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A novel “turn-on” fluorescent probe based on triphenylimidazole-hemicyanine dyad for colorimetric detection of CN^- in 100% aqueous solution

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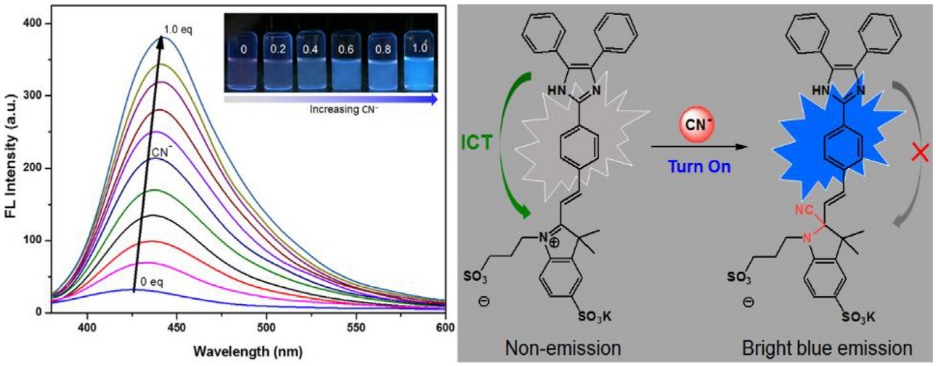
HIGHLIGHTS

- A novel “turn-on” fluorescent probe based on triphenylimidazole and hemicyanine dyad was synthesized for CN^- detection.
- The probe exhibited colorimetric and fluorescent dual responses with CN^- in 100% aqueous solution.
- The detection limit was down to 20.6 nM in 100% aqueous solution.
- The probe has been successfully used to determine CN^- in real water as well as to image CN^- in living cells.

GRAPHICAL ABSTRACT



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ABSTRACT

A new colorimetric fluorescent probe (MCy) for CN^- is designed and synthesized based on triphenylimidazole-hemicyanine dyad. The probe shows high selectivity towards CN^- in 100% aqueous solution even in the presence of other competitive anions such as F^-, Cl^-, AcO^-, NO_2^-, $H_2PO_4^-$, I^-, SCN^-, SO_4^{2-}, NO_3^-, HCO_3^-, Br^- and S^{2-}. Upon nucleophilic addition of CN^- to the indolium group, the probe displays large blue-shift in UV–vis spectrum and remarkable “turn-on” fluorescence owing to the disruption of intramolecular charge transfer. Meanwhile, the probe also undergoes a naked-eye discernible color change from orange to light pink in the sunlight as well as an obvious fluorescence color change from non-emissive to bright blue under a UV lamp. The detection limit of CN^- in aqueous solution can be as low as 20.6 nM, which is much lower than the permissible level of CN^- in drinking water according to the WHO. In addition, the probe has been successfully used to determine CN^- in real water samples as well as to fabricate test paper kit for CN^- detection.

1. Introduction

Recently, the design and synthesis of fluorescent probes for the detection of anions have attracted much attention in the field of chemical and biological analysis owing to their simplicity, flexibility and low cost [1–5]. Among various anions, cyanide anion (CN^-) is particularly concerned due to its extreme toxic-

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ity to human beings and other organisms. The combination of CN^- with cytochrome oxidase can cause the inhibition of oxygen transport to mitochondria and lead to the cytotoxic hypoxia or cellular asphyxiation [6–9]. According to the previous research, the lethal dose for cyanide is as low as 0.5-3.5 mg per kilogram of body weight [10]. Nevertheless, cyanide is widespreadly used in various important industrial processes including electroplating, metallurgy, plastics manufacturing and organic synthesis [11,12]. In most less-developed districts, unfortunately, large amounts of untreated industrial waste was discharged directly into the rivers and lakes, which may lead to severe cyanide contamination in groundwater and even in drinking water. The maximum permissible concentration of CN^- in drinking water regulated by the World Health Organization (WHO) is 1.9 μM [13]. Hence, the development of efficient and economical fluorescent probe for CN^- detection is crucial.

So far, many fluorescent probes for CN^- detection have been explored according to the strategies reported in literatures, such as hydrogen-bonding interaction, metal-displacement and nucleophilic addition reaction [14–22]. Among them, reactive fluorescent probes utilizing the strong nucleophilic property of CN^- stood out among other fluorescent probes, which exhibited high selectivity and high anti-interference ability. Most of the CN^- receptors are electrophilic organic groups containing C=C, C=O, or C=N bonds [23–38]. For example, dicyano-vinyl and cyano-vinyl groups have been widely used as reactive receptors for CN^- detection in many fluorescent probes [39–41]. In addition, the C=O bond in aldehyde and ketone moieties was also adopted to act as recognition site, which exhibited obvious spectrometric response when attacked by CN^- [42,43]. In recent years, indolium moiety has been frequently used as CN^- receptor, which has rooted in the pioneering work of Cheng et al. [44,45]. However, most of the reactive fluorescent probes suffer from several limitations including poor water solubility, poor detection limit, and fluorescent "turn off" response. For the purpose of the practical application of CN^- probes in biological and environmental systems, "turn-on" fluorescent probes for the detection of CN^- in 100% aqueous solution is highly demanded.

Keeping this in mind, we herein designed and synthesized a novel triphenylimidazole-hemicyanine dyad (MCy) as a colorimetric and turn-on fluorescent probe for CN^- detection. The combination of triphenylimidazole and hemicyanine moieties endowed the MCy with an extended π-conjugation, in which intramolecular charge transfer (ICT) from electron-donating triphenylimidazole moiety to electron-withdrawing hemicyanine moiety was expected. The sulfonic group was tethered to hemicyanine moiety for improving water solubility. Nucleophilic attack of CN^- to indolium salt interrupted the ICT process and resulted in a significant spectroscopic response. The obvious color change could be easily observed by naked-eye in the sunlight as well as under a UV lamp. The detection limit was down to 20.6 nM in aqueous solution. This study provides a strategy to construct a colorimetric and "turn-on" fluorescent probe for selective recognition of CN^- in 100% aqueous solution, which may become a practical approach for CN^- detection in biological and environmental systems.

2. Experimental

2.1. Materials and apparatus

All reagents and solvents were purchased from Aladdin (China) and used as received unless otherwise noted. NMR spectra were recorded by a Bruker AV-400 NMR spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEXeIII mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. High resolution mass spectra (HRMS) of the probe and the product of the reaction between MCy and CN^- were recorded on Bruker spectrometer using ESI ionization. Melting point was recorded on an X-5 digital melting-point apparatus. UV–Vis spectra were recorded through an Agilent Cary 100 UV–Vis spectrometer. Photoluminescence emission spectra were recorded by an Agilent QM 100 luminescence spectrometer. The cellular imaging of the probe was performed by an FV 1000-IX81 confocal laser scanning microscope (CLSM, Olympus, Japan) with an excitation wavelength of 368 nm.

2.2. Synthesis of 4-(4, 5-diphenyl-1H-imidazol-2-yl) benzaldehyde (1)

Compound 1 was synthesized according to a literature procedure [40]. The typical route was as follow: under an atmosphere of dry nitrogen, benzil (10.0 mmol, 2.10 g), terephthalaldehyde (20.0 mmol, 2.68 g) and ammonium acetate (100 mmol, 7.71 g) were added to 150 mL acetic acid. The mixture was stirred at 120 °C for 8 h. After cooling to room temperature, the mixture was precipitated in water, filtered and dried in vacuo. The sample was purified by column chromatography using petroleum ether/ethyl acetate (20/1, v/v) as an eluent to achieve a pure yellow solid compound 1 (2.62 g, 81%). m.p.: 195 °C. ^1H NMR (DMSO-d_6, 400 MHz) δ (ppm): 13.03 (s, 1H), 10.04 (s, 1H), 8.31 (d, J = 8 Hz, 2H), 8.02 (d, J = 8 Hz, 2H), 7.57-7.23 (m, 10H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 197.62, 149.46, 143.35, 140.68, 140.58, 140.04, 135.94, 135.32, 134.79, 133.93, 133.77, 133.47, 133.32, 132.36, 132.01, 130.64. MALDI-TOF MS ($C_{22}H_{16}N_2O$) m/z: calcd. 324.375, found 325.176 $[M+H]^+$.

2.3. Synthesis of potassium 5-sulfono-2,3,3-trimethyl-1-(3-sulfonatepropyl)-3H- indolium (2)

Under an atmosphere of dry nitrogen, 5-sulfono-2,3,3-trimethyl-3H-indolium (2.30 g, 8.30 mmol) and 1,3-propanesultone (1.52 g, 12.4 mmol) were added to dichlorobenzene (10 mL), and the mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was diluted with ethyl acetate and the solvent was removed by rotary evaporation. The residue was purified by column chromatography using methanol an eluent, and the desired compound 2 was obtained (2.65 g, 80%). m.p.: 232 °C. ^1H NMR (DMSO-d_6, 400 MHz) δ (ppm): 7.98 (s, 1H), 7.93 (d, J = 8 Hz, 1H), 7.77 (d, J = 8.4 Hz, 1H), 4.59 (t, J = 8 Hz, 2H), 2.79 (s, 3H, CH_3), 2.59 (t, J = 6.4 Hz, 2H), 2.10 (t, J = 7.2 Hz, 2H), 1.50 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 198.26, 149.24, 142.15, 141.67, 126.89, 121.13, 115.53, 54.78, 47.91, 47.23, 24.00, 22.42, 14.53. MALDI-TOF MS ($C_{14}H_{18}KNO_6S_2$) m/z: calcd. 399.524, found 400.062 $[M]^+$.

2.4. Synthesis of the probe MCy

Compound 1 (406 mg, 1.25 mmol) and compound 2 (500 mg, 1.25 mmol) were dissolved in ethanol (20 mL), and then piperidine was added. The reaction mixture was refluxed for 24 h under the protection of pure nitrogen atmosphere. After cooling to room temperature, the solvent was removed by rotary evaporation. The crude product was purified by column chromatography using ethyl acetate/methanol (4/1, v/v) as an eluent, and a pure dark-red solid MCy was obtained (645 mg, 73%). m.p.: 370 °C. ^1H NMR (DMSO-d_6, 400 MHz) δ (ppm): 13.03 (s, 1H), 8.52 (d, J = 16.4 Hz, 1H), 8.46 (d, J = 8.4 Hz, 2H), 8.28 (d, J = 8.8 Hz, 2H), 8.07 (s, 1H), 8.01 (d, J = 16.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.60-7.23 (m, 10H), 4.89 (t, J = 6.4 Hz, 2H), 2.70 (t, J = 6.0 Hz, 2H), 2.21 (m, 2H), 1.85 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 182.69, 153.99, 149.87, 144.94, 144.09, 141.26, 138.87, 135.28, 134.70, 134.66, 132.16, 131.10, 130.22, 129.19, 128.96, 128.74, 127.68, 127.59, 127.32, 127.05, 125.85, 120.76, 115.08, 113.16, 52.75, 49.08, 48.87,