



A substituted spiropyran for highly sensitive and selective colorimetric detection of cyanide ions



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ABSTRACT

A nitrophenyl azo substituted spiropyran was synthesized and characterized spectroscopically. The substituted spiropyran derivative was evaluated for affinity towards different anions in MeCN:water (10 mM HEPES buffer) at different pH. The spiropyran derivative selectively detected cyanide ions by displaying blue or purple color visible to the naked eye and through spectral changes. The ^1H NMR spectra was used to confirm the binding of cyanide ion to the receptor. The nitrophenyl azo group amplified the observed change in color triggered by cyanide binding to the spiropyran derivative enabling high sensitivity. Theoretical methods were used to investigate the experimental observation at the molecular level.

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1. Introduction

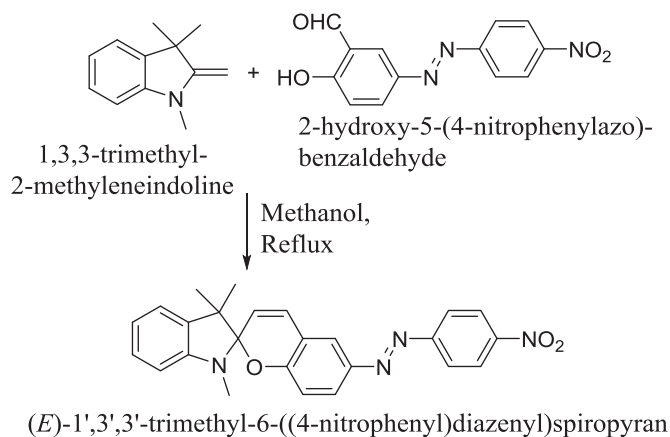
Anions are abundant in the natural world [1,2]. However, the abundance of anions beyond the permissible level is harmful to both humans and the environment [3,4]. Among them, cyanide is the most dangerous and toxic pollutant [3]. The salts of cyanide ion are used worldwide in electroplating, fiber industry, gold mining, and metallurgy producing waste that contaminates the ground water [5]. Cyanide ions act by disrupting electron transport chain inside the human internal system promoting reduced oxidative metabolism through binding with the iron present in cytochrome c oxidase [6,7]. The protection of human health and environment necessitates detection of cyanide ions [8,9]. Due to extreme toxicity associated with cyanide ion, World Health Organization (WHO) recommend tolerable limit of cyanide ion at $1.9\ \mu\text{M}$ [10], while US environmental protection agency recommend tolerable limit at $7.8\ \mu\text{M}$ [11,12]. In view of the extreme toxicity associated with the cyanide ions, there is a growing need to develop sensitive and selective probes for the detection of cyanide ions at trace level. Optical sensors with specific site to hold the selective analyte leading to colorimetric change are promising devices, as they are readily available through synthetic procedures [13]. The obvious incentive for cyanide detection through color change is to devise an

easy and portable cyanide detection kit. Colorimetric change visible to the naked eye is highly practicable in view of its implementation in rural as well as in urban areas. Even though some sensors were reported in the past, the interference with acetate or fluoride make them unsuitable as selective and effective sensors towards cyanide ions [14,15]. The physico-chemical change will be more pronounced and can be distinctively detected by coupling extra conjugated part like azo or nitro group to the original system. The azo group plays an important role in intensifying color change in presence of the analytes of interest.

Photochromic molecules such as spiropyrans which produce distinct color change on interaction with ionic species are viable alternative for cyanide recognition besides their performance in optical and electrical memory devices [16]. The C–O bond is crucial in determining photochromic tendency of the molecule [17]. On light exposure, the closed spiro form transforms itself into open merocyanine form with a partial positive charge. This positive charge can be exploited to bind an important anionic species such as cyanide ion. The most important feature of SP to MC conversion is the generation of distinct color which can be used to confirm the presence of CN^- ion, if this conversion takes place under dark conditions. Recently, a variety of colorimetric and fluorimetric sensors are reported dealing with cyanide ions [18–20]. However, most of the reported receptors display poor selectivity and sensitivity or provide unstable complex limiting their practical use [21,22]. In addition, spiropyran derivatives are also known to produce color change in the presence of acid or base complicating

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Scheme 1. Synthesis of receptor 1.

the detection process [23,24]. Recently, some spiropyran/oxazine based receptors were reported in the literature which either require exposure to UV light or were sensitive to the presence of base or were unusable under aqueous conditions [25–28]. Hence, there is a need to develop a receptor which remains unaffected under such conditions. The spiropyran derivative must display no color change in acidic, basic or neutral conditions and should produce a color change in the presence of anion enabling colorimetric detection. In order to design a colorimetric sensor with improved sensitivity and selectivity towards anions, a spiropyran receptor coupled to nitrophenyl moiety through azo group was designed in anticipation of getting intense color change during anion binding. The anion binding to the receptor and the color change can be further aided by the presence of electron withdrawing nitro group at para position, which can increase the positive charge on the spiro carbon to attract anions.

2. Experimental

Flash column chromatography was performed using Silica Gel (230–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Jeol NMR ECX 400 NMR spectrometer. Chemical shifts are reported in parts per million relative to residual solvent signal or TMS. UV–vis spectra were recorded on an Ocean Optics USB 4000 UV–visible spectrometer.

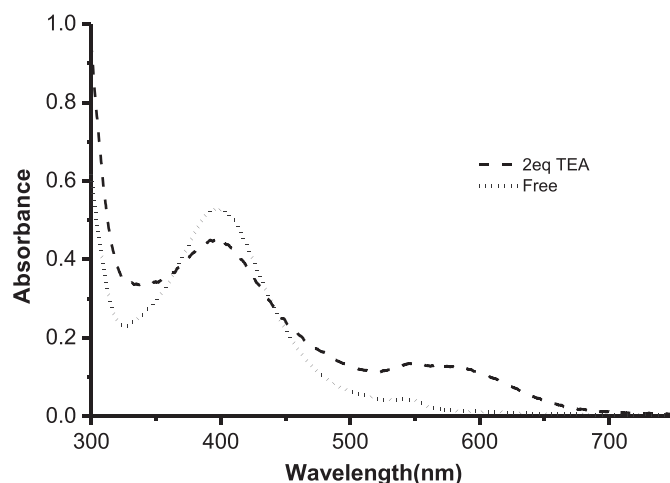


Fig. 1. Spectral change in the UV–vis spectrum of **1** on the addition of two equivalent of trifluoroacetic acid in MeCN followed by the addition of two equivalent triethylamine.

2.1. Synthesis of the receptor 1

In a round bottom flask 1,3,3-trimethyl-2-methyleneindoline (0.7 g, 3.46 mmol) and 2-hydroxy-5-(4-nitrophenylazo)-benzaldehyde (0.88 g, 3.24 mmol) were taken in methanol (50 mL). The reaction mixture was refluxed for 6 h. The solvent was evaporated under reduced pressure. The product was purified through flash column chromatography using 3% ethyl acetate in hexane to yield an orange colored product (0.61 g, 44.1%). m.p. 185–186 °C. IR (KBr, ν/cm^{-1}): 1648. ^1H NMR (DMSO- d_6 , 400 MHz, 298 K, δ): 8.41 (d, 2H, $J=8.4$ Hz, ArH), 8.0 (d, 2H, $J=8.4$ Hz, ArH), 7.89 (s, 1H, ArH), 7.80 (dd, 1H, $J=8.4$ Hz, ArH), 7.22 (d, 1H, $J=10.4$ Hz, C=C–H), 7.14–7.11 (m, 2H, ArH), 6.92 (d, 2H, $J=8.4$ Hz, ArH), 6.80 (t, 1H, $J=7.6$ Hz, ArH), 6.16 (d, 2H, $J=7.6$ Hz, ArH), 5.94 (d, 1H, $J=10.4$ Hz, C=C–H), 2.68 (s, 3H, NCH_3), 1.07–1.23 (two s, 6H, 2 CH_3). ^{13}C NMR (DMSO- d_6 , 100 MHz, 298 K δ): 158.2,

155.4, 147.9, 147.6, 146.2, 136.0, 128.9, 127.6, 126.5, 125.1, 123.1, 121.6, 120.8, 119.3, 119.2, 115.6, 107.0, 105.5, 51.7, 28.6, 25.8, 19.7. HRMS (m/z) [$\text{M}+\text{H}$] $^+$ = 427.1772, calculated for $\text{C}_{25}\text{H}_{23}\text{N}_4\text{O}_3 = 427.1770$. Elemental Analysis: calculated for $\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_3 \cdot 0.5(\text{CH}_3\text{OH})$ C 69.22, H 5.47, N 12.62; found C 69.71, H 5.62, N 12.54.



Fig. 2. Color change upon addition of 1.0 equivalent of tetrabutyl ammonium anions into a solution of spiropyran receptor **1** in MeCN: (10 mM HEPES) water (4:6) at (a) pH = 5.0, (b) pH = 7.6 (c) pH = 9.0. [**1**] = 2.5 μM . From left to right; A = Free receptor, B = CN^- , C = F^- , D = OAc^- , E = Cl^- , F = Br^- , G = I^- , H = NO_3^- , I = H_2PO_4^- , J = HSO_4^- , K = PF_6^- , L = OH^- , M = S^{2-} , N = SH^- .

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