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Reversible “off–on” fluorescent probe for anions based on a facile two-component ensemble

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ABSTRACT

A specific fluorescent switch for anions was successfully constructed. The novel sensing switch is a two-component ensemble, which was combined using a water-soluble conjugated polyelectrolyte and a boronic acid functionalized pyridine salt. In the ensemble, the polyelectrolyte is used as a fluorescent signal unit, and the pyridine boronic acid acts as receptor and quencher. The two-component ensemble shows a fluorescence reversible “off–on” response toward cyanide and phosphate anions based on different binding ways. Furthermore, the facile design and construction of this ensemble presents a novel opportunity for obtaining an efficient and practical probe.

1. Introduction

Optical molecular probes for anions have attracted extensive attention because of their important roles in a wide range of environmental, clinical, chemical and biological applications. Many research results describe well-designed probes which display high sensitivity and selectivity to analytes [1–6]. Among various analytes, anions are of concern because they play important roles in biological processes but are also environmental pollutants [7–10]. Therefore, the development of a multi-functional probe for anion sensing is desired by chemists and biologists.

To date, molecular probes for anions based on fluorescence detection are most promising because they offer advantages of high sensitivity, real-time analysis multiple sensing modes [11,12]. Most of the fluorescence sensors focus on one-component design that contains both fluorophore and receptor groups in the same molecule [13–17]. Combining an analyte with a receptor unit, the light properties of the fluorophore are changes and further realize recognition of the analyte. Despite many highly effective one-component probes have been reported for anions over the past decade [7–9,18,19], practical probes for anions (especially for cyanide and phosphate ions) based on fluorescence spectroscopy were few and had some drawbacks such as poor water solubility and difficult structure modification etc. Therefore, a new mode of probe design to advance this field is in great demand. Here, we describe a new strategy and establish a specific reversible fluorescence ensemble for anions. The probe was a two-component ensemble comprised of a cationic pyridine salt quencher and an anionic conjugated polyelectrolyte (ACP). For the ensemble, the ACP is a signal reporting group and its fluorescence is modulated by the interaction between ACP and the quencher. The cationic pyridine salt is both a quencher and a receptor in the ensemble. It is reasonable believed that the two-component ensemble has many advantages [20–24]. For example, the chemical structure of the quencher can be modified to obtain a highly selective and sensitive probe without having to modify the structure of reporting fluorophore. This sensing approach allows considerable flexibility in choosing the quencher/receptor and fluorophore components depending on the particular requirements of the sensing application.

In this paper, the two-component ensemble is composed of an anionic water-soluble polyelectrolyte (PBPYRSO$_3$Na) and a pyridine salt quencher (*m*-TBPB) with boronic acid (Scheme 1). The anionic conjugated polyelectrolyte PBPYRSO$_3$Na is a reporting group Cationic *m*-TBPB is both a quencher and a receptor in the ensemble. It should be noted that this sensing ensemble has the following unique features: (1) conjugated polyelectrolytes (CP) can offer

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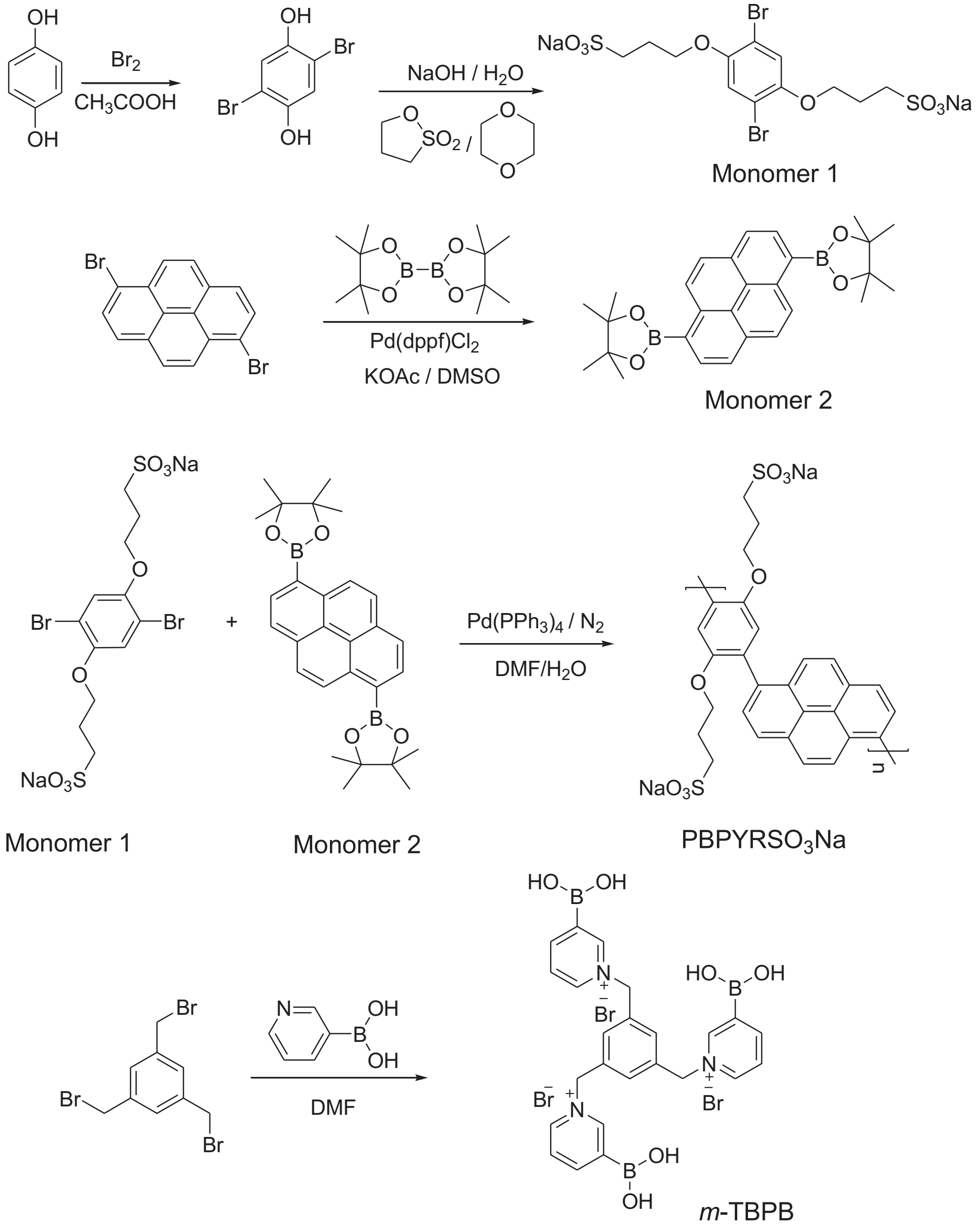

Scheme 1. The synthetic route of polyelectrolyte and *m*-TBPB.

particular properties compared with the normal "neutral" conjugated polyelectrolyte due to their ionic side groups attached to the conjugated main chain. Additionally, the ACP is typically soluble in water which is an environment-friendly solvent [25–27]; (2) a boronic acid functionalized pyridine salt with strong quenching and bonding abilities is used to connect anions; (3) forming a neutral multidimensional complex can provide a specific micro-environment with which to complex anions.

2. Experimental

2.1. Materials and instruments

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. All experiments of water were pure water of selling market. *p*-Hydroquinone, 1,3-propanesultone, 1,6-dibromopyrene, Pd(PPh$_3$)$_4$, Pd(dppf)Cl$_2$ and bis-(pinacolato)diboron were purchased from Aldrich (Steinheim, Germany). 1,3,5-Tris(bromomethyl)benzene and 3-boronic acid-pyridine were obtained form Creasyn Finechem (Tian Jing, China). ^{1}H NMR and ^{13}C NMR were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). ^{11}B NMR spectra were recorded on a Bruker ARX400 were reported in ppm with respect to $BF_3 \cdot OEt_2$ ($\delta = 0$). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.). High-resolution mass spectra (HRMS) were acquired on an Agilent 6510 Q-TOF LC/MS instrument (Agilent Technologies, Palo Alto, CA) equipped with an electrospray ionization (ESI) source. Fluorescence spectra were acquired with a Varian Cary Eclipse fluorescence spectrophotometer, the excitation and emission slit widths were both 5 nm. The excitation wavelength was set at 367 nm according to experimental requirements. All of the experiments were performed at room temperature.

2.2. The solution preparation and fluorescent measurement of the ensemble to anions

The stock solution (1.20 mg/mL) of $PBPYRSO_3Na$ was diluted in 1.0 L measuring flask with pure water to afford the working solution (6.0×10^{-3} mg/mL). The stock solution (0.004 M) of *m*-TBPB was prepared by 0.29 g *m*-TBPB in 100 mL measuring flask. The stock solutions of PO_4^{3-} and CN^- were 0.1 M in 10 mL measuring flask, respectively. The standard stock solutions of low concentrations were prepared by suitable dilution of the stock solution with pure water. The working salts were all sodium salts. All spectra analysis studies were carried out at pure water solution and the working solutions were placed in a quartz cuvette with 1 cm path. The total volume of working solutions was 2 mL. The studies of fluorescence measurements were used titration experiments and the volume added did not exceed 3% of the total. After the mixture solution was shaken for 30 s, the new spectra were measured.

2.3. Synthesis of polyelectrolyte $PBPYRSO_3Na$ and quencher m-TBPB (Scheme 1) [28–31]

2.3.1. 1,4-dibromo-2,5-bis(3′-sulfonatopropoxy)benzene (monomer 1)

A solution of 6.35 g (20.0 mmol) 2,5-dibromobenzene-1,4-diol, 2.0 g (50.0 mmol) sodium hydroxide and water (200 mL) in a Erlenmeyer flask was stirred under nitrogen. Then, a solution of 6.1 g (50.0 mmol) 1,3-propanesultone in 40 mL dioxane was added to the former solution at once. The resulting mixture was then stirred at room temperature overnight, during which time a thick pink slurry formed. The reaction mixture was then stirred at 80–100 °C for another 30 min and then cooled in a water/ice bath. The suspension obtained was vacuum filtered, and the retained solid was washed with cold water followed by acetone. The crude products were purified by recrystallization twice times from water to yield product as white powder (7.61 g, yield 68.4%). ^1H NMR (D_2O, 400 MHz) δ 7.16 (s, 2H), 4.03 (dd, $J = 6.0$, 6.0 Hz, 4H), 3.05 (dd, $J = 4.4$, 5.6 Hz, 4H), 2.21 (m, 4H); ^{13}C NMR (D_2O, 100 MHz) δ 24.24, 47.91, 68.97, 111.03, 119.19, 149.42; IR (KBr) cm^{-1}: 2965, 2922, 2871, 1614, 1479, 1444, 1417, 1392, 1353, 1262, 1144, 1051, 1032, 937, 835, 736, 634, 576; Element Analysis for $C_{12}H_{14}Br_2Na_2O_8S_2$ (Mol. Wt.: 556.15) calcd.: C 25.92; H 2.54; found: C 25.89; H 2.57; HRMS–ESI for $C_{12}H_{14}Br_2Na_2O_8S_2$ (*m*/*z*) 533 [M–23].

2.3.2. 1,6-bis(4′,4′,5′,5′-tetramethyl-1′,3′,2′-dioxaborolane)pyrene (monomer 2)

A mixture of 3.6 g (10.0 mmol) 1,6-dibromopyrene, 7.62 g (30.0 mmol) bis(pinacolato)diboron, 0.58 g (8 mol%) $Pd(dppf)Cl_2$ and 5.88 g (60.0 mol) potassium acetate in DMSO (70 mL) was stirred at 80 °C for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, poured into the 500 mL ice water, filtrated and then purified by column chromatography on silica gel with dichloromethane/petroleum ether (1/4) as the eluant to afford a light green power (3.98 g, 87.6%). ^1H NMR ($CDCl_3$, 400 MHz) δ 9.155 (d, $J = 8.8$ Hz, 2H), 8.572 (d, $J = 7.6$ Hz, 2H), 8.229 (d, $J = 7.6$ Hz, 2H), 8.169 (d, $J = 9.2$ Hz, 2H), 1.517 (s, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.08, 83.91, 124.46, 127.90, 129.13, 133.06, 133.69, 136.42; IR (KBr) cm^{-1}: 3002, 2968, 2819, 1654, 1602, 1546, 1484, 1391, 1385, 1205, 1160, 1058, 1052, 933, 834, 728, 684; Element Analysis for $C_{28}H_{32}B_2O_4$ (Mol. Wt.: 454.17) calcd.: C 74.05, H 7.10, found: C 74.38, H 7.09; HRMS–ESI for $C_{28}H_{32}B_2O_4$ (*m*/*z*): 454 [M^+].

2.3.3. Polymer $PBPYRSO_3Na$

To 100 mL three-neck flask, equipped with mechanical stirrer was added 3.336 g (6.0 mmol) 1,4-dibromo-2,5-bis(3-sulfonatopropoxy) benzene, 2.724 g (6.0 mmol) 1,6-bis(4′,4′,5′,5′- tetramethyl-1′,3′,2′-dioxaborolane)pyrene, dried DMF (60 mL) and 0.224 g (0.18 mmol) $Pd(PPh_3)_4$ under nitrogen. The mixture was stirred under nitrogen for 30 min, and then 20 mL aqueous solution with 3.816 g (36.0 mmol) sodium carbonate was generally added by dropping funnel. The reaction was heated at 80 °C for 48 h. The reaction turned black as Pd(0) particles were liberated. The tan-violet filtrate was collected, precipitated into 1.0 L of acetone, and redissolved in deionized water. The polymer was dialyzed using a dialysis membrane with a 3.5 kDa molecular weight cutoff for 3 days. The final product, a violet dark powder, was obtained after dried in vacuo at 110 °C for 24 h. (1.53 g, 42.8%). ^1H NMR (d_6-DMSO, 400 MHz) δ 8.434–8.102 (broad, 8H), 7.376 (s, 2H), 4.091 (broad, 4H), 2.285 (broad, 4H), 1.721 (broad, 4H); ^{13}C NMR (d_6-DMSO, 100 MHz) δ 25.73, 48.30, 68.34, 99.99, 117.55, 124.65, 125.07, 126.33, 127.82, 129.01, 129.34, 130.52, 134.66, 150.41; IR (KBr) cm^{-1}: 3012, 2911, 2836, 1628, 1600, 1536, 1441, 1343, 1231, 1254, 1022, 1025, 936 845, 728, 635.

2.3.4. 1,3,5-tris[(3′-boronic acid-1′-methylene) pyridine]benzene trisbromide (m-TBPB)

To a solution of 1.794 g (5.0 mmol) 1,3,5-tris(bromomethyl) benzene in 50 mL DMF was added 2.029 g (16.5 mmol) 3-boronic acid-pyridine, and the reaction mixture was stirred at 70 °C for 72 h under nitrogen. The orange precipitate was collected by filtration, washed with DMF, acetone, then ether and dried under a stream of nitrogen to yield 1,3,5-tris[(3′-boronic acid-1′-methylene) pyridine]benzene trisbromide (*m*-TBPB) (2.87 g, 75.3%). ^1H NMR (CD_3OD, 400 MHz) δ 9.019 (d, $J = 18.0$ Hz, 6H), 8.717 (s, 3H), 8.019 (dd, $J = 8.0$ Hz, 14.8 Hz, 3H), 7.804 (s, 3H), 5.962 (s, 6H); ^{13}C NMR (CD_3OD, 100 MHz) δ 62.75, 125.91, 127.81, 130.67, 135.72, 142.59, 143.82, 146.40, 147.94, 149.51; ^{11}B NMR (80 MHz, CD_3OD) δ 18.58. Element Analysis for $C_{24}H_{27}B_3Br_3N_3O_6$ (Mol. Wt.: 725.63) calcd.: C, 39.72; H, 3.75; found: C, 39.42; H, 3.81.

3. Results and discussion

3.1. The interaction of the ensemble with cyanide anion

It is well known that cyanide anion has high nucleophilicity and can form a stable complex with boronic acid. The introduction of cyanide anion to a two-component ensemble resulted in a new intramolecular neutral complex between cyanide anion and the boronic acids of *m*-TBPB (Figs. 1 and 4). At the same time the ground-state intermolecular complex of *m*-TBPB and $PBPYRSO_3Na$ was destroyed or weakened to some extent, which led to the fluorescence recovery of $PBPYRSO_3Na$ (Fig. 1). As seen in Fig. 1, a high signal response of the probe to cyanide anion was observed. The interaction between the cyanide anion and the boronic acid group consisted of nucleophilic addition and nucleophilic substitution. The ability of boronic acid to complex cyanide ion may change from being electron deficient ($R\text{-}B(OH)_2$) in the absence of cyanide to being electron rich ($R\text{-}B\text{-}(CN)_3$) upon cyanide complexation. Therefore, a complex (1:9) can be formed between *m*-TBPB and the cyanide ions. The expected bonding proportion had been verified by the titration of cyanide ions with the ensemble ($PBPYRSO_3Na$: 6.0×10^{-3} g/mL, *m*-TBPB: 1.0×10^{-5} mol/L, Fig. S1). In addition, the detection limit of cyanide anion was depended on the ratio of the ensemble components.

3.2. The interaction of the ensemble with phosphate anion

To our surprise, while introducing phosphate anion to the sensing ensemble, the similar reversible fluorescence “off–on” change was observed (Fig. S2 and S3). Due to the weak nucleophilicity and highly delocalized charges of phosphate anion, the mode of interaction between the sensing ensemble and the

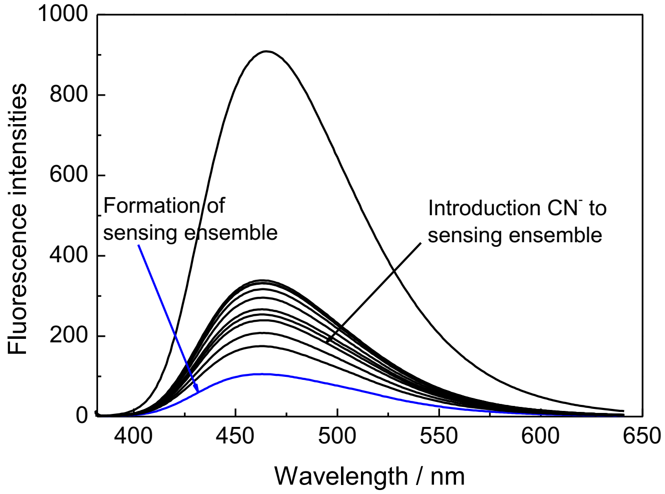

Fig. 1. Characteristic fluorescence response upon introduction of the quencher *m*-TBPB followed by CN^- to a $PBPYRSO_3Na$ solution (6.0×10^{-3} mg/mL). The concentration of *m*-TBPB was 1.0×10^{-5} mol/L and the final CN^- concentration was 1.5×10^{-4} mol/L. The red line indicates unquenched fluorescence and the blue line indicates fluorescence after introduction of the quencher *m*-TBPB. The dark line indicates fluorescence after the introduction of CN^- to the ensemble. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

phosphate anion should be not different to that of the cyanide anion. Given charge delocalized property of the phosphate anion, another probable bonding way for the ensemble and phosphate anions may be proposed. There may be a competition action of phosphate anion and polyelectrolyte sulfonate anions to *m*-TBPB. This competition would lead to a part decomposition of the ground-state complex between $PBPYRSO_3Na$ and *m*-TBPB. The interaction of hydrogen and phosphate anion was another key point to form new complex. Based on the two actions of phosphate anions with *m*-TBPB, the obvious fluorescent recovery of $PBPYRSO_3Na$ was observed. In order to give the exactly bonding modes of the ensemble with cyanide or phosphate anions, many other quenchers have been designed and these synthesis works are underway. Here, the bonding modes only were speculation analysis. Other useful results will be reported in the future.

3.3. The ratio choice of $PBPYRSO_3Na$ and m-TBPB

For the two-component ensemble, another considerable benefit is the ability to vary the ratio of quencher/reporting group to optimize the magnitude of the sensing response. We took a series of tests for the cyanide ion sensing response at different quencher/reporting group ratios (Fig. 2). The experimental results indicated that the high sensitivity response of the sensing ensemble to the anions can be realized by varying the ratio of the quencher to the reporting group. The response sensitivity and the detection limit of the two-component ensemble for the cyanide or phosphate anions would change with an increase in the *m*-TBPB/$PBPYRSO_3Na$ ratio. The relative intensities of fluorescence in the presence of 1.0×10^{-3} mol/L cyanide or phosphate ions were 20–30 times higher than that in the absence of cyanide or phosphate ions. However, some adverse interference factors such as the instability of the baseline, bad repeatability and trace impurity interference emerged in higher quencher/reporting group ratios. Therefore, based on the titration experiments, the optimal components of the sensing ensemble for cyanide and phosphate anions were 6.0×10^{-3} g/mL $PBPYRSO_3Na$ and 1.0×10^{-5} mol/L *m*-TBPB.

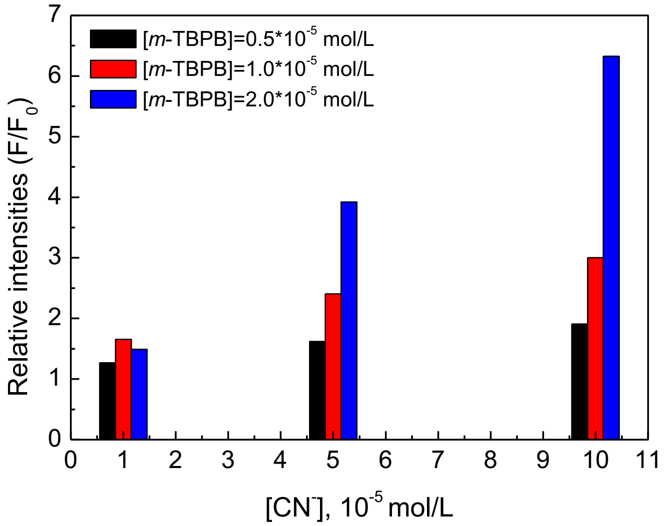

Fig. 2. The response to different components ratios of sensing ensemble with the addition of CN^-. The concentration of $PBPYRSO_3Na$ was 6.0×10^{-3} mg/mL.

3.4. The interactions of the ensemble with other anions

The selectivity of the sensing ensemble for typical nine anions was determined by titration experiments (Fig. 3). As shown in Fig. 3, considerable fluorescence enhancements were observed only in the presence of cyanide and phosphate anions. The enhancement of the relative fluorescence intensities were 10 times for the cyanide ion and 6 times for the phosphate ion compared with that of the other anions. Therefore, the ensemble containing $BPYRSO_3Na$ and *m*-TBPB was a dual-functional fluorescence ensemble for cyanide and phosphate anions. This may be understandable by considering that cyanide has a high nucleophilic ability and that phosphate has a negative charge delocalized property.

3.5. The color changes of ensemble solution

The reversible “off–on” fluorescence state of the sensing ensemble toward cyanide and phosphate anions can be observed

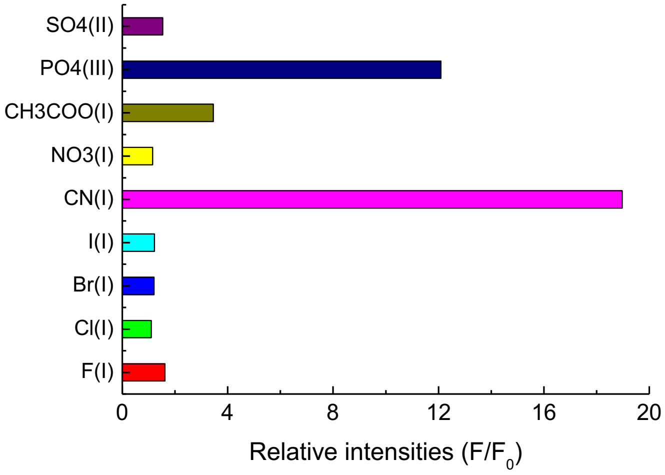

Fig. 3. Variation of the fluorescence relative intensity at 476 nm for the sensing ensemble ($PBPYRSO_3Na$: 6.0×10^{-3} mg/mL, *m*-TBPB: 2.0×10^{-5} mol/L) after the addition of 5.0×10^{-4} mol/L $SO_4^{2-}/PO_4^{3-}/NO_3^-/CN^-/CH_3COO^-/I^-/Br^-/Cl^-/F^-$, respectively, in pure water.

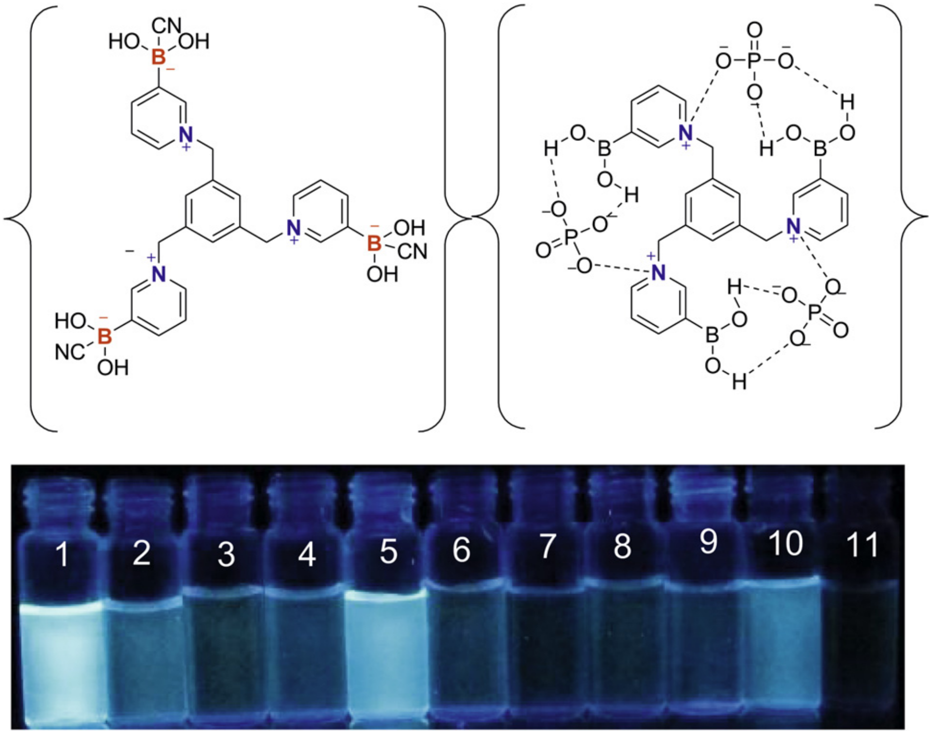

Fig. 4. The conjectural bonding ways of the ensemble with anions and color change for the $PBPRESO_3Na$ (6×10^{-3} mg/mL) solution by the introduction of *m*-TBPB (2.0×10^{-5} mol/L) followed by anions (5.0×10^{-4} mol/L). These solutions were irradiated by λ_{365} nm UV–Vis light. 1, only $PBPRESO_3Na$; 2, $BPRESO_3Na$ + *m*-TBPB; 3, 2 + Cl^-; 4, 2 + Br^-; 5, 2 + PO_4^{3-}; 6, 2 + F^-; 7, 2 + SO_4^{2-}; 8, 2 + CH_3COO^-; 9, 2 + NO_3^-; 10, 2 + CN^-; 11, 2 + I^-. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

visually under λ_{365} nm UV–Vis light (Fig. 4). The original sky-blue solution of $PBPYRSO_3Na$ turned into a dark solution in the presence of *m*-TBPB revealing ground-state complex formation (low-fluorescence). By adding these anions into the dark solution, the solution containing only cyanide or phosphate anions changes into a light blue solution, which demonstrated that a new complex had been formed and the ground-state complex had largely dissociated with a considerable fluorescence recovery of the original $PBPYRSO_3Na$.

4. Conclusion

In summary, we successfully developed a facile fluorescence ensemble for cyanide and phosphate anions and established a new sensing mode. This two-component sensing ensemble can be applied to the detection of anions in a pure water solution with a reversible fluorescence “off–on” state. This optical ensemble may provide a method for the development of highly sensitive and selective fluorescence ensembles for cyanide, phosphate anions and other analytes.

Acknowledgments

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Appendix A. Supplementary data

Synthetic details, ^1H NMR, ^{13}C NMR, High-resolution mass spectra (HRMS) and other fluorescence spectroscopy (PDF) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.dyepig.2013.01.004.

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