



Synthesis of a new fluorescent cyanide chemosensor based on phenothiazine derivative



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ABSTRACT

A new phenothiazine derivative containing two dicyano-vinyl groups as the cyanide receptor on both sides was synthesized and fully characterized. The chemosensor showed an intramolecular charge transfer (ICT) absorption band at 494 nm and emission band at 633 nm in acetonitrile solution. Upon titration with different concentrations of cyanide anion both absorption and emission bands decrease in a ratio-metric manner. This optical response for cyanide anion is due to the nucleophilic Michael addition of CN⁻ on the α -position of the dicyano-vinyl groups present in the chemosensor in both sides and thus converting these electron acceptors to anionic electron donors and consequently breaking the conjugation, which ultimately affect the ICT and the fluorescence of the chemosensor. The result indicated that the chemosensor showed high sensitivity with a fast response of less than 50 s and selectivity toward cyanide anion with a detection limit as low as 3.2×10^{-9} M, which is the lowest ever reported. The chemosensor reaction mechanism with CN⁻ was studied by ¹H NMR and ¹³C NMR, FTIR and mass spectroscopies.

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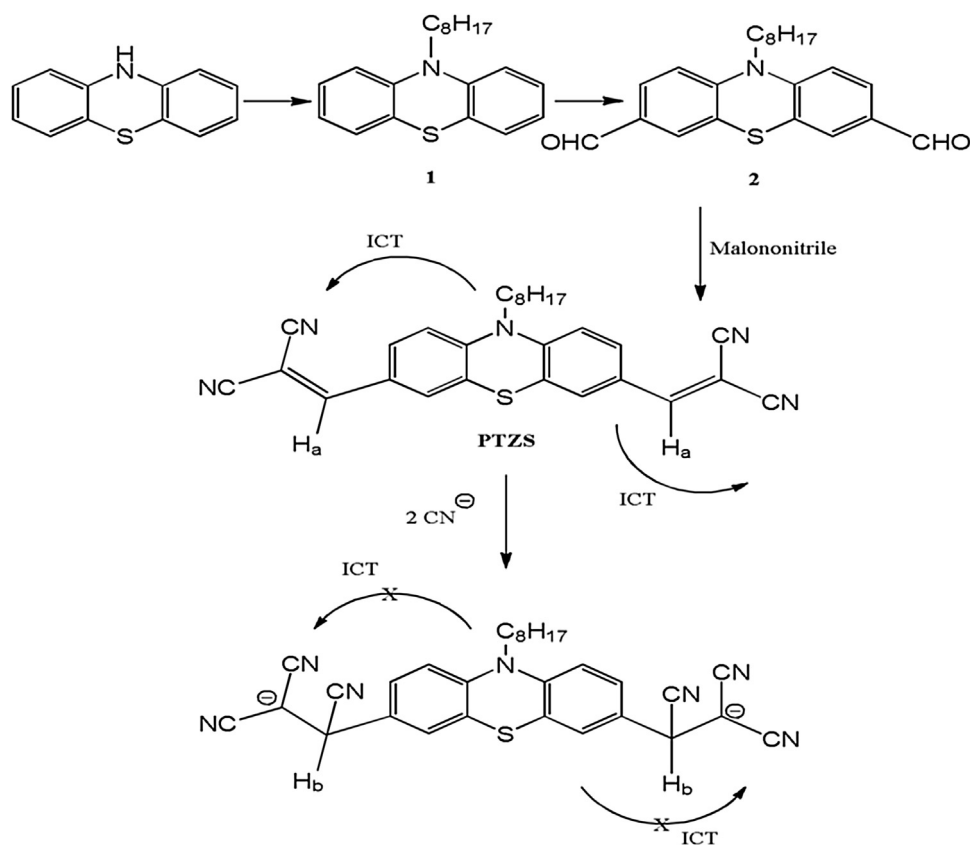
1. Introduction

The high toxicity of cyanide ion has been of continuous concern due its involvement in many applications such as textile manufacturing, metallurgy, herbicides, silver production and gold extraction [1–3]. Ultimately, accidental releases of industrial waste containing cyanide ions into the environment are unavoidable. The maximum allowable level of cyanide ion in the drinking water is 1.9 μ M according to the world health organization (WHO) [4]. Therefore, devising a simple and easy method for the detection of cyanide ion with much lower detection limit than the WHO value is highly desirable. Several methods for the detection of cyanide anions have been reported. Traditionally, methods such as electrochemical and ion chromatography require long processing time [5], whereas chemical sensors provide an easy, simple and low-cost approach with fast response [2]. Therefore, sensitive and easily synthesized optical chemosensors have become desirable for many applications [6,7]. Development of chemosensors that work

in aqueous solution is of growing interest as cyanide anion is a pollutant in aqueous solutions [8–12]. The optical sensing of cyanide anion is happening owing to its characteristic features of being a nucleophile, Lewis base and its propensity of forming hydrogen bonds in aqueous solution. These properties stemmed many scientists to explore various chemical sensors in recent years [13–16]. In the interest of cyanide nucleophilicity, several chemosensors were made in which the π conjugated system get disturbed upon nucleophilic addition of cyanide anion on olefinic double bond causing color change as well as fluorescence response [17–22]. In this regard, we designed and synthesized a new fluorescent chemosensor of an acceptor- π -donor- π -acceptor (A- π -D- π -A) skeleton in which two terminal dicyanovinyl groups are acting as acceptors and phenothiazine derivative as the donor. Upon interaction with cyanide anion, the chemosensor intramolecular charge transfer (ICT) that exist between A- π -D- π -A get broken due to the nucleophilic attack of cyanide anion on dicyanovinyl groups, resulting in a rapid optical response with very high sensitivity and selectivity. To the best of our knowledge, this is the first cyanide chemosensor based on phenothiazine A- π -D- π -A skeleton.

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Scheme 1. Synthesis of PTZS and the sensing mechanism.

2. Experimental

2.1. General

All solvents and reagents were of the highest purity available, purchased from Sigma-Aldrich Company and used as received. ^1H and ^{13}C NMR spectra were recorded in $\text{CDCl}_3\text{-d}_6$ solution on a Bruker Avance 600 MHz spectrometer for compounds 1 and 2 and for PTZS ^1H and ^{13}C NMR spectra were recorded in $\text{DMSO-D}_2\text{O-d}_6$ solution on a Bruker Avance 400 MHz spectrometer. Infrared spectra were performed on PerkinElmer spectra 100 FTIR spectrometer. Mass spectroscopy was performed using Agilent GC 7000 mass spectrometers. UV absorption spectra were determined in different solvents on Shimadzu UV-vis Spectrophotometer. Fluorescence spectra were recorded on PerkinElmer LS 55 Fluorescence Spectrometer.

2.2. Synthesis and characterization

2.2.1. Synthesis of 10-octyl-10H-phenothiazine (1)

Potassium hydroxide (2.003 g, 35.7 mmol) was added to a solution of 10-phenothiazine (2.91 g, 11.9 mmol), 1-bromooctane (17.9 mmol), and potassium iodide (catalytic) in 50 ml dimethyl sulfoxide (DMSO). The reaction mixture was stirred for 5 h at r.t and then 200 ml of water was added. The crude product was extracted with CHCl_3 (3×50 ml) and the organic layer washed with saturated ammonium chloride aqueous solution and then water. The organic layer was dried over anhydrous sodium sulfate. After removing the solvent, the residue was purified by column chromatography (eluent: n-Hexane) on silica gel to give 3.2 g, 86.2% yield as a colorless oil. ^1H NMR (600 MHz, CDCl_3) δ 0.91 (3H, t, $J=7.2$ Hz, CH_3), 1.27–1.36 (8H, m, CH_2), 1.47 (2H, quin, $J=7.2$ Hz, CH_2), 1.84 (2H, quin,

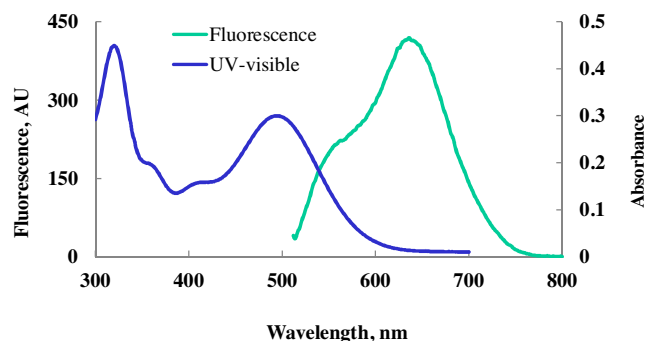


Fig. 1. Absorption and fluorescence spectra of 2×10^{-5} M PTZS in acetonitrile-water (50:50).

$J=7.2$ Hz, CH_2), 3.87 (2H, t, $J=7.2$ Hz, N-CH_2), 6.89 (2H, d, $J=7.8$ Hz, Ar-H), 6.94 (2H, t, $J=7.8$ Hz, Ar-H), 7.17–7.19 (4H, m, Ar-H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.13, 22.65, 26.98, 29.23, 29.24, 31.77, 115.59, 115.69, 121.72, 127.19, 131.82, 132.94; IR ν/cm^{-1} : (C–H olefinic) 3064.41, (C–H aliphatic) 2922.91, 2853.02, (C=C) 1594.4, 1571.80, 1457.23 cm^{-1} .

2.2.2. 10-Octyl-10H-phenothiazine-3,7-dicarbaldehyde (2)

To an ice cooled flask containing *N,N*-dimethylformamide (70 ml) was added POCl_3 (26 ml) dropwise with stirring. After addition, the solution was stirred at room temperature for 90 min. Then the flask was cooled again in ice-bath and compound d (6 mmol) was added. The reaction mixture was warmed gradually to run at 75°C for 2 h. Then cooled to room temperature and poured onto ice-water, basified (sat. aqueous K_2CO_3 solution) and extracted with CHCl_3 (4×30 ml) washed, dried (MgSO_4) and evaporated, purified by column chromatography using (PE/EtOAc, 8:2) as elu-

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