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Near-infrared chemodosimetric probes based on heptamethine cyanine dyes for the "naked-eye" detection of cyanide in aqueous media

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ABSTRACT

Two simple chemodosimetric probes (P1 and P2) based on heptamethine cyanine dyes have been synthesized for highly sensitive and selective detection of cyanide anions (CN^-) in aqueous media. The probes with an immobilized indolium salt as the specifically nucleophilic addition reaction site for CN^- exhibit absorption bands in the near-infrared (NIR) region (650–850 nm). Upon the addition of CN^-, the probes display a blue-shifted spectrum and result in apparent color change from green to brilliant yellow that can be easily observed by the naked eye even in the presence of other interfering anions such as F^-, AcO^-, Br^-, NO_2^-, Cl^-, SO_4^{2-} and I^-. There are good linear relationships between the fluorescence intensity of the probes and CN^- concentrations, and the detection limits for P1 and P2 are estimated to be 0.017 μM and 0.2 μM, respectively. The sensing mechanism of the nucleophilic addition is confirmed by ^1H NMR and mass spectroscopic analysis. In addition, the probe P2 is employed for cell imaging and the detection of CN^- in living cells L929 is successfully realized.

1. Introduction

The design and synthesis of chemodosimetric probe for the detection of anions have drawn considerable attention due to their high sensitivity, selectivity, and real-time monitoring in recent decades [1–6]. Cyanide compounds are widely used in mineral extraction, electroplating, polymer production and other industrial activities. However, cyanide anion (CN^-) is one of the most toxic anions, which can affect many functions in human body and lead to vomiting, convulsions, loss of consciousness, and eventual death. As we know, the fatal dose of cyanide is estimated to be 0.5–3.5 mg/kg of body weight for an adult [7]. The extensive use of cyanide along with its easy diffusion causes serious water contamination, which increases the potential risks to humans. According to the World Health Organization (WHO), the highest permissible level of cyanide in drinking water is 1.9 μM [8]. Therefore, it is important to design and synthesize simple chemodosimetric probe to recognize CN^- highly efficient.

In recent years, various fluorescent cyanide probes have been developed based on the mechanism of metal coordination, hydrogen-bonding interaction, and specific chemical reactions [9–18]. Among which, the nucleophilic addition reaction was the most popular strategies for designing cyanide probes because of their highly enhanced selectivity over other interfering anions. Many fluorescent probes containing coumarin [19–23], phenazine [24,25], triarylborane [26], carbazole [27,28], triphenylamine [29–31] and triphenylimidazole [32] as fluorophores and dicyanovinyl, indolium, benzothiazol as recognition sites were developed based on nucleophilic addition of cyanide to carbon-carbon/heteroatom double bonds. For example, Yin et al. have synthesized the coumarin-Meldrum's acid conjugate, which showed a reduced emission peak at 641 nm and concurrently displayed a new strong emission peak at 491 nm due to the blocked intramolecular charge transfer (ICT) process when the alkylidene Meldrum's acid was attacked by CN^- [19]. Guo and coworkers reported a hybrid coumarin–hemicyanine dye with diethylamino-coumarin and indolium group as the electron-donating and electron-withdrawing groups, respectively. The addition of CN^- on the indolium group of probe interrupted the π-conjugation and resulted in a color change from purple to colorless due to the disruption of ICT [21]. Although the above mentioned coumarin derivatives and other fluorophores are excellent fluorescent signal units for fluorescent cyanide probes, their absorption and emission spectra are in short-wavelength regions, which are not beneficial to reduce scattering and background emissions.

NIR fluorophores with absorption and emission spectra in the

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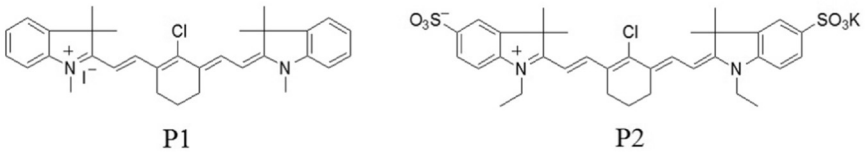

Scheme 1. The molecular structure of P1 and P2.

wavelength range of 650–900 nm have attracted wide interest because of their low-level background interferences. Cyanine dyes are the famous NIR fluorophores with large extinction coefficients, strong fluorescence, easily tunable absorption and emission spectra, which have been extensively used in bio-marker, optical data storage, electrochemical fluorescence switching and photosensitizer in dye-sensitized solar cells [33–36]. However, there are only few reports about the fluorescent cyanide probes based on cyanine dyes. For example, Cheng et al. have reported the nucleophilic addition of CN^- to the iminium cation moiety of the commercial cyanine dye (Cy5). However, the detection of CN^- in water need the assistance of phase-transfer catalyst [37]. Inspired by their work, we design two simple heptamethine cyanine-based fluorescent probes, namely P1 and P2, in which one indolium moiety acts as electron-donating group and the other indolium salt acts as electron-withdrawing group. Meanwhile, methine group and 1-chloro-cyclohexene act as π-linkers to enhance the stability of the probes. Compared to P1, P2 is designed with sulfonic groups decorating on both indolium groups at the 5-position for better water-soluble (Scheme 1). The D-π-A molecular structure of the P1 and P2 should possess an expanded π-conjugation as well as a strong ICT within two indolium groups. When CN^- is added to the iminium cation moiety of indolium salt, a distinct spectroscopic response and color change would be occurred because the disruption of π-conjugation as well as the ICT process. In the present study, rapid "naked-eye" recognition of the probes towards CN^- is realized in aqueous media with high selectivity and sensitivity. The cell imaging is also performed to demonstrate the biological application of probe P2.

2. Experimental

2.1. Reagents and apparatus

All reagents and solvents were purchased from commercial source and used without further purification unless otherwise noted. NMR spectra were measured with a Bruker AV-400 NMR spectrometer. MALDI-TOF mass spectra were tested on a Bruker BIFLEXeIII mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. UV–vis spectra were recorded with an Agilent Cary 100 UV–vis spectrometer. Photoluminescence emission spectra were recorded with an Agilent QM 100 luminescence spectrometer. The detection of CN^- in living cells with the probe was also tested by a FV 1000-IX81 confocal laser scanning microscope (CLSM, Olympus, Japan) with an excitation wavelength of 635 nm.

2.2. Synthesis of P1

Probe 1 was synthesized with N-methyl-2, 3, 3-trimethylindolenine and 2-chloro-1-formyl-3-hydroxymethylene cyclohexene according to the reported literatures [38,39]. The synthetic routes to P1 are outlined in Scheme 1 (1). Under an atmosphere of dry nitrogen, N-methyl-2, 3, 3-trimethylindolenine (3.012 g, 10.0 mmol), 2-chloro-1-formyl-3-hydroxymethylene cyclohexene (0.863 g, 5.0 mmol) and sodium acetate trihydrate (0.820 g, 10.0 mmol) in 30 mL acetic acid were refluxing for 12 h. After cooling to room temperature, the reaction mixture was poured into ether, filtered, and dried under vacuum. The crude product was recrystallized in methanol to give pure compound of P1 (2.690 g, 69.4%). ^{1}H NMR (400 MHz, DMSO-d6) δ (ppm): 8.27-8.24 (d, 2H, CH), 7.65-7.63 (d, 2H, ArH), 7.46-7.45 d, 2H, ArH), 7.32-7.28 (m, 4H, ArH), 6.33-6.29 (d, 2H, CH), 3.70 (s, 6H, CH_3), 2.74-2.71 (t, 4H, CH_2), 1.88-1.85 (t, 2H, CH_2), 1.68 (s, 12H, CH_3); ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 172.48, 147.52, 142.70, 142.52, 140.84, 128.40, 125.95, 124.98, 122.24, 111.29, 101.76, 48.73, 39.43, 31.49, 27.19, 25.77, 20.28; MALDI-TOF MS($C_{32}H_{36}ClIN_2$) m/z: calcd for 610.16, found: 483.29 $[P1\text{-}I]^+$.

2.3. Synthesis of P2

Probe 2 was synthesized with the similar routes for P1 (Scheme 1 (2)). Under an atmosphere of dry nitrogen, N-ethyl-2, 3, 3-trimethylindolenine-5-sulfonic acid potassium salt (843 mg, 2.20 mmol), 2-chloro-1-formyl-3-hydroxymethylene cyclohexene (188 mg, 1.10 mmol) and sodium acetate trihydrate (90.0 mg, 1.10 mmol) were added to 10 mL acetic acid and refluxed for 12 h. After cooling to room temperature and the solvents were evaporated under vacuum. The residue was dissolved in a small amount of methanol, and then the solution was added to 100 mL of ether with violent stirring, filtered, washed with ether and dried under vacuum. The crude product was purified by silica gel chromatography using chloroform/methanol (4/1, v/v) as an eluent to gain pure compound of P2 (0.664, 64.4%). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm): 8.28-8.24 (d, 2H, CH), 7.81 (s, 2H, ArH), 7.68-7.66 (d, 2H, ArH), 7.40-7.38 (d, 2H, ArH), 6.35-6.31 (d, 2H, CH), 4.27-4.22 (m, 4H, CH_2), 2.73-2.71 (t, 4H, CH_2), 1.87-1.84 (t, 2H, CH_2), 1.67 (s, 12H, CH_3), 1.32-1.28 (t, 6H, CH_3); ^{13}C NMR (100 MHz, DMSO-d6) δ (ppm): 171.96, 147.97, 145.32, 142.95, 141.65, 140.57, 126.52, 126.28, 119.86, 110.43, 101.64, 48.93, 39.43, 27.28, 25.84, 20.31, 12.14; MALDI-TOF MS ($C_{34}H_{39}ClN_2O_6S_2$) m/z: calcd for 670.19, found: 671.11 $[P2+H]^+$.

2.4. General spectroscopic procedures

The probe solution of P1 (5 μM) and P2 (5 μM) were prepared in CH_3CN, CH_3CN/H_2O (9/1, v/v) and DMF/H_2O (7/3, v/v) mixed solvent, respectively. Then 3.0 mL of the solution P1 or P2 was placed in a quartz cell (10.0 mm width) and the absorption and fluorescent spectra were recorded. Titration experiments were carried out in 10 mm quartz cell at room temperature. The cyanide solution (as the tetrabutylammonium salt) was prepared in CH_3CN or DMF/H_2O (7/3, v/v) for P1 or P2, respectively. Other anions solutions (as the sodium salt or potassium salt) were added to the host solution and used for the titration experiments.

2.5. Binding stoichiometry

The binding stoichiometry of P1 with CN^- was investigated through the Job's plot titration. For the Job's plot analyses, a series of solutions with varying mole fraction of CN^- were prepared by keeping the total concentration of P1 and CN^- at 5 μM. Fluorescence spectra of these solutions were measured for each sample at