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# Colorimetric sensing of cyanide and fluoride ions by diaminomalenonitrile based Schiff bases

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ABSTRACT

Two new diaminomalenonitrile (DMN) based Schiff bases have been synthesized and explored as a highly efficient receptor for fluoride and cyanide anions. Detection of anions induced by deprotonation of $-NH_2$ followed by transfer of proton to the electron deficient nitrogen atom of –CN which induce the strong charge transfer (CT). Anion selectivity was controlled by the fluorophore attached to the DMN, the fluorophore can tune the electron push–pull property. This phenomenon was confirmed by $^1$H NMR and DFT calculations.

## 1. Introduction

Design and development of molecular probes for anion recognition is very much interesting topic of research till date [1–7]. Among various anions, cyanide and fluoride ions are the most toxic inorganic anions to living organisms and is harmful to the environment. Absorption of cyanide, lead to various types of physiological disorders like convulsions, loss of consciousness and eventually death [8,9]. Further, the binding of cyanide with cytochrome-c oxidase reduces its activity. According to the World Health Organization(WHO), the permissible level of cyanide in drinking water is 1.9 μM [10]. Unfortunately, the use of cyanide ions cannot be avoided due to its widespread applications in various industrial processes, such as gold mining, electroplating, metallurgy, and production of organic chemicals and polymers and plastics [11,12]. Keeping in view the utility of cyanide ions, there is a great need for receptors that can selectively detect cyanide ions. Among various types of chemosensors reported so far, the reaction based chemosensors showing ratiometric response toward cyanide are advantageous owing to their high selectivity and sensitivity. Ratiometric responses are attractive because the ratio between the two emission intensities can be used to measure analyte concentration and provide built-in correction for environmental effects and stability under illumination. Thus, reaction based chemosensors showing ratiometric responses toward cyanide ions are highly desirable. Most of the reported reaction based chemosensors suffer from several limitations, such as poor selectivity, require high temperature or basic medium, slow response toward cyanide ions high detection limits, risk of releasing HCN, irreversibility (based on reaction), and require an organic environment to function.

The low level of fluoride in toothpaste and in drinking water is beneficial to the dental health and treatment of osteoporosis, while excess intake of fluoride can result in fluorosis and urolithiasis [13–15]. Due to small size and high electronegativity the fluoride ion usually forms a strong H-bond, and exhibit greater affinity with silicon. These unique chemical properties make these sensors exhibit excellent selectivity for $F^-$ over other anions. As the result, the major features of the reported fluoride sensors so far are based on three recognition elements according to the interaction mode: hydrogen bonding, Lewis acid–base interaction, and specific reactivity with silicon. Thus, development of a quick, facile, reversible and ratiometric reaction based fluorogenic sensor, with remarkable selectivity and sensitivity for toxic analytes like fluoride and cyanide ions in aqueous media with low detection limit is still on demand [16–18].

Anion receptors associated with colorimetric and fluorescent perturbations are highly preferred because of their high sensitivity and convenience for monitoring the anion recognition. It has

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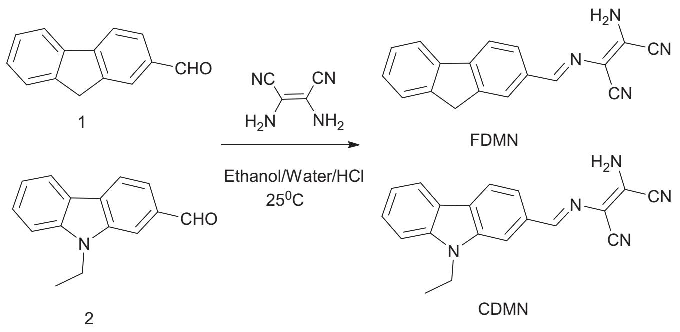

**Scheme 1.** Synthesis of FDMN and CDMN fluorophores.

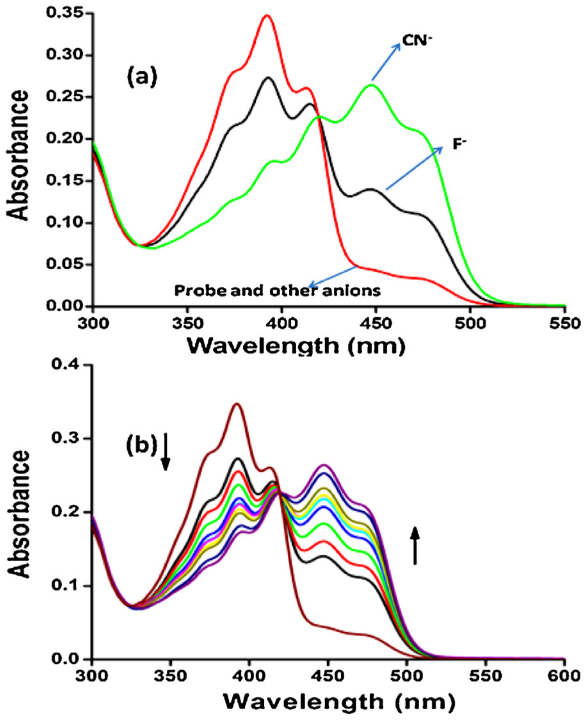

**Fig. 1.** UV–vis spectra of **FDMN** (10 $\mu$M) (a) upon the addition of different anions, (b) change in absorbance of **FDMN** (10 $\mu$M) during the titration with CN$^-$ (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1.0 eq.) in DMF:Water (80:20) solution.

been established that the photophysical properties of these chromophores are highly dependent on the electron donor/acceptor strength. Consequently, if the anion binding site itself is a part of a donor (D) or acceptor (A) in the ICT based receptor design, a highly effective signal communication could be expected [19]. 2-(((*E*)-(9H-fluoren-2-yl)methylene)amino)-3-aminomaleonitrile (FDMN) and (*E*)-2-(amino(((9-ethyl-9H-carbazol-2-yl)methylene)amino)methylene)maleonitrile (CDMN) (Scheme 1) represent a class of organic π-conjugated compounds with electronic donor (D) and acceptor (A) parts connected by single and double bonds, exhibiting interesting electronic properties due to an intramolecular charge transfer (ICT). To the best of our knowledge, this work represents the example of recognition of two different ions by varying the conjugated fluorophore.

## 2. Experimental section

Receptors **CDMN** and **FDMN** have been synthesized by a new and an easy methodology. This method is simple and efficient without involving any noxious organic solvents either for the synthesis or purification.

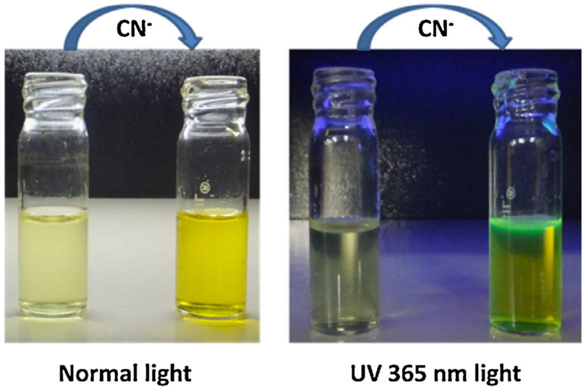

**Fig. 2.** Color change of **FDMN** (10 $\mu$M) upon adding 1.0 eq. CN$^-$ (a) normal light, (b) under 365 nm UV light.

### *2.1. Synthesis of 2-(((E)-(9H-fluoren-2-yl)methylene)amino)-3-aminomaleonitrile*

To the stirring solution of fluorene-2-aldehyde (1) (1.5 mmol, 0.3 g) in ethanol/water mixture (5 mL) at 25 °C, 2–3 drops of conc. HCl were added, followed by the drop wise addition of an ethanolic solution of diaminomaleonitrile (**DMN**) (1.5 mmol, 0.166 g), The addition proceeded with the immediate precipitation of the Schiff base product. The precipitate was filtered, washed with methanol and dried to get **FDMN** with 90% of yield**. FDMN** were characterized by mass and NMR spectroscopic techniques. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.31 (s, 1H), 8.26 (s, 1H), 8.03- 7.96 (m, 3H), 7.92 (s, 2H), 7.63- 7.61 (d, *J* = 7.2 Hz, 1H), 7.43–7.35 (m, 2H), 3.97 (s, 2H). $^{13}$C NMR (DMSO-*d*6, 300 MHz): δ = 155.28, 144.43, 144.04,143.42, 140.28, 134.15, 128.80, 127.73, 126.99, 126.50, 125.30, 125.20, 120.81, 120.22, 114.49, 113.79, 102.97, 36.27 ppm calculated mass = 284.32. LCMS-ESI [M$-$H$^+$] = 283.06 *m*/*z*.

### *2.2. Synthesis of (E)-2-(amino(((9-ethyl-9H-carbazol-2-yl)methylene)amino) methylene)maleonitrile*

To the stirring solution of carbazole-2-aldehyde (2) (0.9 mmol, 0.2 g) in ethanol/water mixture (5 mL), 2–3 drops of conc. HCl were added, followed by the drop wise addition of an ethanolic solution of diaminomeleonitrile (**DMN**) (0.09 g, 0.9 mmol), The addition proceeded with the immediate precipitation of the Schiff base product. The precipitate was filtered, washed with methanol and dried to get **CDMN** with 88% of yield**. CDMN** were characterized by mass and NMR spectroscopic techniques. $^1$H NMR (400 MHz, DMSO) $\delta$ 8.83 (s, 1H), 8.42 (s, 1H), 8.20-8.14 (dd, *J* = 15.1, 7.8 Hz, 2H), 7.76 (s, 2H), 7.69- 7.66 (dd, *J* = 11.5, 8.5 Hz, 1H), 7.52-7.48 (t, *J* = 7.5 Hz, 1H), 7.29-7.25 (t, *J* = 7.4 Hz, 1H), 4.50- 4.44 (q, *J* = 6.9 Hz, 2H), 1.34- 1.31 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (DMSO-*d*6, 300 MHz): δ = 156.10, 141.64, 140.13, 126.98, 126.77, 126.41, 125.32, 122.52, 122.44, 122.31, 120.57, 119.68, 114.76, 113.98, 109.66, 109.40, 103.60, 37.23, 13.72 ppm. Calculated mass = 313.36. LCMS-ESI [M$-$H$^+$] = 312.08 *m*/*z*.

### *2.3. UV–vis titration of FDMN with CN$^-$*

**FDMN** (1.7 mg) was dissolved in DMF (1.5 mL) and 0.27 mL of this solution (7 mM) was diluted with 99.9 mL DMF/water (8: 2, v/v) and 2.5 mL of this solution was diluted with 2.5 mL DMF/water (8:2, v/v) to make the final concentration of 10.0 $\mu$M. NaCN (3.2 mg, 0.1 mmol) was dissolved in DMF/water (8: 2, v/v, 0.5 mL). Then, 0.5 mL of the cyanide solution was dissolved in 25 mL of DMF/water (8: 2, v/v) to get the final concentration of 20 $\mu$M solution and added