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A Chemosensor for Fe^{3+} Detection Derived from Pyrene

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Abstract

It is of great significance to find a suitable method to detect Fe^{3+} due to its essential role in human and animal health. Artificial chemosensors have been a suitable method in view of simple preparation, fast response, et al. [Aim]: A selective Fe^{3+} chemosensor was designed. [Method]: A novel Fe^{3+}-selective chemosensor was rationally designed based on pyrene derivative by the introduction of benzoyl hydrazine. [Results] The proposed chemosensor presented the good selectivity for Fe^{3+} in prescence of other common metal ions. [Conclusions]: The proposed idea can be used for reference to enrich chemosensors.

Keywords: Fe^{3+}; Chemosensor; Turn on.

1. Introduction

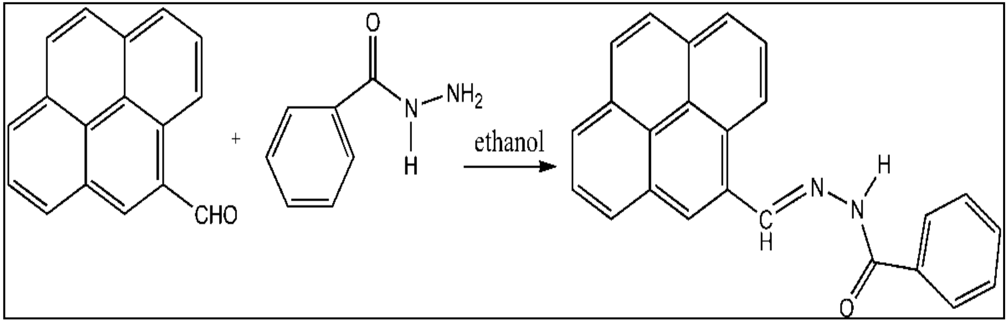
Fe^{3+} plays an essential role in human and animal health, which becomes apparent with recognition of Fe^{3+} as a body constituent and understanding of the relationship between intake and certain diseases[1, 2]. It is widely known that deficiencies or excesses of Fe^{3+} are toxic or can lead to a variety of diseases, such as Parkinson's disease and Alzheimer's disease [3, 4]. Therefore, it is of great significance to find a suitable method to detect this biologically important and cytotoxic ion in biological and environmental concerns.

In recent years, considerable efforts have been devoted to the development of artificial chemoensors due to their nondestructive and prompt detection by a simple signal response [5-7]. Which is applied broadly to detect some biologically and environmentally important ionic species, especially heavy transition-metal (HTM) ions [7-10].

The chemosensor comprises a signal unit and an identification unit, the former is used for selective binding with target molecules, while the latter shows this binding through specific signal forms. The design idea of our chemosensor is as follows: 1) Pyrene is used as the signal element in view of its excellent photophysical properties and easy modification on the molecular structure [11, 12]. Meanwhile, construction of C=N isomerization by Schiff base reaction has been used as the recognition mechanism in photophysical process because it is easy to design "off-on" chemosensors by some simple organic preparations. Particularly, the chelating group C=N displays good affinity for heavy metal ions [13, 14]. O and N atoms are excellent coordination units which have rich lone pair electrons. In the structure of Schiff base, O atom of the carbonyl group (-C=O), N atom of the imine group (-N=CH) could participate in coordination with metal ions [15-20], and consequently produce stable coordination complexes according to hard and soft acid base theory [21].

Inspired by this platform, a selective Fe^{3+} chemosensor based on pyrene derivative was synthesized as shown in Scheme 1.

Scheme-1. The synthetic route of chemosensor P



2. Experimental Section

2.1. Reagents and Instruments

All reagents and solvents are of analytical grade and used directly.

Absorption spectra were measured by a Hitachi U-2910 spectrophotometer. Electrospray ionization (ESI) analyses were performed on a Thermo TSQ Quantum Mass Spectrometer. Nuclear magnetic resonance (NMR) spectra were measured with a Brucker AV 400 instrument and chemical shift were given in ppm from tetramethylsilane (TMS).

2.2. Synthesis of P

Benzoyl hydrazine (0.0370 g, 0.027 mmol) and 1-pyrenecarboxaldehyde (0.065 g, 0.28 mmol) were mixed in ethanol (40 mL). The reaction mixture was stirred and refluxed for 4 h, and then cooled slowly to room temperature. Precipitate so produced was obtained by filtering and washed with ethanol, which was used directly. MS (ESI+) *m*/*z*: 349.28 $[M+H]^+$. ^1H NMR (d_6-DMSO): 12.01 (s, 1H), 10.75 (s, 1H), 9.47 (s, 1H), 9.32 (d, 1H), 8.75 (d, 1H), 852 (t, 1H), 8.39 (t, 1H), 8.30 (d, 2H), 8.19 (t, 2H), 8.13 (d, 1H), 8.06, (t, 1H), 7.97 (d, 2H), 7.57 (d, 1H), 7.54 (d, 1H). ^{13}C NMR (d_6-DMSO): 194.26, 163.57, 147.07, 133.97, 132.40, 131.45, 131.37, 131.16, 0.65, 129.29, 129.11, 128.93, 128.16, 127.93, 127.80, 127.45, 127.13, 126.64, 126.29, 125.78, 125.55, 125.40, 124.67, 124.29, 123.07, 122.92.

2.3. General Spectroscopic Methods

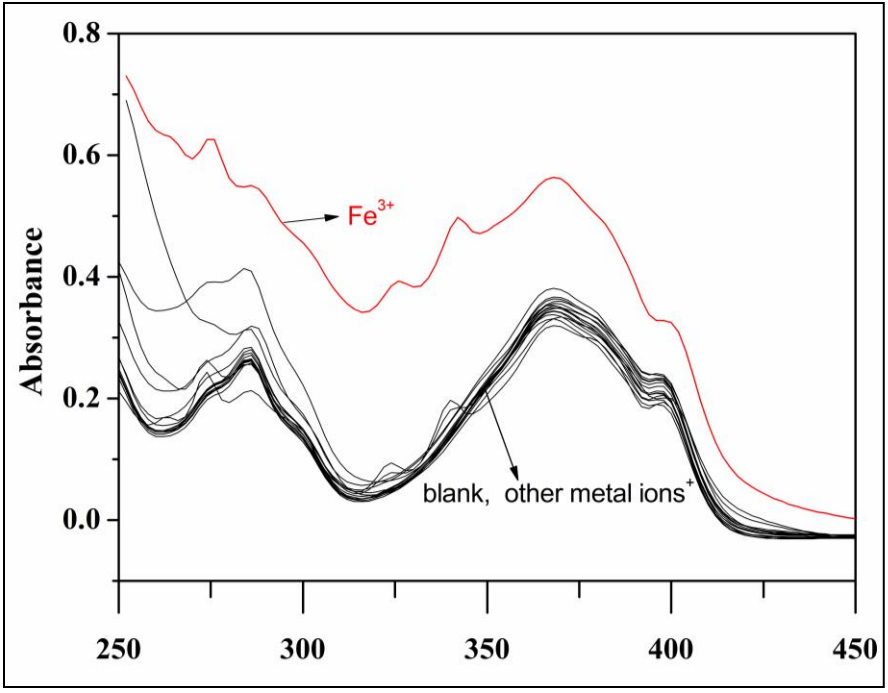
The absorption spectra were measured at room temperature. Test solutions were prepared by adding 25 μL the chemosensor stock solution (2 mM) and an appropriate volume of each analyte into a test tube, and then diluting the solution to 5 mL with ethanol.

3. Results

3.1. Selectivity of P

Absorption spectra of P in prescence of various common metal ions were illustrated in Fig. 1. In the wavelength range of 250 nm to 450 nm, free P exhibited three absorption bands with peaks at 368 nm, 325 nm and 280 nm. When 100 μM of metal ions, such as Hg^{2+}, Ag^+, Ni^{2+}, Cu^{2+}, Co^{2+}, Ca^{2+}, Na^+, K^+, Mg^{2+}, Al^{3+}, Cd^{2+}, Cr^{3+}, Zn^{2+}, Ba^{2+}, Pb^{2+} and Fe^{3+} was added to the ethanol solution of P, it was found that only Fe^{3+} triggered an appreciable spectral increase change at 368 nm, 325 nm and 280 nm, other metal ions did not show any obvious absorption change under similar conditions.

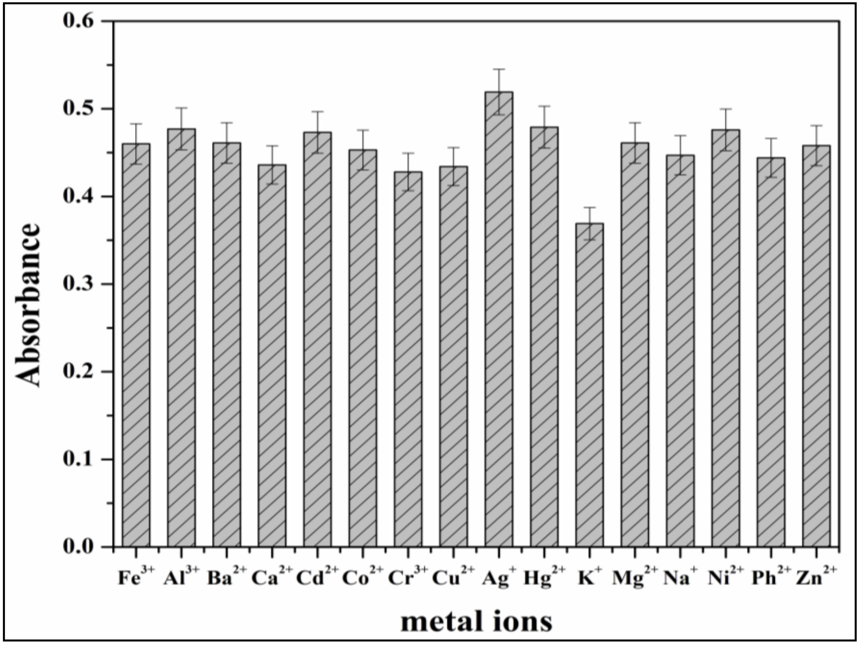
Fig-1. The UV absorption spectra of various metal ions (100 μM) added to chemosensor P (10 μM) in ethanol



3.2. Competitive Capacity of P

In order to explore the potential application to real samples, the interference from other metal ions was measured. The competition experiments by adding 10 μM Fe^{3+} to P solution in the presence of other metal ions with 100 μM were illustrated in Fig. 2. The absorbance at 368 nm as the standard was adopted, which showed that the absorbance responses at 368 nm by the Fe^{3+}-induced reaction with P was not suppressed by other above-mentioned metal ions.

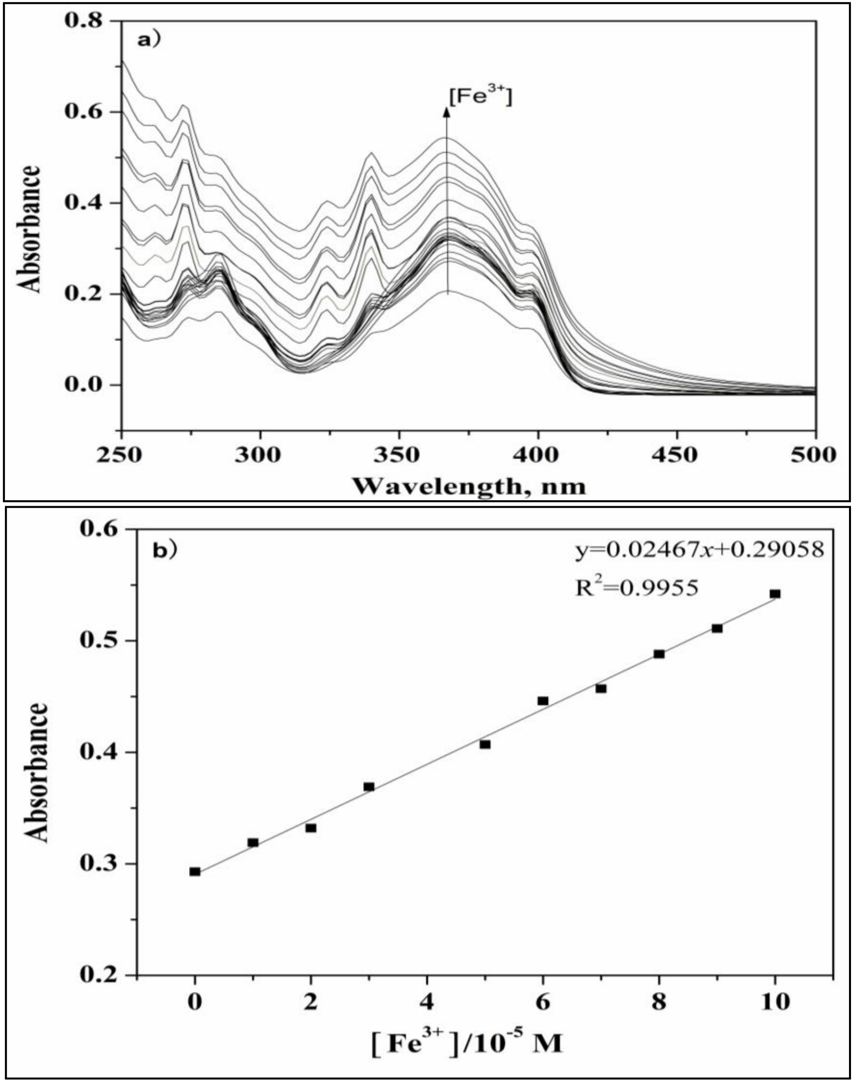
Fig-2. Absorption response of P (10 µM) to 10 µM Fe^{3+} or 100 µM of other metal ions with 10 µM of Fe^{3+} in ethanol



3.3. Sensitivity of P

Furthermore, absorption titrations of P upon addition of different concentration of [Fe^{3+}] were conducted in Fig. 3. With increasing [Fe^{3+}], the absorbance gradually increased at a broad absorption band in the range of 250 nm to 400 nm as seen in Fig. 3a.

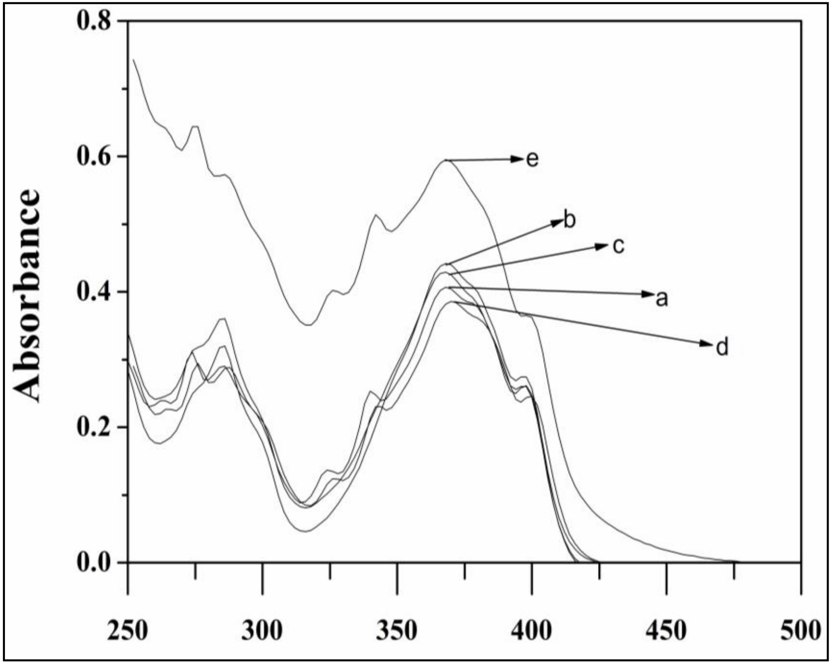
Fig-3.a) Absorption spectra of chemosensor P (10 µM) upon addition of different concentrations of Fe^{3+} (0-100 µM) in ethanol; b) A linear correlation with P (10 µM) upon addition of Fe^{3+} (10-100 µM)



3.4. Reversibility of P

The reversibility of P by EDTA as reagent to explore the potential for practical recycling was conducted as shown in Fig. 4.

Fig-4. The reversibility of P in ethanol: a) P (10 μM); b) P (10 μM) + Fe^{3+} (10 μM); c) P (10 μM)+Fe^{3+} (10 μM) + EDTA (10 μM); d. P (10 μM) + Fe^{3+} (10 μM) + EDTA (100 mM); e) P (10 μM) + Fe^{3+} (10 μM) + EDTA (10 μM) + Fe^{3+} (100 μM)



4. Discussion

4.1. Selectivity of P

These results demonstrated the binding between P and Fe^{3+} from absorption spectra of P. Meanwhle, as is well-known that Fe^{3+}-selective “off-on” chemosensor was favored over those showing “on-off” for analytes in the matter of interference factor, sensitivity, background concerns [22-25]. The designed chemosensor had some advantages.

4.2. Competitive Capacity of P

In order to explore the potential application to real samples, the interference from other metal ions was measured. The results revealed that the chemosensor had the prospect of application in the complicated medium.

4.3. Sensitivity of P

The absorbance at 368 nm was well proportional to a [Fe^{3+}] -dependent way (10-100 μM), which displayed with R^2=0.9955, and also the desired detection limit with 3.3 μM in ethanol as demonstrated in Fig. 3b. The results showed that the chemosensor can be used for qualitative and quantitative determination of Fe^{3+}.

4.4. Reversibility of P

The reversibility of P by EDTA displayed that the chemosensor P had somewhat stronger binding force toward Fe^{3+} than that of EDTA, which was proved that chemosensor P had certain reversibility.

5. Conclusions

In summary, a new simple pyrene derivative was developed to be a chemosensor, which could specifically recognize Fe^{3+} over other common metal ions. Furthermore, it also showed a “turn-on” type response.

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