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A novel Cr^{3+} turn-on probe based on naphthalimide and BINOL framework

Shengying Wu, Kewei Zhang, Yefeng Wang, Dan Mao, Xin Liu, Jianjun Yu, Limin Wang *

Key Laboratory for Advanced Materials and Institute of Fine Chemicals, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, PR China

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ABSTRACT

Naphthalimide and BINOL framework based fluorescent probe NP-B was rationally designed and synthesized. NP-B exhibited 'turn-on' fluorescence for Cr^{3+} and high selectivity over other metal ions. 1:1 binding mode between NP-B and Cr^{3+} was proposed and the mode was verified through MALDI-TOF mass spectrum. The detection limit was calculated to be 0.20 μM, which indicated the good sensitivity for Cr^{3+}.

Trivalent chromium (Cr^{3+}) is an essential nutrient for humans and plays an important role in the metabolism of carbohydrates, lipids, proteins, and nucleic acids.[1] Insufficient intake of Cr^{3+} increases the risk for diabetes[2] and cardiovascular diseases,[3] whereas excessive intake causes genotoxic effects.[4] Accurate and rapid determination of Cr^{3+} amount in the environment is therefore necessary. Traditional analytical methods for Cr^{3+} employ expensive instruments such as atomic absorption spectrometry[5] and inductively-coupled plasma atomic emission spectrometry.[6] Although these methods enable accurate and specific detection of Cr^{3+}, they are usually time-consuming and require complicated and tedious sample preparation.[7]

The fluorescence method has more advantages over above-mentioned methods such as facile operation, high selectivity, enhanced sensitivity, rapid and high frequency sample detection, nondestructive methodology, enhanced sensitivity, high sampling frequency and low cost of equipment, and direct visual perception.[8] For example, an efficient fluorescent sensor in a recent report has shown high selectivity toward the target ion with a significant fluorescent intensity change observed.[9]

Thus, the detection and estimation of Cr^{3+} always constitute an active area of research.[10] Although a lot of chemosensors for Cr^{3+} have been developed, most of them are turn-off chemosensors for Cr^{3+} due to the paramagnetic nature of Cr^{3+}.[11] Turn-off sensors showed poor sensitivity and selectivity for the cations,[12] comparing with turn-on chemosensors. Furthermore, naphthalimide and its derivatives are widely employed in the construction of chemosensors.[13] So far, few fluorescent probes for Cr^{3+} based on the naphthalimide and BINOL derivatives are reported. Herein, we designed and synthesized a new highly selective and turn-on fluorescent probe for detection of Cr^{3+} based on naphthalimide derivative.

The synthesis of NP-B was started from [1,1′-binaphthalene]-2,2′-diol (BINOL) and 4-bromo-1,8-naphthalic anhydride, as shown in **Scheme 1**. **A4**[14] and **B3**[15] have been synthesized from [1,1′-binaphthalene]-2,2′-diol (BINOL) or 4-bromo-1,8-naphthalic anhydride according to literature procedures, respectively. **A4** and **B3** were condensed to furnish the desired Schiff base NP-B as a yellow solid in 96% yield. Metal ions are readily avaliable from corresponding chloride, nitrate, sulfate, or perchlorate salts.

The interaction of probe NP-B with the cations was investigated through fluorescence spectra. All the fluorescence behavior of probe NP-B was studied in THF/H_2O solutions (85/15, v/v). Fluorescence titration of NP-B with Cr^{3+} was performed and the responding spectra are shown in Figure 1. Free NP-B exhibited a slight fluorescence response with a maximum at 491 nm ($\Phi = 0.08$), due to efficient photoinduced electron transfer (PET) process from the electro-rich receptor to the excited NP-B fluorophore. Upon addition of Cr^{3+}, fluorescence enhancement and a red-shift of emission band centered at 498 nm could be observed ($\Phi = 0.27$). The fluorescence enhancement was attributed to the formation of a NP-B/Cr^{3+} complex and PET mechanism was quenched, while the red-shift to 498 nm was caused by a change of the internal charge transfer process (ICT). A continuous enhancement of fluorescence intensity could be observed along

* Corresponding author. Tel./fax: +86 21 64253881.
E-mail address: wanglimin@ecust.edu.cn (L. Wang).

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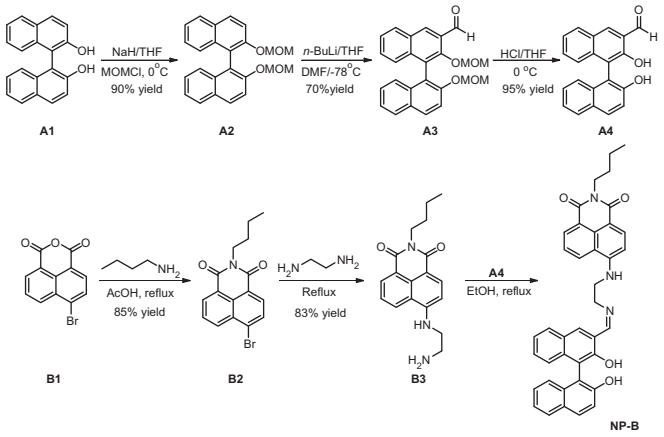


Scheme 1. The synthetic route of NP-B.

with the increasing of the Cr^{3+} concentration (Fig. 1) and this enhancement was saturated upon the addition of 14 equiv of Cr^{3+}.

Figure 2 shows there was a good linearity between the emission at 498 nm and concentrations of Cr^{3+} in the range from 20 to 120 μM, indicating that sensor NP-B can detect nearly quantitatively relevant concentrations of Cr^{3+}. The linear equation was found to be $y = 34.9645x + 165.2441$ ($R^2 = 0.9979$), where y was the emission at 498 nm measured at a given Cr^{3+} concentration and x represented the concentration (10^{-5} mol/L) of Cr^{3+} added. According to IUPAC, the detection limit was determined from three times the standard deviation of the blank signal (3s) as 0.20 μM. The result indicated that NP-B was sensitive to Cr^{3+}.

In order to further understand the coordination of NP-B with Cr^{3+}, MALDI-TOF-MS was carried out (Fig. S4). The unique signal at $m/z = 679.1392$ corresponding to $[probe + Cr\text{-}3H + Na]^+$ was clearly observed when 14 equivalents of Cr^{3+} was added to NP-B, whereas NP-B without Cr^{3+} exhibited a different signal at $m/z = 608.2547$ (calcd for 608.2549) (Fig. S3).

Figure 3 shows the fluorescence spectra ($\lambda_{ex} = 420$ nm) of NP-B (1×10^{-5} M) measured in THF/H_2O (85/15, v/v) with a buffer solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 10 mM, pH = 7.0), with 14 equiv of respective metal cations such as Ca^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Na^{+}, K^{+}, Al^{3+}, and Cr^{3+}. Without cations, NP-B showed weak fluorescence due to efficient photoinduced electron transfer (PET) process from the electron-rich receptor to the excited NP-B fluorophore. After addition of Cr^{3+}, the PET mechanism was

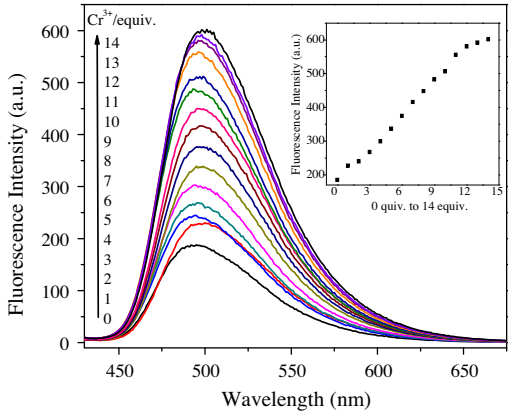


Figure 1. Fluorescence spectra of NP-B (1×10^{-5} M) in THF/H_2O (85/15, v/v) with a buffer solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 10 mM, pH = 7.0) in the presence of different concentrations of Cr^{3+} (0–14 equiv), $\lambda_{ex} = 420$ nm. Inset: fluorescence intensity at 498 nm of NP-B as a function of Cr^{3+} concentration.

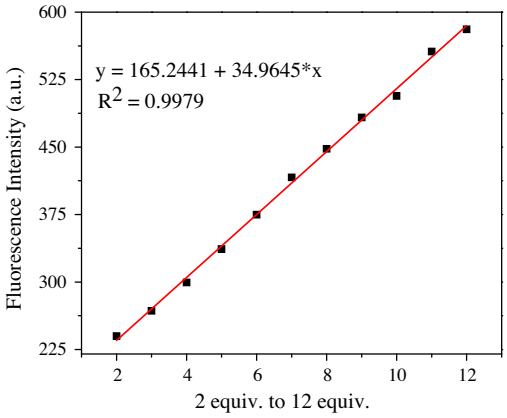


Figure 2. Curve of fluorescence intensity at 498 nm of NP-B (1×10^{-5} M) versus increasing concentrations of Cr^{3+} (2–12 equiv).

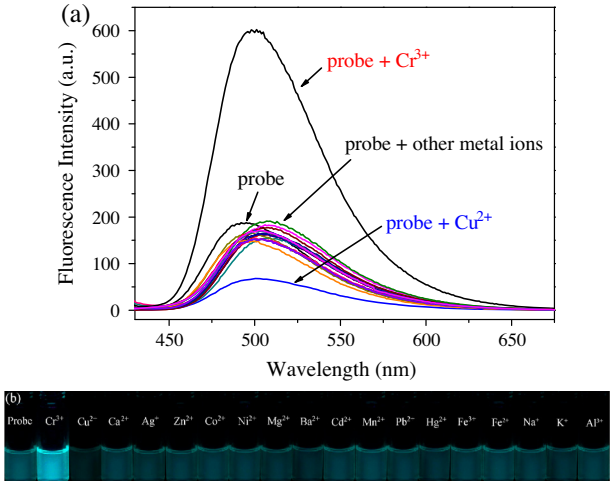


Figure 3. (a) Fluorescent response of NP-B (1×10^{-5} M) to various metal ions at 14 equiv concentration in THF/H_2O (85/15, v/v) with a buffer solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 10 mM, pH = 7.0). (b) A photograph showing the color change of NP-B (1×10^{-5} M) at 365 nm in THF/H_2O (85/15, v/v) upon addition of 14 equiv of various metal ions.

quenched. Thus, a strong fluorescence emission enhancement with a red-shift was observed. As shown in Figure 3b, green fluorescence was observed upon Cr^{3+} addition. In contrast, addition of other metal cations could not cause a significant enhancement in fluorescence emission, especially, the copper ions could even quench the fluorescence. We suspected the quench was caused by the magnetic properties of copper ions and π–π stacking. π–π Stacking was induced by the dimer which was formed by copper ions and probe.[16] With Cr^{3+}, the enhancement factor is determined to be 600. In contrast, other metal ions quenched fluorescence of NP-B or had little influence on NP-B, which suggested that the factor of Cr^{3+} was more than 3.5 times greater than that of other metal cations, as shown in Figure 4. The above-mentioned findings clearly indicated that NP-B behaved as a highly selective turn-on fluorescent probe for Cr^{3+}. In addition, the fluorescence enhancement took place immediately after Cr^{3+} addition (within 10 s), indicating that NP-B enabled rapid detection of Cr^{3+}. As for the high selectivity for Cr^{3+}, we reasoned that the following two factors might play critical roles. On one hand, avoiding the use of sulfur atom in our scaffold could prevent interference from other metal ions especially from mercury.[17] On the other hand, the receptor of NP-B was relatively rigid and cavity-like, which could specifically fit for Cr^{3+} but not metal ions.

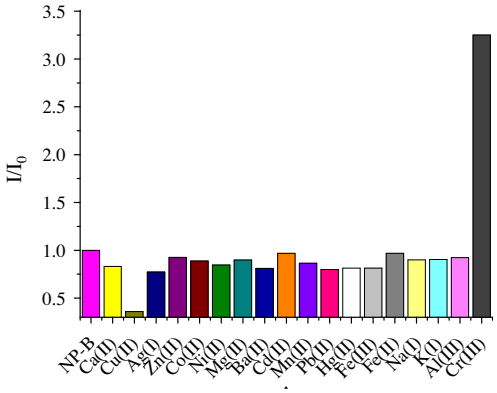


Figure 4. Fluorescent emission changes of NP-B (1×10^{-5} M) upon addition of 14 equiv of each relevant analyte (Ca^{2+}, Cu^{2+}, Ag^{+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Ba^{2+}, Cd^{2+}, Mn^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}, Fe^{2+}, Na^{+}, K^{+}, Al^{3+}, Cr^{3+}) in THF/H_2O (85/15, v/v) with a buffer solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 10 mM, pH = 7.0). λ_{ex} = 420 nm.

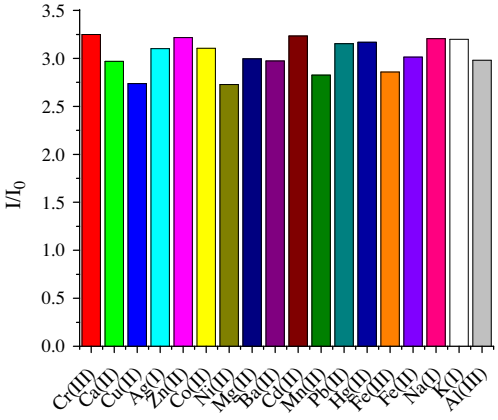
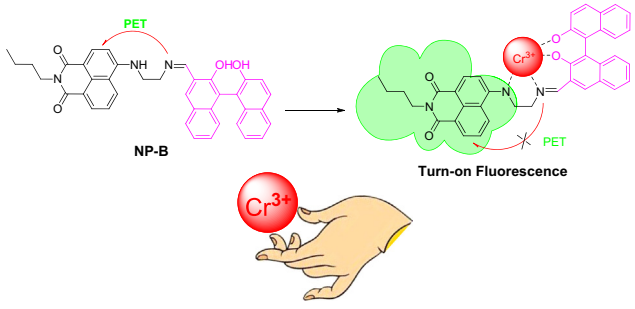


Figure 5. Fluorescent emission changes of NP-B (1×10^{-5} M) with 14 equiv of Cr^{3+} and 14 equiv of various metal ions in THF/H_2O (85/15, v/v) with a buffer solution of 3-(*N*-morpholino) propanesulfonic acid (MOPS, 10 mM, pH = 7.0). λ_{ex} = 420 nm.



Scheme 2. Proposed binding mode of NP-B with Cr^{3+}.

To examine whether probe NP-B still retains sensitivity to Cr^{3+} under the potential competition from relevant analytes, the probe was treated with Cr^{3+} in the presence of other metal ions. As displayed in Figure 5, all the relevant analytes tested had virtually little influence on the detection of Cr^{3+}. Thus, probe NP-B could be particularly applicable to Cr^{3+}, even in the presence of these relevant analytes.

As observed from the fluorescence titration spectra, the Cr^{3+} induced a red shift in emission. This phenomenon usually occurred when the nitrogen, which was also the donor of the push-pull system, chelated with metal ions, which eventually induced the change of the internal charge transfer process (ICT)[18]. Therefore, we reason that the ethylenediamine nitrogen that linked to the naphthalimide ring was involved in Cr^{3+} chelation. According to this factor and the MALDI-TOF-MS spectrum, we proposed a plausible binding mode of the probe NP-B with Cr^{3+} as shown in Scheme 2, and the association constant between NP-B and Cr^{3+} was determined to be $2.4 \times 10^4\ M^{-1}$ in THF/H_2O (85/15, v/v) by using nonlinear least-square analysis.

In conclusion, Naphthalimide and BINOL framework based "turn-on" fluorescence probe NP-B was successfully developed. NP-B displayed a fluorescence enhancement and a little red-shift response to Cr^{3+} via a 1:1 binding mode. Fluorescence intensity was linear with the concentration of Cr^{3+} cation in a range from 20 to 140 μM. As a probe, NP-B exhibited high selectivity and sensitivity for Cr^{3+}. The detection limit was calculated to be 0.20 μM.

Acknowledgments

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Supplementary data

Supplementary data (these data include copies of ^1H NMR, ^{13}C NMR spectra, and mass spectra of compounds described in this Letter) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.11.024.

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