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Highly selective colorimetric/fluorometric chemodosimeters for cyanide ions in aqueous solution based on Michael addition to C-atom possessing different polar substituents

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ABSTRACT

Two simple chemosensors, 3-(4-aminophenyl)-2-cyanoacrylic acid (**1**) and 3-(3-aminophenyl)-2-cyanoacrylic acid (**2**), exhibited visual colour and fluorescence changes selectively with cyanide ions in aqueous solution. Their anion sensing properties were investigated using UV–vis, fluorescence and ^{1}H & ^{13}C NMR spectral studies and theoretical studies. The mechanism of sensing involves Michael addition of CN^- to C=C bond. The addition reaction was found to occur relatively easier with p-$NH_2C_6H_4$ group (Taft's σ^* 0.16) substituted C=C bond than that with m-$NH_2C_6H_4$ group (σ^* 0.58) substituted compound. The detection limits were calculated to be 33 pM and 0.2 nM for the receptors **1** and **2**, respectively, which are lower than the maximum permissible concentration of cyanide ion in drinking water (1.9 μM) set by the World Health Organization (WHO).

Anion recognition is an area of growing interest in supramolecular chemistry due to its crucial role in a wide range of chemical, biological and environmental processes.[1–4] Among various anions cyanide is one of serious concerns due to its high toxicity to human and aquatic life.[5,6] According to the World Health Organization (WHO) the permissible level of cyanide in drinking water is 1.9 μM.[7] The discharge from chemical industries, metal mining processes as well as waste water treatment facilities are the sources of cyanide in water.[8] The production of nitrile, nylon and acrylic plastics is also associated with environmental concerns caused by cyanide.[9,10] Biological sources of cyanide include bacteria, fungi and algae, which produce this ion as part of their nitrogen metabolic pathways.[11] Thus, there is a considerable interest in the development of effective detection methods of high selectivity and sensitivity for cyanide ion especially in water. There are several approaches to the design of selective probes for cyanide anion, such as hydrogen bonding interaction,[12,13] deprotonation,[14] co-ordination of cyanide ion with metal ion,[15–18] boronic acid derivatives,[19–23] luminescence life time measurements,[24] demetallation of preassembled complexed sensors[25,26,15,27] and nucleophilic attack of cyanide ion on activated carbonyl groups.[28,29] Very recently Wang et al.[30] have reviewed the recent progress in the development of fluorometric and colorimetric chemosensors for the detection of cyanide ions. They concluded that those methods which utilise chemical reaction that produce chromo/fluorogenic responses have proven to be the most convenient due to their simplicity, high selectivity and inexpensive nature. Hence, over the past few years, strategies to design these types of receptors have attracted significant attention.

In the present endeavour we report two simple ways to make Michael addition reaction based chemosensors for selective detection of cyanide ions in aqueous solution. These receptors work on the '*turn-off*' intramolecular charge transfer (ICT) transition along with '*turn-on*' fluorescence mechanism. Attempts have also been made to investigate the cyanide ion sensing behaviour of these acceptors using various spectral techniques (UV–vis, fluorescence and ^{1}H & ^{13}C NMR) and theoretical studies. The effect of position of the substituent (electron donor) on the sensing property has also been discussed.

The two receptors (**1** and **2**) were synthesised from commercially available *para* and *meta* aminobenzaldehydes (Schemes S1 and S2).

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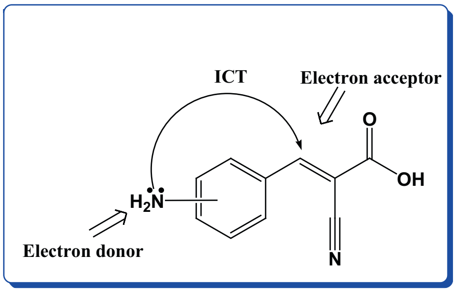

Receptor-**1**: *p*-NH_2; **2**: *m*-NH_2

In both these receptors there will be intramolecular charge transfer transition from amine N-atom (donor) to 2-cyanoacrylic acid (acceptor) through the π-conjugation. As the electron donating property of the amino group strongly depends on the position, both *para*-(Hammett's σ-0.57) and *meta*-(σ 0) derivatives were selected for the study. All attempts to prepare the *ortho* derivative were in vain; only cyclic molecules were obtained as products (Scheme S3). Hence, this molecule was not considered for further studies. Though we are not able to prepare the *ortho* substituted compound with the –NH_2 group, we prefer to have the –NH_2 group in the receptors rather than the –NMe_2 group. This is because the electron donating property of the –NH_2 group significantly differs according to the position. But, the –NMe_2 group will behave as electron donating both in *para*-(σ-0.63) and *meta*-(σ-0.15) positions and of course with varying intensities. The electron acceptor moiety 2-cyanoacrylic acid was selected based on the fact that it is a well-known Michael acceptor. It is presumed that Michael addition of CN^- to the C=C bond in the acceptor moiety will terminate the ICT transition ('*turn-off*') and thus imparts a visible colour change. In line with our expectation, addition of CN^- ions (in the form of NaCN) to both these receptors in aqueous solution (with HEPES buffer of pH 7.4 in DMSO 1:1 v/v) exhibited a visible colour change from yellow to colourless. Addition of other common anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$ and NO_3^- to **1** and **2** does not produce any such colour change (Fig. 1).

In the electronic spectra of the receptors in HEPES buffer of pH 7.4 in DMSO 1:1 v/v, the band appeared at 387 and 377 nm for **1** and **2**, respectively, corresponding to the ICT transition (Fig. 2).[31] From Hammett's substituent constant values, it is clear that the –NH_2 group at the *para*-position is relatively a better electron donor than that at the *meta*-position. In line with this point, the ICT transition in the receptor **1** occurred at a relatively higher wavelength (387 nm) than that in the receptor **2** (377 nm). The electronic spectral changes observed for the receptor **1** upon addition of the chosen anions (in the form of tetra butyl ammonium salts) in DMSO are shown in Figure S1. It is evident from the figure that the receptor is highly selective towards cyanide ions. The UV–vis spectral changes observed for both these receptors **1** and **2** with incremental addition of CN^- ion in DMSO–HEPES buffer (1:1 v/v) are depicted in Figure 2. As shown in Figure 2a, the receptor **1** displayed a λ_{max} at 387 nm (ICT), when CN^- was gradually titrated to the solution of **1**, the absorption peak at 387 nm decreased while a new absorption band at 336 nm appeared, with the colour of the solution turning from yellow to colourless. A clear isosbestic point was observed at 353 nm. The receptor **2** also exhibited similar electronic spectral and colour changes upon addition of incremental amounts of CN^- ions (Fig. 2b). This observation is attributed to

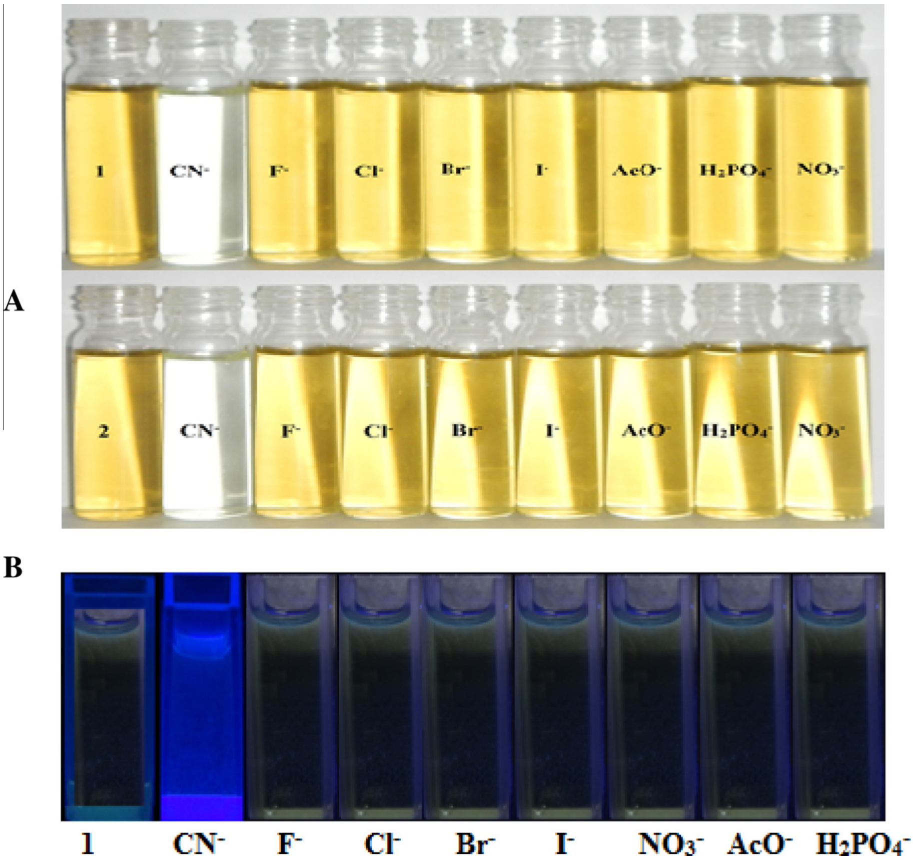

Figure 1. (A) Colour changes upon addition of (1 equiv) of various anions in DMSO solution of **1** and **2** (6.25×10^{-4} M); (B) photograph of **1** taken under irradiation with UV light after addition of the indicated anions.

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