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**A Water Soluble Fluorescent Chemosensor Based on Asp
Functionalized Naphthalimide for Successive Detection Fe^{3+}
and H_2PO_4^-**

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Complete List of Authors:	Zhang, You-Ming; NW Normal Univ, Chen, Xiao-Peng; College of Chemistry and Chemical Engineering, Northwest Normal University Lanzhou, Liang, Guo-Yan; College of Chemistry and Chemical Engineering, Northwest Normal University Zhong, Kai-Peng; nwnu Yao, Hong; College of Chemistry and Chemical Engineering, Northwest Normal University Lanzhou, Wei, Tai-Bao; College of Chemistry and Chemical Engineering, Northwest Normal University Lanzhou, Lin, Qi; Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China; Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical Engineering, Northwest Normal University,, ;
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3 **H_2PO_4^-**

4 You-Ming Zhang*, Xiao-Peng Chen, Guo-Yan Liang, Kai-Peng Zhong , Hong Yao,
5 Tai-Bao Wei and Qi Lin*

6 *Key Laboratory of Eco-Environment-Related Polymer Materials, Ministry of Education of China;*

7 *Key Laboratory of Polymer Materials of Gansu Province; College of Chemistry and Chemical*

8 *Engineering, Northwest Normal University, Lanzhou, Gansu, 730070. P. R. China*

9
10 *Corresponding author: You-Ming Zhang; Qi Lin*

11 *E-mail :zhangnwnu@126.com; linqi2004@126.com*

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Abstract:

The selective recognition of target ions in water is very important and the development of novel water soluble chemosensor is still an intriguing challenge. Herein, a novel water soluble fluorescent sensor based on aspartic acid (**Asp**) functionalized 1,8-naphthalimide derivative (**Asp-NI**) has been designed and synthesized. The sensor **Asp-NI** could dissolve in water and successively detect Fe^{3+} and H_2PO_4^- in water solution with high selectivity and sensitivity. The detection limits are 4.97×10^{-7} M for Fe^{3+} and 5.27×10^{-6} M for H_2PO_4^- . Other coexistent competitive metal ions (Hg^{2+} , Ag^+ , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Mg^{2+}) showed no interference in the Fe^{3+} detection process. The sensor **Asp-NI** could act as a Fe^{3+} and H_2PO_4^- controlled “On-Off-On” fluorescent switch. More interestingly, the Fe^{3+} induced fluorescence quenching process could be totally reversed by the addition of H_2PO_4^- , this “On-Off-On” switching process could be repeated several times with little fluorescence loss. Notably, the actual usage of sensor **Asp-NI** was further demonstrated by test kits.

Keywords:

water soluble fluorescent sensor; 1,8-naphthalimide derivative; Fe^{3+} recognition; H_2PO_4^- recognition; successive fluorescent detection.

1. Introduction

As we all know, iron ions play a fundamental role in many chemical, biological, medical, environmental and technological processes^[1]. Most of all, in the human body, iron, the most abundant and versatile transition metal in cellular systems^[2], is present in numerous numbers of enzymes and proteins and it is essential for various biological processes^[3], such as oxygen uptake, oxygen metabolism, electron transfer, and transcriptional regulation^[4]. In addition, recognition of bioactive ions has come into limelight since they play significant roles in bioprocesses.^[5] In particular, phosphates are crucial anions since they are used in energy storage devices and signal transducers. Besides, phosphates are also well known anions used in industrial processes^[6]. Hence, the development of new methods for efficient monitoring of iron and H_2PO_4^- is very necessary. Recently, a large number of methods have been reported for detecting Fe^{3+} and H_2PO_4^- , such as, colorimetry^[7], atomic absorption spectroscopy^[8], voltammetry^[9], and spectrophotometry.^[10] Among of these methods, colorimetric and fluorimetric sensors have attracted considerable interest owing to their simple, inexpensive, rapid implementation and high sensitivity^[11]. However, there is still a vexing problem. Generally, most of biological or environmental procedures are carried out in water system, and due to the poor water solubility of chemosensors, most of those couldn't work in aqueous solution or water.^[12,13] Therefore, much attention has been paid to developing Fe^{3+} and H_2PO_4^- sensors that work in the aqueous phase. But, most of the sensors often employ sophisticated structures and complicated synthetic method, and the progress of its targeted detection need high temperature and long reaction time.^[14]

In view of this and as a part of our research effort devoted into ions recognition,^[15] we want to develop a fluorescent chemosensor for efficient detection Fe^{3+} and H_2PO_4^-

in water. Herein, we report the aspartic acid (**Asp**) functionalized 1,8-naphthalimide derivative (**Asp-NI**, Scheme 1), which act as a hydrosoluble fluorescent sensor for the detection of Fe^{3+} and H_2PO_4^- . The strategy for the design of sensor **Asp-NI** as follows. Firstly, we introduced aspartic acid (**Asp**) into the sensor molecular as a hydrophilic group, which can enhance the water-solubility of sensor **Asp-NI**. Moreover, the aspartic acid moiety employ two carboxyl groups act as binding sites for iron ions. Secondly, owing to the excellent optical properties of 1,8-naphthalimide derivatives, we introduced 1,8-naphthalene dicarboxylic anhydride groups as the signal groups to achieve fluorescent recognition. Finally, the sensor **Asp-NI** is designed easy to make, the synthesis process of the sensor only need one step reaction. As a results, the nice thing here is that the sensor **Asp-NI** could successively detect Fe^{3+} and H_2PO_4^- in water solution with high selectivity and sensitivity.

(Insert Scheme 1)

2. Experimental

2.1 Materials and instruments

All reagents and solvents were commercially available at analytical grade and were used without further purification. Fresh double distilled water was used throughout the experiment. ^1H NMR spectra were recorded on a Mercury-400BB spectrometer at 600 MHz and ^{13}C NMR spectra were recorded on a Mercury-400BB spectrometer at 150 MHz. Chemical shifts are reported in ppm down field from tetramethylsilane (TMS, δ scale with solvent resonances as internal standards). Infrared spectra were performed on a Digilab FTS-3000 FT-IR spectrophotometer. Mass spectra were recorded on an esquire 6000 MS instrument equipped with an electrospray (ESI) ion source and version 3.4 of Bruker Daltonics Data Analysis as the data collection system.

2.2 General procedure for fluorescence experiments

All fluorescence spectra were recorded on a Shimadzu RF-5301 fluorescence spectrometer after the addition of perchlorate metal salts in water, while keeping the ligand concentration constant (2.0×10^{-5} M). The excitation wavelength was 330 nm. Solutions of metal ions were prepared from the perchlorate salts of Fe^{3+} , Hg^{2+} , Ag^{+} , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Mg^{2+} (4×10^{-4} M). Solutions of anions were prepared from tetrabutylammonium salt of anions (F^{-} , Cl^{-} , Br^{-} , I^{-} , AcO^{-} , $\text{H}_2\text{PO}_4^{-}$, HSO_4^{-} and ClO_4^{-}) and sodium salt of anions (CN^{-} and SCN^{-}).

2.3 Synthesis and characterization of sensors Asp-NI

A mixture of 1,8-naphthalenedicarboxylic anhydride (1.98 g, 10 mmol) and aspartic acid (1.331 g, 10 mmol) in DMF (20 mL) was stirred at 140°C reflux for 24 h. After cooling to room temperature, water (50 mL) was added and the precipitate was filtered, washed three times with hot DMF, then get light yellow powder product **Asp-NI1** (2.31 g). Then, the **Asp-NI1** (5 mmol, 0.156 g) and sodium hydroxide (10 mmol, 0.40 g) were dissolved in water (50 mL). The reaction mixture was stirred for 30 minutes under room temperature. Then the water (50 mL) was evaporates by drying oven to afford the desired product; N,N-bis (1,8-naphthalene dicarboxamide) aspartic sodium salt, that is the sensor molecule **Asp-NI**.

Asp-NI1: yield: 74%; m.p. , 254°C ; ^1H NMR (D_2O , 400 MHz, ESI, Fig. S1†) d 8.37-8.35 (2H, ArH), d 8.19-8.18 (2H, ArH), d 7.65-7.64 (2H, ArH) 5.82-5.79 (1H, CH) 3.09-3.06 (1H, CH_2) 2.84-2.80 (1H, CH_2). ^{13}C NMR (D_2O , 400 MHz, ESI, Fig. S2†) d 179.89, 176.99, 165.54, 134.98, 134.57, 134.54, 129.94, 127.98, 127.56, 126.95, 125.68, 125.06, 121.36, 53.89, 38.43. IR (KBr, cm^{-1} , ESI, Fig. S3†) v: 3437,

(-OH); 1699, (COOH, C=O); 1656, (C=O) ; 1238, (-N-CH) cm^{-1} . In the IR spectra of **Asp-NI**, upon the addition of Fe^{3+} , the stretching vibration absorption peaks of carboxyl shifted from 1699 cm^{-1} to 1651 cm^{-1} as show in ESI, Fig. S4† ESI-MS m/z: [**Asp-NI** +H] $^{+}$. Cold for $\text{C}_{16}\text{H}_{11}\text{NO}_6$ 313.0586; Found 313.0540, (ESI, Fig. S5†).

3. Results and Discussion

In order to investigate the ions recognition capacity of the sensor **Asp-NI** in pure water, a series of recognition experiments were carried out. The recognition profiles of the chemosensor **Asp-NI** toward various metal ions, including Fe^{3+} , Hg^{2+} , Ag^{+} , Ca^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} , Cd^{2+} , Pb^{2+} , Zn^{2+} , Cr^{3+} and Mg^{2+} were primarily investigated using fluorescence spectroscopy in water. As shown in Fig. 1, in the fluorescence spectrum, the emission of **Asp-NI** appeared at the maximum emission wavelength was 385 nm in pure water when excited at 330 nm. When 20 equivalents of Fe^{3+} (4×10^{-4} M) and the other cations were added to the water solution of sensor **Asp-NI**, respectively. Only the Fe^{3+} could induce the solution of sensor **Asp-NI** fluorescent quenching, other competitive metal ions couldn't induce similar response. Moreover, as shown in Fig. 2a, the photographs show the change in the fluorescence of **Asp-NI** after the addition of various metal ions in water.

(Insert, Fig. 1 and Fig. 2a)

Interestingly, the quenched fluorescence of **Asp-NI** in solutions by Fe^{3+} was turned on after addition of $\text{H}_2\text{PO}_4^{-}$. To evaluate the $\text{H}_2\text{PO}_4^{-}$ selective nature of the **Asp-NI-Fe** $^{3+}$ complex, the influence of other anions such as F^{-} , Cl^{-} , Br^{-} , I^{-} , AcO^{-} , CN^{-} , HSO_4^{-} , ClO_4^{-} , CN^{-} and SCN^{-} was investigated. (Fig. 2b) Interestingly no significant change in fluorescence emission was observed with other anions. The resulting **Asp-NI-Fe** $^{3+}$ complex showed high selectivity for $\text{H}_2\text{PO}_4^{-}$ in the same media as well

(Figure 3).

(Insert Fig. 2b and Fig. 3)

The binding affinity of sensor **Asp-NI** with Fe^{3+} was estimated by performing emission titration experiments when excited at 330 nm. The sensor **Asp-NI** showed strong fluorescence at 385 nm. As shown in Fig.4, upon the addition of increasing concentrations of Fe^{3+} (0-20 equiv.), the emission peak at 385 nm gradually diminished intensity, and the fluorescence of **Asp-NI** was essentially quenched by 20 equiv. of Fe^{3+} , moreover the signal saturation was observed. The detection limit of the sensor towards Fe^{3+} , obtained according to fluorescence titration on the basis of $3S_B/S$, was $4.97 \times 10^{-7} \text{ M}^{[16]}$ (Fig. S6 in the ESI). The binding constants for the formation of the respective complexes were evaluated using the Benesi - Hildebrand (B - H) plot^[17].

$$1/(I - I_0) = 1/\{K(I_{\text{max}} - I_0)C\} + 1/(I_{\text{max}} - I_0)$$

I_0 is the emission intensity of Asp-NI at emission maximum ($\lambda = 396 \text{ nm}$), I is the observed emission intensity at that particular wavelength in the presence of a certain concentration of the metal ion (C), I_{max} is the maximum emission intensity value that was obtained at $\lambda = 396 \text{ nm}$ during titration with varying metal ion concentration, K is the binding constant (M^{-1}) and was determined from the slope of the linear plot, and C is the concentration of the Fe^{3+} ion added during titration studies. The binding constant for the formation of the Asp-NI- Fe^{3+} complex was calculated on the basis of the change in emission at 385 nm by considering a 1 : 1 binding stoichiometry. The binding constant (K) determined by the B-H method was found to be $2.9 \times 10^4 \text{ M}^{-1}$.

(Insert Fig. 4)

To further exploit the utility of the chemosensor **Asp-NI** as an ion-selective sensor for Fe^{3+} , competitive experiments were carried out in the presence of 20 equiv. of Fe^{3+}

154 and 20 equiv. of various cations in pure water. As shown in Fig. 5, it is noticeable that
155 the miscellaneous competitive cations did not lead to any significant interference. The
156 fluorescence selectivity was examined at an excitation wavelength of 330 nm, and
157 none of the competing cations interfered in the detection of Fe^{3+} . This result displays
158 the highly selectivity of the sensor **Asp-NI** toward iron over the other analytes
159 mentioned above. Further, the interference experiments were carried out to study the
160 selectivity of **Asp-NI**. The fluorescence spectroscopy was carried out just after the
161 addition of KCl and NaCl in water solution. As shown in Figure S7, the fluorescence
162 emission peak at 385 nm was no obvious changed compare with the solution of free
163 **Asp-NI**. The result indicated that the existence of Na^+ , K^+ have not interference with
164 identification process of **Asp-NI** to Fe^{3+} . Then we added the solutions of KHCO_3 and
165 KNO_3 to **Asp-NI** + Fe^{3+} . As shown in Figure S11, the sensor behavior of H_2PO_4^- to
166 **Asp-NI** + Fe^{3+} could not be influenced even existence the HCO_3^- and NO_3^- . All these
167 facts confirmed that **Asp-NI** can be capable of selectivity and sensitivity detection
168 Fe^{3+} .

169 (Insert Fig. 5)

170 Moreover, the pH dependence of the **Asp-NI** in the HEPES buffer system was
171 verified using fluorescence spectroscopy, as shown in Fig.6, Fe^{3+} detection was
172 successful in the pH ranged from 2.0 to 10.0 in HEPES buffered solution.

173 (Insert Fig. 6)

174 The reversibility of the sensor was tested by addition of various anions to the
175 **Asp-NI-Fe³⁺** solution. The addition of H_2PO_4^- to the solution of **Asp-NI-Fe³⁺** showed
176 the detection process of the sensor **Asp-NI** for Fe^{3+} is reversible, and the reversible

process could be repeated at several times with the little fluorescent efficiency loss. (Fig. 7) Thus, the sensor **Asp-NI** could act as not only a reversible Fe^{3+} and H_2PO_4^- sensor, but also a Fe^{3+} and H_2PO_4^- controlled “On-Off-On” fluorescent switch. Besides, the reversibility of the chemosensor is a very important aspect for its practical application. To further investigate the practical applications of chemosensor **Asp-NI**, test strips were fabricated by immersing filter paper into water of **Asp-NI** (2×10^{-3} M) followed by drying them in air. The test strips containing **Asp-NI** were utilized to sequential sense Fe^{3+} and H_2PO_4^- . As shown in Fig. S8, when Fe^{3+} was first added to the test strips, an obvious color change was observed. After the addition of H_2PO_4^- the color of the test strips recovered, which served as a convenient and efficient sequential Fe^{3+} and H_2PO_4^- test kits. which indicated that the test strips could act as a recyclable test kits for sequential detection of Fe^{3+} and H_2PO_4^- .

(Insert Fig. 7)

As **Asp-NI** showed specific selectivity for Fe^{3+} and H_2PO_4^- in water, a series of experiments such as Job’s method, IR, and MS were carried out to investigate the Fe^{3+} and H_2PO_4^- recognition capability and mechanism of the sensor **Asp-NI**. To gain an insight into the stoichiometry of the **Asp-NI-Fe** $^{3+}$ complex, the method of continuous variations (Job’s method) was used (Fig. 8). As expected, when the molar fraction of sensor **Asp-NI** was 0.50, the absorbance value approached a minimum, which demonstrated the formation of a 1:1 complex between the sensor **Asp-NI** and Fe^{3+} .

(Insert Fig. 8)

The practical utility of the probe was carried out by detection of Fe^{3+} in tap water. As shown in Fig. 9 and S9, firstly, the standard curve of the **Asp-NI** for Fe^{3+} was obtained by fluorescent titration of **Asp-NI** solutions with different concentrations Fe^{3+} (5.0×10^{-7} M, 1.0×10^{-6} M, 1.5×10^{-6} M, 2.0×10^{-6} M, 2.5×10^{-6} M, 3.0×10^{-6} M,

3.5 $\times 10^{-6}$ M, 4.0 $\times 10^{-6}$ M). Then, the concentration of Fe³⁺ in tap water was investigated by standard curve method and obtained as 1.42 $\times 10^{-6}$ M. In order to verify this result, we also used inductively coupled plasma (ICP) experiments to measure the concentration of Fe³⁺ in tap water. The ICP results show that the concentration of Fe³⁺ in tap water is 1.09 $\times 10^{-6}$ M, which supported the result obtained by standard curve method. Moreover, the special advantage of this sensor is water soluble. A comprehensive comparison on synthetic method of probe, suitable solvents, and LOD (limit of detection) of the probe **Asp-NI** with reported probes were listed in Table S1.

(Insert Fig. 9)

The recognition mechanism of the sensor **Asp-NI** with Fe³⁺ was also investigated by IR spectra. In the IR spectra of **Asp-NI** (ESI, Fig. S3†), upon the addition of Fe³⁺, the stretching vibration absorption peaks of carboxyl shifted from 1699 cm⁻¹ to 1651 cm⁻¹ as show in ESI, Fig. S4†, which indicated that **Asp-NI** complexed with Fe³⁺ via the carboxyl group of **Asp-NI** (Scheme 2). In addition, the ESI Mass results are in good agreement with this finding. The peak at m/z 312.0940 (Fig. S5) is corresponding to [**Asp-NI** + H]⁺ and the peak at m/z 736.9666 demonstrate the presence of [**Asp-NI** + Fe³⁺ + 3(ClO₄⁻) + DMF] (ESI, Fig. S11). According to the Job's method, IR and ESI Mass, the ions response mechanism of **Asp-NI** with Fe³⁺ and H₂PO₄⁻ could be presumed as Scheme 2.

(Insert Scheme 2)

4. Conclusions

In conclusion, we rationally design and synthesis a water-soluble, easy-to-make and efficient Fe³⁺ fluorescent sensor **Asp-NI**. By rationally introduce carboxyl moiety into 1,8-naphthalimide-based chemosensor molecular, the obtained chemosensor shown well solubility in water and specific fluorescent selectivity for Fe³⁺ and H₂PO₄⁻ in

water. The detection limits are 4.97×10^{-7} M for Fe^{3+} and 5.27×10^{-6} M for H_2PO_4^- (ESI, Fig. S11†). Other ions had nearly no significant influence on the sensing behavior, which indicated that the sensor **Asp-NI** may be useful as a sensor for monitoring Fe^{3+} levels in biological, medical, environmental and technological systems. Interestingly, the sensor **Asp-NI** could act as not only a reversible Fe^{3+} sensor, but also a Fe^{3+} and H_2PO_4^- controlled “On-Off-On” fluorescent switch. The distinct color changes under UV light (365 nm) and rapid reversible fluorescent changes can be detected by the naked eye. More interestingly, the Fe^{3+} induced fluorescence quenching process could be totally reversed by the addition of H_2PO_4^- , this “On-Off-On” switching process could be repeated several times with little fluorescence loss. Notably, the actual usage of sensor **Asp-NI** was further demonstrated by test kits.

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Scheme 1 Synthesis of the chemosensors **Asp-NI**.

Fig.1 Fluorescent emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) spectra of **Asp-NI** ($2 \times 10^{-5} \text{ M}$) with various cations in water in response to Fe^{3+} (20 equiv).

Fig. 2 The change in the fluorescence of (a) **Asp-NI** ($2 \times 10^{-5} \text{ M}$) after the addition of cations ($4 \times 10^{-4} \text{ M}$) in water. (b) **Asp-NI-Fe³⁺** ($2 \times 10^{-5} \text{ M}$) after the addition of various anions ($2 \times 10^{-5} \text{ M}$) in water under 365nm UV light.

Fig. 3 Fluorescent emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) spectra of **Asp-NI-Fe³⁺** ($2 \times 10^{-5} \text{ M}$) with various anions in water in response to H_2PO_4^- (20 equiv.).

Fig.4 Fluorescence emission spectra of **Asp-NI** ($2 \times 10^{-5} \text{ M}$) in the presence of different concentration of Fe^{3+} anions (0.00–20.00 equiv.) in pure water. Inset: A plot

of fluorescent intensity depending on the concentration of cyanide in the range from 0 to 20 equivalents. ($\lambda_{\text{em}} = 385 \text{ nm}$)

Fig. 5 Fluorescence of sensor **Asp-NI** ($2 \times 10^{-5} \text{ M}$) at 385 nm with addition of 20 equiv. of Fe^{3+} in the presence of 20 equiv. of other anions in water solution. ($\lambda_{\text{ex}} = 330 \text{ nm}$)

Fig. 6 Effect of pH on the fluorescence spectra (385 nm) of Fe³⁺ (20 equiv.) from 2.0 to 13.0 in water solution. ($\lambda_{\text{ex}} = 330 \text{ nm}$)

Fig. 7 Fluorescent emission ($\lambda_{\text{ex}} = 330 \text{ nm}$) spectra showing the reversible complex between **Asp-NI** ($2 \times 10^{-5} \text{ M}$) and Fe^{3+} (20 equiv.) by introduction of H_2PO_4^- (20 equiv.) in water solution.

Fig. 8 The Job's plot examined between Fe^{3+} and Asp-NI, indicating the 1:1 stoichiometry, which was carried out by fluorescence spectra ($\lambda_{\text{ex}} = 330 \text{ nm}$, $\lambda_{\text{em}} = 385 \text{ nm}$).

Fig. 9 The Fe^{3+} concentration and fluorescence intensity function diagram. ($\lambda_{\text{em}} = 385 \text{ nm}$).

Scheme 2 The proposed mechanism of Asp-NI bonding with the Fe^{3+} in DMF solution.