



Spectroscopic and theoretical evaluation of solvent-assisted, cyanide selectivity of chromogenic sensors grounded on mesitylene platform and their biological applications



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ABSTRACT

A series of mesitylene based ratiometric chromogenic sensors (**1–3**) have been synthesized and evaluated for selective cyanide detection in aqueous medium. Low hydration energy and high basicity of CN⁻ in water is shown to be responsible for selective behavior of probes in the aqueous medium. Spectroscopic and theoretical studies endorse frozen proton transfer as the sensing mechanism. The compounds also show considerable antimicrobial activity.

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1. Introduction

Currently, the development of colorimetric sensors for anions especially for cyanide has enticed much attention, because the color change can be observed easily by naked eyes and no special equipment is required [1–3]. Then again, ratiometric chromogenic sensors permit signal rationing by performing the measurement of absorption intensities at two different wavelengths and thus increase the dynamic range [4]. The sensors that can work in aqueous phase are required more frequently due to their use in biological and environmental systems [5]. Hence, construction of ratiometric colorimetric anion sensors that can work in both organic as well as in aqueous phase is the need of the hour. The continued use of cyanide ion in various industrial processes [6] causes its inevitable release in the environment though it is toxic beyond 2 μM in drinking water with 20 μM being its lethal level [7], making search for CN⁻ sensors preordained. Most of the known chemosensors for CN⁻ ion suffer from an uncalled for interference

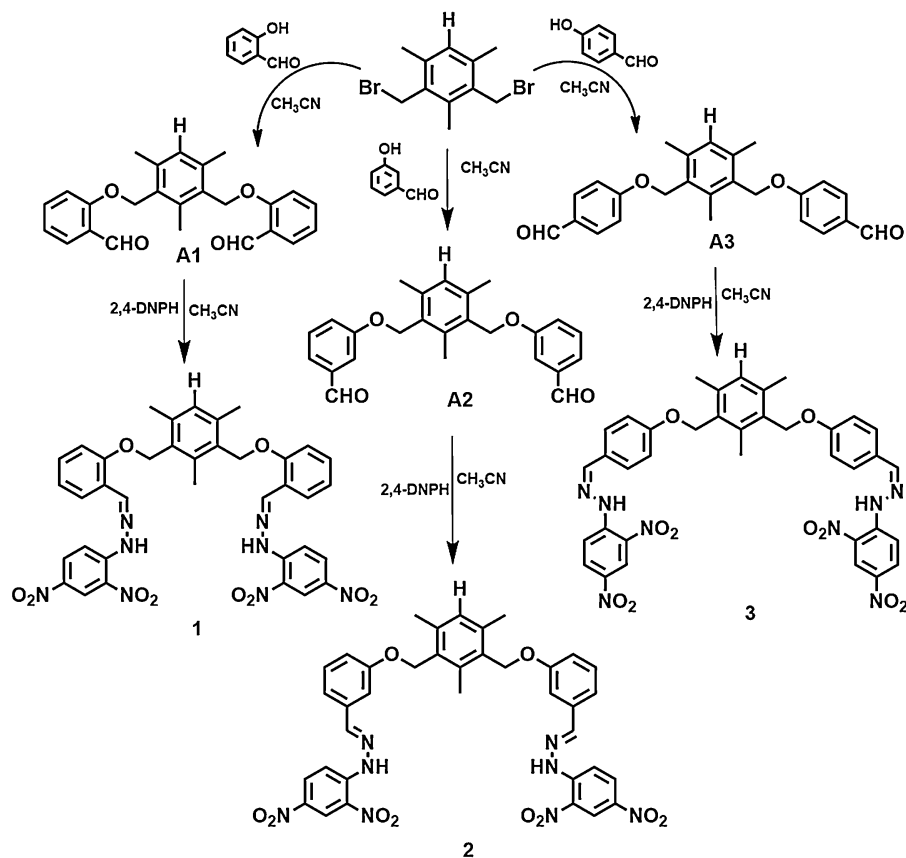
from other ions, particularly the F⁻ ion, therefore the selectivity of the sensors is a vital concern in all future developments [8].

In literature [9], the colorimetric anion sensors generally used groups such as amide, urea, thiourea, pyrrole, etc., for sensing purposes. The sensing mechanism involved in the probes with these functional groups depends upon the acidity of the protons of –NH groups, which can be regulated by introducing electron-withdrawing groups. Hence, designing of probes to detect CN⁻ ions, which can operate through deprotonation of the –NH proton of a hydrazone group and enhancing its acidity by incorporation of the electron withdrawing –NO₂ groups, is a good synthetic approach. The addition of anions causes charge transfer transitions between the anion-H-bonded NH units and the electron-deficient NO₂ moiety, yielding optical responses. From literature's point of view, reports on use of hydrazone moiety as sensors, are rather scarce [10] and the reported designs are mostly monopodal with one hydrazone unit in it. In continuation with our ongoing work on ion sensing with di- and tri-podal Schiff's bases [11] we present here mesitylene based, isomeric, hydrazone containing dipodal Schiff bases (**1**), (**2**) and (**3**) (Scheme 1), giving ratiometric response with nitro groups as signaling units. These highly acidic sensors are envisaged to be exceedingly selective and sensitive for greatly basic CN⁻ ions, over a wide range of interfering anions in the aqueous medium.

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Scheme 1. Synthesis of sensors.

2. Experimental

All the commercially available chemicals were purchased from Aldrich and used without further purification. All solvents were dried by standard methods. TLC was carried out on glass sheets pre-coated with silica gel. Elemental analyses (C, H, N) were performed on a Perkin-Elmer model 2400 CHN analyzer. The ^1H and ^{13}C NMR spectra were carried out in $\text{DMSO}-d_6$ with TMS as an internal reference, on a JEOL-FT NMR-300 MHz and/or Bruker Topspin-FT NMR-500 MHz spectrometer. The infrared spectra (KBr pellet) were recorded using Perkin-Elmer FT-IR C92035 spectrophotometer in the range $400\text{--}4000\text{ cm}^{-1}$. The electronic absorption spectra were recorded on a Shimadzu Pharmaspec UV-1700 UV-vis spectrophotometer with a quartz cuvette (path length, 1 cm). The absorption spectra have been recorded between 1100 and 200 nm. The cell holder of the spectrophotometer was thermostatted at 25°C for consistency in the recordings. HRMS spectra were recorded on a Bruker's microTOF-QII spectrophotometer.

2.1. Synthetic procedures

2.1.1. Synthesis of 3,3'-(((2,4,6-trimethyl-1,3-phenylene)bis(methylene))bis(oxy))dibenzaldehyde, **A2**

This compound was prepared by taking 1 g of K_2CO_3 in dry acetonitrile along with 244 mg of 3-hydroxybenzaldehyde (2 mmol). The reaction mixture was refluxed for 30 min and then 306 mg of 2,4-bis(bromomethyl)-1,3,5-trimethylbenzene (1 mmol) was added slowly. The reaction mixture was refluxed for another 24 h and the progress of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was filtered and the filtrate was concentrated. Again filtered off the precipitate, washed with methanol and dried. The crude product was

recrystallized from $\text{CHCl}_3\text{--CH}_3\text{OH}$ mixture to get pure white material. Yield 85%; mp = $194\text{--}200^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ): 2.33 (s, 9H, $-\text{CH}_3$), 5.15 (s, 4H, $-\text{CH}_2$), 7.02 (s, 1H, $-\text{Ar}$), 7.39 (s, 2H, $-\text{Ar}$), 7.57 (d, 2H, $-\text{Ar}$, $J = 10.8$), 10.00 (s, 2H, $-\text{CHO}$); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, δ): 15.1 ($-\text{CH}_3$), 19.5 ($-\text{CH}_3$), 65.0 ($-\text{CH}_2$), 113.8 ($-\text{Ar}$), 121.7 ($-\text{Ar}$), 130.1 ($-\text{Ar}$), 130.6 ($-\text{Ar}$), 130.9 ($-\text{Ar}$), 138.3 ($-\text{Ar}$), 138.7 ($-\text{Ar}$), 193.3 ($-\text{CHO}$); FTIR (KBr, cm^{-1}) 1701, 1591, 1443, 1250; Elemental analysis calculated for $\text{C}_{25}\text{H}_{24}\text{O}_4$: C, 77.30; H, 6.23 Found: C, 77.12; H, 6.04%; HRMS m/z : 411.1532 $[\text{M}+\text{Na}]^+$ ion (calc. 411.1572).

2.1.2. Synthesis of 4,4'-(((2,4,6-trimethyl-1,3-phenylene)bis(methylene))bis(oxy))dibenzaldehyde, **A3**

Same procedure as for **A2** except that 2 mmol of 4-hydroxybenzaldehyde was used instead of 2-hydroxybenzaldehyde. Yield 56%; mp = $136\text{--}138^\circ\text{C}$; ^1H NMR (300 MHz, $\text{DMSO}-d_6$, δ): 2.31 (s, 3H, $-\text{CH}_3$), 2.33 (s, 6H, $-\text{CH}_3$), 5.20 (s, 4H, $-\text{CH}_2$), 7.04 (s, 1H, $-\text{Ar}$), 7.26 (dd, 4H, $-\text{Ar}$, $J = 8.55$), 7.91 (dd, 4H, $-\text{Ar}$, $J = 8.55$), 9.89 (s, 2H, $-\text{CHO}$); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$, δ): 15.1 ($-\text{CH}_3$), 19.5 ($-\text{CH}_3$), 66.2 ($-\text{CH}_2$), 115.2 ($-\text{Ar}$), 129.9 ($-\text{Ar}$), 130.1 ($-\text{Ar}$), 130.6 ($-\text{Ar}$), 132.0 ($-\text{Ar}$), 138.5 ($-\text{Ar}$), 138.7 ($-\text{Ar}$), 164.0 ($-\text{Ar}$), 191.5 ($-\text{CHO}$); FTIR (KBr, cm^{-1}) 1701, 1609, 1517, 1241; Elemental analysis calculated for $\text{C}_{25}\text{H}_{24}\text{O}_4$: C, 77.30; H, 6.23 Found: C, 77.26; H, 6.21%; HRMS m/z : 389.1738 $[\text{M}+1]^+$ ion (calc. 389.1675).

2.1.3. Synthesis of 2,2'-((((2,4,6-trimethyl-1,3-phenylene)bis(methylene))bis(oxy))bis(2,1-phenylene))bis(methanylylidene)bis(1-(2,4-dinitrophenyl)hydrazine)

1.020 g (0.515 mmol) of compound **A1** was dissolved in 10 ml of dry acetonitrile, to which a solution of 0.204 g (1.03 mmol) of 2,4-dinitrophenylhydrazine in 90 ml of acetonitrile was added. The

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