Dalton Transactions

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATIONS

Rational design of a highly sensitive and selective "turn-on" fluorescent sensor for PO_4^{3-} detection

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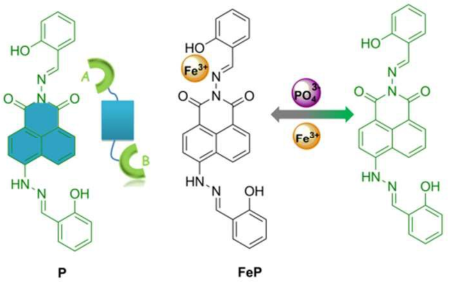
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

An efficient turn-on fluorescent sensor for PO_4^{3-} has been developed by rationally designing an *in situ*-generated iron(III) complex with 1,8-naphthalene-based schiff base unit. The sensor exhibits high sensitivity and selectivity in both solution and solid-state film, even in the presence of other phosphate anions such as HPO_4^{2-} and $H_2PO_4^{-}$.

Rapid and selective detection of a certain ion in aqueous media is of great importance for environmental protection, biological process monitoring as well as disease diagnosis. Among various detection methods, the photoluminescence (PL)-based sensing technique has attracted increasing attention due to its simplicity, sensitivity, cost-effectiveness and short response time.[1] To date, a number of fluorescent/phosphorescent sensors along with the design strategies have been developed for detecting different ions.[2] Phosphate anions (PO_4^{3-}), an integral part of nucleotides, plays crucial roles in signal transduction and energy storage in biological systems.[3] The excess of PO_4^{3-} released into the environment can lead to contamination of the aquatic system.[4] Thereby, development of a sensitive and selective sensor response to phosphate anions is highly desirable. Recently, such sensors based on the emission quenching (turn-off) mechanism have been designed, which requires the materials showing high PL efficiencies.[4a, 5] However, the conventional materials used in the turn-off sensors always undergo aggregation-caused quenching effect in aquatic systems, resulting in drastically negative effects on the efficiency and sensitivity.[6] In contrast, the emission "turn-on" sensors used to detect phosphate anions have been less explored due to lack of design concept, despite they possess the advantage over their turn-off counterparts. For example, the turn-on sensors are less likely to generate false-positive and readily discerned by the naked eye from the dark background.[7] To date, only few turn-on sensors to detect PO_4^{3-} have been reported and they suffer from the relatively poor selectivity. Thus, the development of new materials as the turn-on sensors with high sensitivity and selectivity for detection of PO_4^{3-} still remains a challenge.

It is known that schiff bases are readily obtained by simple synthesis procedures and usually exhibit strong emission in aggregation state.[8] Moreover, they show the excellent ability of recognizing metal ions. It is thus speculated that the turn-on sensors may be achieved if PO_4^{3-} can capture the metal ion from a non-emissive metal-coordinated schiff base complex, resulting in emission. [7b, 9]It will be simple and efficient way to design a turn-on sensor to sense PO_4^{3-}. Keeping this in mind, we herein report the design and synthesis of a 1,8-naphthalene-based schiff base (**P**) with two coordination units (A and B), as shown in Scheme 1. The schiff base can form 1:1 complex with Fe^{3+} ion, namely **FeP**, which is almost non-emissive in the aqueous media as well as solid-state. Interestingly, **FeP** exhibits highly sensitive and selective towards PO_4^{3-}, even in the presence of other phosphate-based anions such as HPO_4^{2-} and $H_2PO_4^{-}$. To our best knowledge, this is the first example of a turn-on sensor used to selectively detect PO_4^{3-}.



Scheme 1. Chemical structure of **P** and **FeP**.

Briefly, the schiff base **P** was synthesized in high yield through a consideration reaction between salicylic aldehyde and 1, 8-naphthalimide derivative. Detailed procedures, characterizations and the excitation and emission spectra of **P** are given in the ESI† (see Fig. S1 and Experiment section). Herein, we choose Fe^{3+} as the metal reource to coordinate with this schiff base due to its excellent coordination ability and effective emission quenching effect.[1c, 9] Naturally, the expected non-emissive complex generates. To test this hypothesis and understand coordination behavior, the titration experiment was carried out in THF–water by adding aliquots of different concentrations of Fe^{3+} ions to the solution of **P**. As shown in Fig. S2†, with increasing concentrations of Fe^{3+}, the PL intensity at 531 nm is gradually diminished and essentially quenched when 1 equiv of Fe^{3+} is added. The effect of 1 equiv of other metal ions on the emissions of **P** is also investigated (see Fig. S3†). Clearly, only Fe^{3+} can effectively form an almost non-emissive complex (**FeP**) with **P** but others exhibit no interference on the luminescent intensity of **P**. The PL quantum yields (PLQY, Φ) of **P** and **FeP** were estimated to be 0.32 and 0.06, respectively.

Although the designed shciff base has two possible chelating sites with metal ions, it is found that the stoichiometric ratio between **P** and **Fe^{3+}** is 1:1, as determined by the titration curve. This result is further supported by the UV-Vis spectra data and Job's plot of the complexation between **P** and Fe^{3+} (see Figs. S4 and S5†). The association constant was calculated to be 9.46×10^{3} M^{-1} according to Benesi-Hildebrand plot (Fig. S6†).[10] For the further materials design and investigation of the binding site, the control experiments using three structurally similar shicff bases **P1**, **P2** and **P3** were performed, respectively (see Fig.S7†). As shown in Fig. S7, the compounds **P2** and **P3** contain the binding site of B and A, which is same as that of **P,** respectively. However, such binding site A or B is absent in compound **P1**. The Fe^{3+} ions have been also added into the solutions of compounds **P1**, **P2** and **P3** for better comparison. Under the same experimental conditions, no obvious emission changes are observed for **P1** and **P2** upon addition of **Fe^{3+}**, however, **P3** exhibits evident emission quenching phenomenon, as shown in Fig. S8†. Therefore, we can conclude that the binding sites between **P** and Fe^{3+} should occur on the point A.

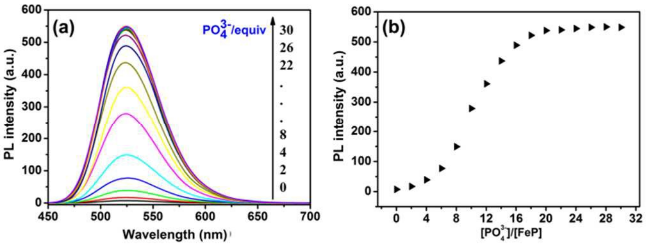


Fig.1 (a) Fluorescence spectra of **FeP** (1.0×10^{-4} M) in the presence of different concentration of PO_4^{3-} ($0–3.0\times10^{-3}$ M) in THF–water (9.5:0.5, v/v) solution. (b) Fluorescence intensity at 531 nm as a function of PO_4^{3-} concentration.

Considering PO_4^{3-} anion could coordinate with Fe^{3+}, the addition of PO_4^{3-} to the solution of **FeP** complex will lead to the release of the emissive **P** due to the competing displacement effect. Thus, **FeP** is supposed to be a potential turn-on sensor with minimum background interference for PO_4^{3-}. To evaluate the utility of **FeP** as a turn-on sensor for PO_4^{3-}, the PL spectra of **FeP** toward different concentrations of PO_4^{3-} were investigated. As shown in Fig. 1, **FeP** maintains an emission "off" state in the mixtures. With increasing proportions of PO_4^{3-}, the PL spectrum of **FeP** is progressively intensified. It was about 80-fold PL enhancement when 30 equiv of PO_4^{3-} was added. The PLQY of the resulting solution is 0.31, which is similar to that of free shciff base **P**. The corresponding detection limit for PO_4^{3-} was estimated to be 1.721×10^{-6} M on the basis of reported methods,[11] indicating the high sensitivity of the sensor (see Fig.S9).

Excepting sensitivity, a given sensor should exhibit the excellent selectivity toward the targeting analytes. To investigate its selectivity, **FeP** was thus treated under identical conditions with other metal ions as well as anions such as Cu^{2+}, Ag^{+}, Ca^{2+}, Cd^{2+}, Fe^{2+}, Ba^{2+}, K^{+}, Mg^{2+}, Pb^{2+}, Mn^{2+}, Zn^{2+} ,Na^{+}, F^{-}, Cl^{-}, Br^{-}, I^{-}, NO_3^{-}, AcO^{-}, SO_4^{2-}, HPO_4^{2-}, $H_2PO_4^{-}$, CO_3^{2-} and HCO_3^{-}. As can be seen from Fig.2a and 2b, no significant change in emission intensity was observed after treatment with other ions. It is known that the ratio of PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^{-}$ usually depends on the pH of the solution. Besides, the PO_4^{3-} and $H_2PO_4^{-}$ are hardly to coexist in the large component due to their intrinsic ionization constants and hydrolysis abilities. From Fig. 2b, it is found that the $H_2PO_4^{-}$ and HPO_4^{2-}have little effect on the emission behaviors of **FeP**. By analyzing the above experiments carefully, we deduced that the unprecedented selectivity of **FeP** towards PO_4^{3-} than other ions, even in the presence of other phosphate-based anions. It is noted that, however, further addition of a small amount of PO_4^{3-} into other ions containing systems result in remarkable emission enhancement. This result clearly demonstrates the unprecedented selectivity of **FeP** for PO_4^{3-} than other ions. The competition experiments were also conducted for the studied system composed of **FeP** and 30 equivalents of $PO_4^{3-}$by adding 100 equivalents of other cations and anions. The emission intensity was almost not affected by a 10-fold excess of other ions (Fig. S10 ESI†). Moreover, the solution colour changed with addition of PO_4^{3-}, which was similar to that of free **P** and evidently observed by naked eyes (see Fig. 3). In the corresponding UV-vis spectra, the characteristic absorption peaks at ca. 332 nm and 452 nm gradually reduce and increase, respectively. The absorption at ca. 452 nm is also slightly blue-shifted upon addition of PO_4^{3-}**.** In other words, **FeP** can be utilized as a colorimetric chemsensor in the same way to detect PO_4^{3-}.

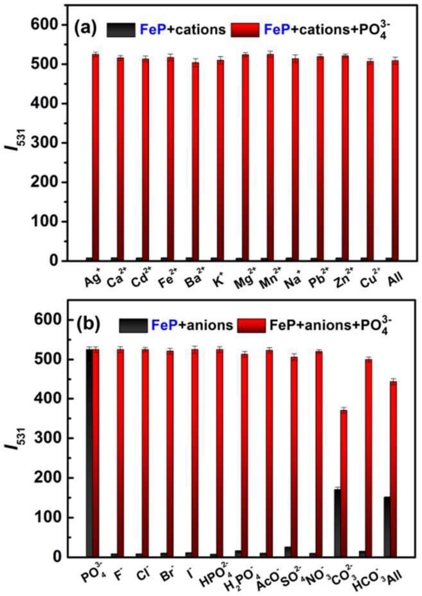


Fig.2 Fluorescence emission spectra (λ = 531 nm) of **FeP** in THF–water mixtures upon addition of various cations (a) and anions (b).

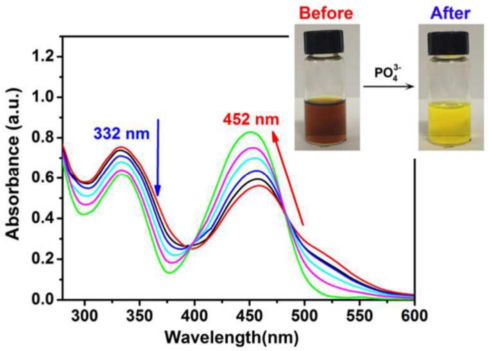


Fig.3. UV–vis spectra of **FeP** (5.0×10^{-5} M) with increasing amounts of PO_4^{3-} in THF–water solution. Inset: naked eye color of **FeP** before and after addition of PO_4^{3-}.

To facilitate the use of **FeP** in the real-world applications, a TLC thin-film was prepared by dip-coating solution of **FeP** on the TLC plate, followed by dying in the air for about 5 min. The resulting TLC plate is non-emissive, as shown in Fig. 4. By dropping the aqueous solutions of PO_4^{3-} with a concentration of 5.0×10^{-3} M on the above TLC plate, the spot on the plate containing PO_4^{3-} shows bright luminescent (see Fig. 4, No. 1). In sharp contrast, other TLC plates treated by the interfering ions still remain dark and no obvious emission is found. To the best of knowledge, this is the first example of a solid film used to sensing PO_4^{3-} in aquenous solution.

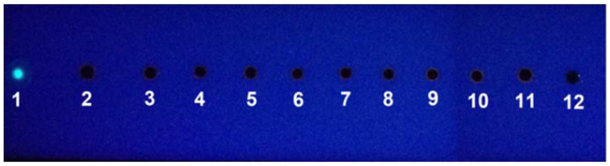


Fig.4 Selective detection of PO_4^{3-} (1) by a **FeP** spot on a TLC plate. Data for other anions are shown for comparison (2, F^-; 3, Cl^-; 4, Br^-; 5, I^-; 6, NO_3^-; 7, AcO^-; 8, SO_4^{2-}; 9, HPO_4^{2-}; 10, $H_2PO_4^-$; 11, CO_3^{2-}; 12, HCO_3^-. Photographs were taken under illuminations of 365 nm UV light.

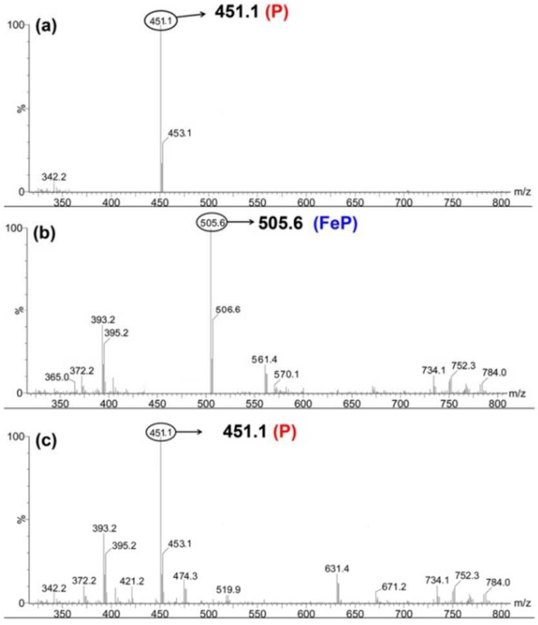


Fig.5 MS-spectra of **P** (a) and **FeP** (b), repectively. (c) MS-spectrum of **FeP** solution after addition of PO_4^{3-} anions.

Due to the above results of good reversible change in emission intensity and color, we propose that the displacement of Fe^{3+} from the **FeP** upon addition of PO_4^{3-} may be attributed to the present turn-on response mechanism. For the purpose of mechanistic understanding, the electrospray source HRMS was studied before and after addition of PO_4^{3-} anion. As shown in Fig. 5, obvious signals (m/z) at 505.6 and 451.1 attributed to the species of $[\mathbf{FeP}+H]^+$ and free shiff base $[\mathbf{P}+H]^+$ are observed respectively, suggesting that **P** forms again when PO_4^{3-} anions are added (see Fig.5a and Fig. 5c). In view of these previous works, herein, we tentatively suppose that the probing mechanism of **FeP** towards PO_4^{3-} is assigned to the PO_4^{3-}-induced displacement effect of **FeP**. Further addition of Fe^{3+} ions into the PO_4^{3-}-containing **FeP** solution, the emission is quenched again, which is also assigned to Fe^{3+} coordinating with **P**. This intrinsic characteristic enables **FeP** to act as a PO_4^{3-} and Fe^{3+} controlled fluorescent switch. The emission "ON" and "OFF" states can be switched by ingenious alternation of PO_4^{3-} and Fe^{3+} ratios. The simple experiment has been performed to testify this issue. By modifying the addition of PO_4^{3-} and Fe^{3+} ions, such switch can be reversibly achieved for several times without any deterioration (Fig. S11, ESI†). In other words, the free **P** can be also an efficient chemical sensor for Fe^{3+} ions. The detection limit of **P** towards Fe^{3+} was estimated to be 1.282×10^{-6} M (Fig. S12, ESI†).

Conclusions

In summary, a 1,8-naphthalene-based schiff base that can efficiently coordinate with Fe^{3+} ions to generate a non-emissive complex, has been rationally designed and synthesized. Benefiting from strong interaction between PO_4^{3-} and obtained complexes, the highly sensitive and selective sensor towards PO_4^{3-} in both solution and solid state is achieved. To our best knowledge, this is the first example of a turn-on sensor used to selectively detect PO_4^{3-}. The sensing mechanism and the structure-properties relationship for such sensor have also been systematically investigated. We hope that the present study will provide a new insight into the development of the effective turn-on type PO_4^{3-} sensors in the future.

The authors gratefully acknowledge the financial support from National Science Foundation of China (NSFC) of Nos. 20703008, 21303012, 21273030 and 21131001 and the Natural Science Foundation of Shandong Province of China (No. ZR2009BL024).

Notes and references

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† Electronic Supplementary Information (ESI) available: the details of synthesis and characterization of the studied complexes; the photophysical properties of Fep towards different ions. See DOI: 10.1039/b000000x/

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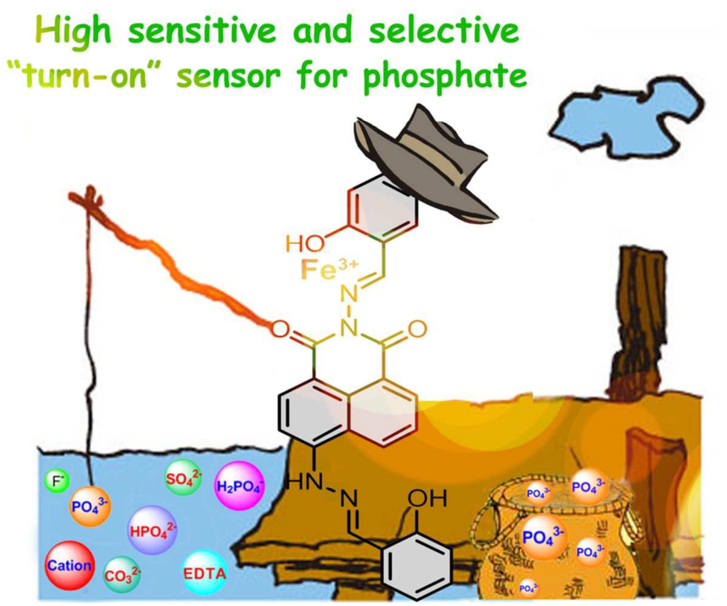

An *in situ*-generated iron(III) complex with 1,8-naphthalene-based schiff base unit has been rationally designed, which exhibits a highly selective response and excellent sensitivity for the turn-on detection of PO_4^{3-} anions.