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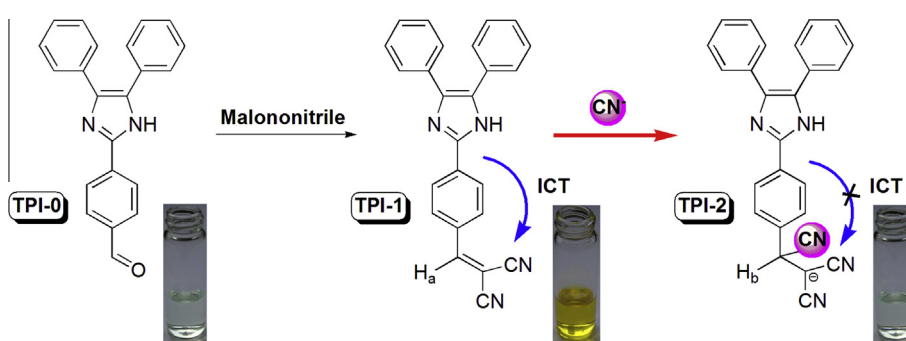
Colorimetric fluorescent cyanide chemodosimeter based on triphenylimidazole derivative

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HIGHLIGHTS

- A triarylimidazole-based colorimetric chemodosimeter for CN⁻ was demonstrated.
- The chemodosimeter can recognize CN⁻ with obvious color and fluorescence change.
- The chemodosimeter exhibits a very low limit of detection (0.11 μM) for CN⁻.
- The chemodosimeter allows naked eye detection of CN⁻.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we demonstrated a highly selective colorimetric chemodosimeter for cyanide anion detection. This chemodosimeter having a triphenylimidazole group as a fluorescent signal unit and a dicyano-vinyl group as a reaction unit was synthesized by the Knoevenagel condensation of 4-(4,5-diphenyl-1H-imidazol-2-yl)benzaldehyde with malononitrile in a reasonable yield. The probe exhibited an intramolecular charge transfer (ICT) absorption band at 420 nm and emission band at 620 nm, respectively. Upon the addition of cyanide anion, the probe displayed a blue-shifted spectrum and loss in color due to the disruption of conjugation. With the aid of the fluorescence spectrometer, the chemodosimeter exhibited a detection limit of 0.11 μM (*S/N* = 3). Interferences from other common anions associated with cyanide anion analysis were effectively inhibited.

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Introduction

Cyanide is considered the most toxic of all anions and can be absorbed through inhalation, ingestion, or skin contact [1]. Even a trace amount of cyanide intake will lead to lethal damage to the human body, since cyanide is a powerful inhibitor of the activity of cytochrome c oxidase. The binding of cyanide to this cyto-

chrome can prevent transport of electrons from cytochrome c oxidase to oxygen, causing cytotoxic hypoxia in the presence of normal hemoglobin oxygenation [2–4]. Consequently, tissues that depend highly on aerobic respiration, such as the central nervous system and the heart, are particularly affected. Nowadays, the concern over the effect of cyanide on humans was heightened by the fact that the use of cyanide salts remained widespread, particularly in gold and silver mining, electroplating, plastics manufacturing, and metallurgy [5–8]. Unfortunately, accidental releases of cyanide into the environment do occur although safeguards and increasing levels of monitoring and control. In addition, certain plastics, especially those derived from acrylonitrile, release hydrogen cyanide

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when heated or burnt [9]. Therefore, the development of novel methods for the determination of cyanide at trace concentrations has become one of the most attractive subjects of investigation in analytical chemistry because of the practical applications.

Traditionally, cyanide has been determined by using ion chromatography, electrochemical analysis, and spectroscopic techniques [10–13]. However, most of these strategies require either multiple experimental steps with tedious sample pretreatments or sophisticated instrumentation. In addition, these methods often suffer from interference by other anions, such as NO_3^- , AcO^- , H_2PO_4^- , HSO_4^- , ClO_4^- and halides. Specifically, the discrimination of cyanide from halides is rather problematic [14,15]. In this regard, analytical methods based on colorimetric chemosensors present many advantages, including high sensitivity, easy detection, inexpensive, and rapid in real-time monitoring. The sensing process is often accompanied by changes in absorption or fluorescence spectra that can be precisely monitored and sometimes detected by the naked eye [16–21].

Compared to the relatively well-developed cyanide chemosensors, colorimetric chemodosimeters based on the special nucleophilicity of cyanide have emerged as a research area of significant importance. Generally, colorimetric chemodosimeters are used to detect an analyte through a highly selective and irreversible chemical reaction between the dosimeter molecule and the target analyte, leading to signal changes in both the absorption wavelength and color that has an accumulative effect and hence is directly related to the concentration of the analyte. Taking advantage of the unique nucleophilicity of cyanide, various colorimetric cyanide chemodosimeters have been demonstrated, in which the chemodosimetric molecule contains a π -conjugated chromogenic unit and a reactive subunit. Hitherto, dicyano-vinyl group [22–26], diketone group in benzyl [27], salicylaldehyde group [28–31], benzamide group [32–34], trifluoroacetyl group [19,35], N-acyl triazines [17,36], and [1,3]oxazine ring [37,38] have been adopted as the reactive subunit. Among these, dicyano-vinyl group is a popular reaction counterpart for cyanide nucleophilic addition reactions owing to its high efficiency. Although the design of colorimetric cyanide chemodosimeters with dicyano-vinyl groups as the recognition site has currently attracted attention, there are only a few examples of fluorescent chemodosimeters for cyanide [22–26]. Therefore, it is still a challenge to fabricate new colorimetric cyanide chemodosimeters adopting dicyano-vinyl group as the reactive subunit.

Herein, we demonstrated a highly sensitive colorimetric fluorescent chemodosimeter for the detection of cyanide by covalent linking triphenylimidazole and dicyano-vinyl units. As is well known, arylimidazole derivatives have attracted considerable attention in recent years because of their unique properties and diverse applications such as photographic materials, luminescent materials, optical materials, and therapeutic agents [39–41]. In particular, 2,4,5-triphenylimidazole (TPI) is a typical fluorophore, which shows a maximum absorption wavelength at 308 nm ($\epsilon = 2.62 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$), fluorescence emission wavelength at 385 nm, and fluorescence quantum yield of 0.10 in CH_3CN solution, anthracene in cyclohexane used as a standard ($\Phi_F = 0.31$; excitation wavelength 366 nm) [49]. (Figs. S1 and S2, see Supporting Information, SI). Additionally, TPI contains an imidazole ring with dicoordinate nitrogen atom, which can potentially build complexes assembled by hydrogen bonds with a molecule containing hydrogen-bond donor, such as a carboxylic acid. The chemical flexibility of this class of compounds allows the preparation of a large variety of related structures and, consequently, the tailoring of their optical properties. Therefore, one would expect that novel chemodosimeter based on directly linked arylimidazole-dicyano-vinyl units might result in new potential applications in cyanide detection. In the present work, we describe the synthesis and the

spectroscopic evaluation of the new colorimetric fluorescent cyanide chemodosimeter in detail.

Experimental

Reagents and apparatus

All reagents and solvents were purchased from commercial source and used without further purification unless otherwise noted. Triethylamine (Et_3N) was distilled and kept over potassium hydroxide. NMR spectra were recorded with a Bruker AV-400 NMR spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEXIII mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. UV-vis spectra were recorded with a Perkin-Elmer Lambda-25 UV-vis spectrometer. Photoluminescence emission spectra were recorded with a Perkin-Elmer LS-50b luminescence spectrometer.

Synthesis of 4-(4,5-diphenyl-1H-imidazol-2-yl)benzaldehyde (TPI-0)

Under an atmosphere of dry argon, benzil (2.10 g, 10 mmol), terephthalaldehyde (1.34 g 10 mmol) and ammonium acetate (6.16 g, 80 mmol) in 50 mL acetic acid were refluxing for 6 h. After cooling to room temperature, the reaction mixture was poured into water, filtered, and dried in vacuo. The crude product was purified by silica gel chromatography using ethyl acetate/dichloromethane (1/10, v/v) as an eluent to isolate pure compound TPI-0 (2.60 g, 80%). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 12.99 (s, 1H, NH), 10.01 (s, 1H, CHO), 8.29–8.27 (d, 2H, ArH), 8.01–7.99 (d, 2H, ArH), 7.55–7.21 (m, 10H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 192.8, 144.7, 138.6, 135.9, 131.2, 130.5, 129.1, 128.7, 127.6, 125.9. MALDI-TOF MS ($\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}$) m/z : calcd for 324.12, found: 325.20 [$\text{M} + \text{H}$] $^+$.

Synthesis of 2-(4-(4,5-diphenyl-1H-imidazol-2-yl)benzylidene)malononitrile (TPI-1)

Under an atmosphere of dry argon, compound TPI-0 (325 mg, 1.0 mmol) and malononitrile (132 mg, 2.0 mmol) in 20 mL absolute ethanol were refluxing overnight with trace Et_3N as catalyst. After cooling to room temperature, the reaction mixture was poured into water, filtered, and dried in vacuo. The crude product was purified by silica gel chromatography using ethyl acetate/dichloromethane (1/20, v/v) as an eluent to isolate pure compound TPI-1 (240 mg, 65%). ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 13.05 (s, 1H, NH), 8.51 (s, 1H, $\text{CH}=\text{C}$), 8.27–8.25 (d, 2H, ArH), 8.06–8.04 (d, 2H, ArH), 7.5–7.2 (m, 10H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm): 160.8, 144.4, 135.7, 131.7, 130.5, 128.9, 126.1, 114.9, 114.0, 80.8. MALDI-TOF MS ($\text{C}_{25}\text{H}_{16}\text{N}_4$) m/z : calcd for 372.13, found: 373.21 [$\text{M} + \text{H}$] $^+$.

General spectroscopic procedures

A solution of TPI-1 (10 μM and 20 μM) was prepared in CH_3CN solution. Titration experiments were carried out in 10-mm quartz cell at room temperature. Anions (as the tetrabutylammonium salt) in CH_3CN were added to the host solution and used for the titration experiments.

Binding stoichiometry

The binding stoichiometry of TPI-1 with cyanide ion was investigated through the Job's plot. For the Job's plot analyses, a series of solutions with varying mole fraction of cyanide ion were prepared by keeping the total concentration of TPI-1 and cyanide ion

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