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Research Paper

Fluorescence turn-on NapTp in CTAB micelles for efficient detecting ferric ions in aqueous system

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ABSTRACT

Naphthalimide-based probe (NapTp) has poor solubility and remain essentially none missive in water. This paper describes a rapid and simple route to encapsulate the probe NapTp into the hydrophobic core of cetyltrimethylammonium bromide (CTAB) micelles, while ensuring solubility of the NapTp-CTAB assembly in water. Due to the hydrophobic character of the micelles core, the NapTp becomes fluorescent in water as it behaves in organic solvents. Importantly, the NapTp-CTAB assembly displays distinct fluorescence "turn-on" for sensing Fe^{3+} ions in 100% aqueous system. The probe most clearly reveals 1:1 multiplexing characteristics for aqueous analytes with an excellent selectivity. The detection limit of NapTp-CTAB for Fe^{3+} ions is estimated to be of 8.05×10^{-7} M.

1. Introduction

Ferric ion (Fe^{3+}) is one of the most important analytes because of its severe vomiting, diarrhea, abdominal pain, and heart/liver damage effects. Its redox-active form catalyzes the generation of highly reactive oxygen species to trigger damage to biological macromolecules and metabolites if cellular iron homeostasis is compromised [1–3]. An enforceable drinking water standard is given by the EPA (United States Environmental Protection Agency) for a secondary iron standard of 0.3 mg L^{-1} [4]. Hence, it is necessary and significant to accurately detecte the level of Fe^{3+} ions in drinking water. Some analytical methods, such as inductively coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectroscopy (FAAS), and so on, can be achieved to detect Fe^{3+} ions [5–8]. In comparison with above-mentioned techniques, molecular probe with fluorescence OFF-ON signal for specific events provides more efficient, more convenience, greater sensitivity, and less invasiveness [9–11]. Furthermore, the fluorescence "turn-on" probe is an ideal measurement tool for detecting Fe^{3+} ions in the environment comparing with "turn-off" probe [12–14]. However, many of the available Fe^{3+} ions probes are based on fluorescence quenching mechanisms due to the paramagnetic nature of Fe^{3+} ions [15–18]. At present, only a few "turn-on" probes have been reported to measurement Fe^{3+} ions with a selective response [19–23]. Moreover, most of these "turn-on" probes for Fe^{3+} ions detection are usually organic solvent-based, and have poor solubility in water. The hydrophobicity greatly limits their applications. Therefore, as an overall strategy, it is necessary to design "turn-on" sensors for measurement Fe^{3+} ions with both high sensitivity and selectivity in 100% aqueous system.

Herein we design a rapid and simple route to encapsulate Naphthalimide-based probe (NapTp) into water soluble surfactant micelle for sensing Fe^{3+} ions in 100% aqueous system. The cetyltrimethyl ammonium bromide (CTAB), containing a positively charged surface and a hydrophobic interior micro heterogeneous environment, was introduced into the aqueous phase as the water soluble surfactant micelle [24,25], and looked forward to a good performance in this work. Due to the hydrophobic character of the micelles core, NapTp can be physically trapped inside the hydrophobic core and ensure solubility of the assembly in water as it behaves in organic solvents. As expected, NapTp trapped in CTAB micelle (as NapTp-CTAB assembly) displays chemodosimeter optical change with the change of concentration gradient of Fe^{3+} ions, accompanied with distinct color change from pale green to bottle green with exciting at 365 nm.

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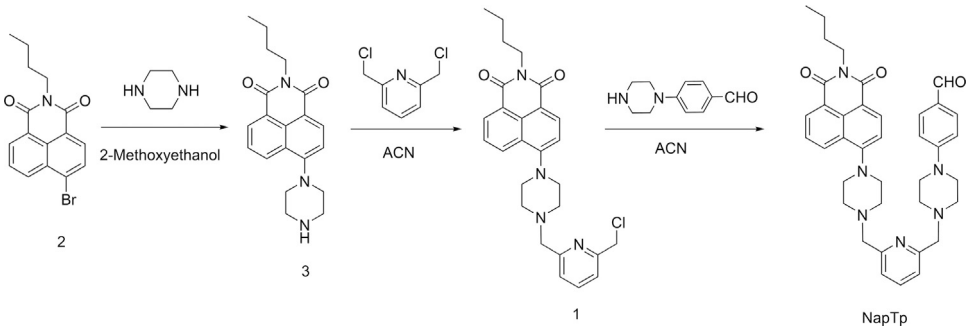

Scheme 1. Synthetic route of probe NapTp.

2. Experimental

2.1. Materials and methods

All reagents and solvents were used as received without further purification. Deionized water was used in the experiments throughout. Silica gel (100–200 mesh) was used for column chromatography. High resolution mass spectra measurements were performed on a LCMS-IT-TOF MS spectrometry. NMR spectra were recorded on a Varian 400 MHz with chemical shifts reported as ppm (in DMSO-*d6* or $CDCl_3$, TMS as internal standard). Fluorescence measurements were performed on a FS-5 spectrophotometer (Edinburgh, Britain) and the slit width was set as 2 nm for excitation and emission, respectively. Absorption spectrum was measured on a SHIMADZU UV-3600 spectrophotometer. Solvents were generally dried and distilled prior to use. The measurements were performed at room temperature on air-equilibrated solutions (10^{-5} M). The CTAB-dependent fluorescence studies were performed according to the literature [26].

2.2. Synthesis and characterization

Synthesis of 1,8-Naphthalimide-4-piperazine-2,6-bis(chloromethyl)pyridine-(*p*-piperazine-benzaldehyde) (NapTp).

Reference to the literatures [27], the imidation of 2 (1.0 g, 3.0 mmol) with pyperizine (0.52 g, 6.0 mmol) in 2-methoxyethanol (15.0 mL) at refluxing under nitrogen atmosphere for 8 h, after removal of 2-methoxyethanol, the residues was purified by silica gel column chromatography using chloroform/methanol (3:1, v/v) as eluent to afford 3, Yield: 0.4 g (54.0%). 3 (163.0 mg, 0.44 mmol) was dissolved in acetonitrile (50.0 mL), then added 2,6-dichloromethylpyridine (35.2 mg, 0.2 mmol), after stirred and refluxed for 10 h under nitrogen atmosphere, the mixture was cooled to room temperature to afford a yellow solid after filtration, which was purified by silica gel column chromatography using chloroform/ethyl acetate (10:1, v/v) as eluent to afford 1, Yield: 138 mg (82.0%).

200.0 mg (0.42 mmol) compound 1, 87.0 mg (0.46 mmol) *p*-Benzaldehyde-Piperazine [28] and 20.0 mL of acetonitrile were placed into a 50 mL flask, the mixture was refluxed for 6 h. After cooled down to room temperature, the mixture was filtered, and the filtrate was concentrated by evaporating the solvent to get a viscous liquid. Flash chromatography on silica gel using CH_2Cl_2/ethyl acetate (5:1, v/v) yielded compound NapTp (161.0 mg, 61.0%) as a yellow powder. HRMS (ESI) calcd for $C_{38}H_{42}N_6O_3$: 631.3397; found: 631.3408. $[M+H]^+$. ^1H NMR ($CDCl_3$, 400 MHz) δ ppm: 9.80 (br s, 1H), 8.61–8.59 (d, 1H), 8.54–8.52 (d, 1H), 8.44–8.42 (d, 1H), 7.78–7.70 (m, 4H, Ph), 7.45–7.40 (m, 2H, Ph), 7.25–7.23 (d, 1H), 6.94–6.92 (m, 2H, Ph), 4.21–4.17 (t, J = 7.60 Hz, 2H, $-CH_2CH_2CH_2CH_3$), 3.87 (s, 2H, $-CH_2$), 3.79 (s, 2H, $-CH_2$), 3.48–3.45 (t, J = 4.40 Hz, 4H), 3.35 (m, 4H), 2.89 (m, 4H), 2.72 (m, 4H), 1.75–1.73 (m, 2H), 1.49–1.44 (q, J = 7.60 Hz, 2H), 1.01–0.97 (t, J = 7.20 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 190.33, 164.46, 164.01, 157.90, 157.73, 155.90, 155.05, 136.95, 131.81, 131.02, 130.19, 129.88, 127.18, 126.18, 125.59, 123.36, 121.58, 116.84, 114.91, 113.52, 64.37, 53.39, 53.03, 52.88, 47.13, 40.07, 30.26, 29.67, 20.38, 13.83.

3. Results and discussion

We utilized naphthalimides platform, a prototype ICT fluorophore, as the signal transducer, which can be tuned by varying the functional group (Scheme 1) [29–31]. Fluorescence increasing probe NapTp has a broad absorption band resulting from an internal charge-transfer (ICT) process (Fig. S1, ESI) [28,32]. NapTp is synthesized by 4-piperazine-naphthalimide (1) and 4-piperazine-benzaldehyde (2), 1 and 2 are linked by 2,6-

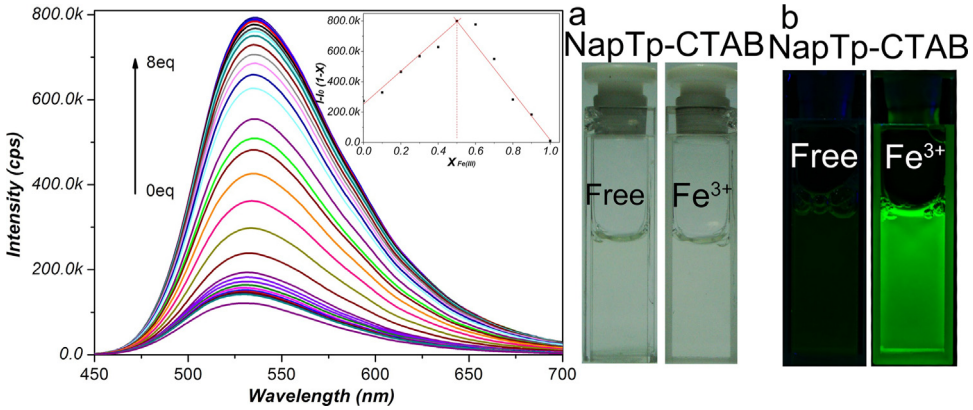

Fig. 1. Fluorescence response of NapTp-CTAB assembly (1×10^{-5} M) to 8 equiv. of Fe^{3+} ions (λ_{ex} = 390 nm, Slits: 2/2 nm). Inset: job's plot. (a) Visualized images of NapTp-CTAB and NapTp-CTAB + Fe^{3+}. (b) Fluorescence images of NapTp-CTAB and NapTp-CTAB + Fe^{3+} under U. V. (λ = 365 nm).

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