 156.7, 160.1, 163.4; MS (ESI): calcd for $C_{82}H_{93}NO_9$ [M+K-H]$^+$ 1273.64, found 1273.70.

Experimental Procedure for 8

A mixture of **7** (1.4 g, 1.13 mmol), **2** (0.4 g, 1.49 mmol) and imidazole (2.0 g, 29.4 mmol) in toluene (20 mL) was refluxed under N_2 for 4 h. After the solvent was evaporated, the residue was dissolved in chloroform and washed with water to remove the imidazole. The chloroform was then removed, and the residue was purified by column chromatography on silica gel using CH_2Cl_2/EtOH as the eluent, afforded product as a red solid (0.89 g, yield 53%). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (s, 3H), 1.25-1.28 (m, 66H), 1.68 (s, 2H), 4.11 (s, 2H), 5.16 (s, 4H), 6.79-6.83 (m, 12H), 6.93 (s, 2H), 7.17-7.26 (m, 8H), 7.42 (s, 2H), 8.19 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.3, 28.3, 29.5, 29.7, 29.8, 31.6, 32.0, 34.4, 34.5, 40.8, 46.9, 119.3, 119.5, 119.6, 119.8, 119.9, 120.3, 120.4, 121.3, 122.1, 122.8, 126.7, 126.8, 127.1, 127.4, 128.2, 130.1, 133.0, 133.1, 137.4, 147.4, 147.4, 152.9, 153.0, 154.5, 155.8, 156.3, 163.5, 163.7; MS (ESI): calcd for $C_{96}H_{106}N_6O_9$ [M-H]$^-$ 1486.80, found 1486.67.

Experimental Procedure for PBI-1

A solution of **8** (0.32 g, 0.21 mmol) and MeI (4 mL) was stirred at room temperature for 72 h. Then remaining MeI was evaporated to dryness under reduced pressure, the residue was dissolved in methanol (10 mL) at RT and solution of NH_4PF_6 (88 mg, 0.54 mmol) in water (1 mL) was added drop wise. The solution was allowed to stir for 24 h. The separated black solid was filtered and washed with water and hexane to afford PBI-**1** (0.19 g, yield 50%). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8 Hz, 3H), 1.22-1.27 (m, 66H), 1.65 (s, 2H), 3.66 (s, 6H), 4.09 (s, 2H), 5.21 (s, 4H), 6.72-6.80 (m, 8H), 7.00 (s, 2H), 7.10-7.21 (m, 12H), 8.11 (s, 2H), 8.14 (s, 2H), 8.56 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.3, 28.3, 29.5, 29.7, 29.8, 31.6, 32.1, 34.3, 34.5, 36.3, 40.9, 48.8, 119.0, 119.4, 119.7, 119.9, 120.1, 120.8, 120.8, 121.8, 121.4, 122.9, 123.6, 124.6, 124.6, 126.7, 126.7, 132.2, 132.2, 132.9, 133.2, 136.6, 147.2, 147.7, 152.7, 153.3, 155.3, 156.6, 163.4, 163.7; HR-MS: m/z calcd

for $C_{98}H_{112}F_{12}N_6O_9P_2$ $[M\text{-}2PF_6^-]^{2+}/2$ 758.4245, found 758.4265.

Experimental Procedure for 9

9 was prepared in the same way as **8** (yield 44%). mp > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8 Hz, 3H), 1.22-1.29 (m, 66H), 1.65-1.68 (m, 2H), 3.65 (s, 3H), 4.10 (t, J = 8.0 Hz, 2H), 5.21 (s, 4H), 6.81-6.84 (m, 10H), 6.90 (s, 2H), 7.05 (s, 2H), 7.20-7.24 (m, 8H), 7.60 (s, 2H), 8.16 (s, 2H), 8.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.2, 28.2, 29.4, 29.6, 29.7, 31.5, 32.0, 34.4, 34.5, 40.8, 45.6, 61.7, 119.4, 119.4, 119.8, 119.9, 120.3, 120.4, 121.3, 122.0, 122.8 ,126.7, 126.8, 129.6, 130.1, 131.4, 132.3, 133.0, 133.1, 137.7, 147.5, 152.9, 155.6, 155.9, 156.3, 163.4; MS (ESI): calcd for $C_{97}H_{108}N_6O_9$ $[M]^+$ 1501.82, found 1501.26.

Experimental Procedure for PBI-2

PBI-**2** was prepared in the same way as PBI-**1** (yield 55%). mp: 267-269 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8 Hz, 3H), 1.17-1.28 (m, 66H), 1.68 (s, 2H), 3.63 (s, 6H), 3.85 (s, 3H), 4.10 (s, 2H), 5.30 (s, 4H), 6.55-6.69 (m, 8H), 7.00-7.21 (m, 14H), 7.61(s, 2H), 7.98 (s, 4H), 8.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.3, 28.3, 29.5, 29.8, 29.8, 31.5, 32.0, 34.4, 34.5, 36.3, 40.8, 48.1, 62.8, 118.6, 119.2, 119.3, 119.5, 119.8, 120.0, 120.8, 120.9, 121.2, 122.3, 124.0, 126.5, 126.6, 128.9, 132.2, 132.5, 132.7, 133.0, 136.9, 147.0, 147.5, 152.4, 153.3, 154.7, 156.7, 157.0, 163.1, 163.4; HR-MS: m/z calcd for $C_{99}H_{114}F_{12}N_6O_9P_2$ $[M\text{-}2PF_6^-]^{2+}/2$ 765.9363, found 765.9356.

Experimental Procedure for PBI-3

PBI-**3** was prepared in the same way as **8** (yield 50%). mp > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, J = 8Hz, 3H), 1.23-1.29 (m, 66H), 1.65-1.69 (m, 2H), 4.10 (t, J = 8Hz, 2H), 6.81-6.85 (m, 10H), 7.04 (s, 2H), 7.21-7.25 (m, 8H), 8.23 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 22.8, 27.3, 28.3, 29.5, 29.8, 31.6, 31.6, 32.1, 34.5, 40.9, 116.5, 119.4, 119.5, 119.9, 120.0, 120.5, 121.1, 122.5, 122.8, 126.8, 129.2, 133.2, 147.5, 153.0, 156.1, 156.2, 156.3, 163.6, 164.1; HR-MS: m/z calcd for $C_{88}H_{98}N_2O_9$ $[M+H]^+$ 1327.7351, found 1327.7333.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

Graph for anions induced color change and fluorescence titrations of sensors PBI-**1** and PBI-**2** are available.

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