A simple yet highly selective colorimetric sensor for cyanide anion in an aqueous environment†

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The nucleophilic nature of cyanide is used to create a simple, sensitive, and highly effective sensor, 2-(trifluoroacetylamino)anthraquinone 2 (2-TFAQ), for the easy "naked-eye" detection of very low concentrations of cyanide in an aqueous environment.

Anions are ubiquitous in both the organic and mineral worlds, and play important roles in biology, medicine, catalysis, and in the environment.[1] Considerable attention has been paid to the design and synthesis of abiotic receptors for anionic species in the past two decades, which makes anion recognition one of the fastest growing disciplines in the field of supramolecular chemistry.[2] In particular, cyanide is one of the most toxic anions and is harmful to the environment and human health. The binding of cyanide to cytochrome oxidase reduces the activity of this enzyme and inhibits oxygen utilization by cells.[3] However, the use of cyanide can not be avoided completely due to its wide application in the production of organic chemicals and polymers, such as nitriles, nylon, and acrylic plastics.[4] In addition, it is critical to the gold-extraction process.[5] For these reasons, receptors capable of sensing or binding cyanide selectively are highly desirable. While a number of receptors for anions have been designed and synthesized, relatively few have been developed for cyanide, especially in the aqueous environment.

Several strategies have been developed to detect cyanide, including the formation of cyanide complexes with transition metals,[6] boron derivatives[7] and CdSe quantum dots,[8] nucleophilic addition reactions to carbonyl groups,[9] the displacement approach,[10] hydrogen-bonding interactions,[11] deprotonation[12] and luminescence lifetime measurement.[13] However, many receptors for cyanide reported to date have several limitations as follows: (i) poor selectivity, especially in the presence of fluoride or acetate, (ii) requiring specific conditions, such as high temperature or basic media, (iii) not instantaneously registering the addition of cyanide, (iv) requiring the use of instruments such as luminoscopes, or UV light, (v) running the risk of releasing HCN, (vi) only working in an organic environment, and (vii) complicated synthesis. With these considerations in mind, we now report a simple yet effective colorimetric sensor 2-(trifluoroacetylamino)anthraquinone **2** (2-TFAQ), which overcomes the above limitations, and can achieve the so-called "naked eye" detection of cyanide in an aqueous environment. Our strategy is based on the fact that cyanide is a well known nucleophile and can attack the carbon atom of a electron-deficient carbonyl group easily.

Compounds 1-(trifluoroacetylamino)anthraquinone **1** (1-TFAQ) and 2-(trifluoroacetylamino)anthraquinone **2** (2-TFAQ) (Fig. 1) were synthesized in a single step according to the literature method:[14] 1-aminoanthraquinone/2-aminoanthraquinone and trifluoroacetic anhydride were stirred in nitrobenzene at room temperature for one hour. Then the mixture was filtered and purified *via* column chromatography (yield >90%). Both compounds were characterized by ^{1}H NMR, ^{13}C NMR, elemental analysis and mass spectra. A single crystal of **2** suitable for X-ray diffraction analysis was obtained by diffusion of water into a DMSO solution of **2**. In the solid state, two intramolecular hydrogen bonds (C1AB–H1AB···O3AB and N2AB–H2AB···F1AB hydrogen bonds in Fig. 2a) are present, and a one-dimensional chain is formed through intermolecular C–H···O hydrogen bonds (Fig. 2a). Fig. 2b shows the trimer induced by one DMSO molecule through one N–H···O hydrogen bond and two C–H···O hydrogen bonds. Selected hydrogen bond parameters are listed in the ESI (Table S2)†.

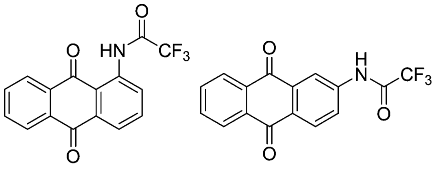

Fig. 1 Structures of anthraquinone-based receptor 2-TFAQ **2** and reference compound 1-TFAQ **1**.

Addition of cyanide to an organic–aqueous solution (acetonitrile–water mixture) of **2** (50 μM) causes a color change from colorless to yellow accompanying a new absorption band at $\lambda_{max} = 429$ nm. To confirm the interaction mechanism between the cyanide and the receptor, ^{1}H NMR titration experiments were carried out by addition of Bu_4NCN to a acetonitrile-d_3 solution of **2** (Fig. 3). All the aromatic protons exhibited an upfield shift, which is compatible with the proposed switching mechanism (Scheme 1). The UV-vis spectra changes and the corresponding color changes of **2** are highly solvent sensitive, especially to the amount of water present in the medium, probably due to the strong solvation effect in water. Consequently, a 95 : 5 (v/v) CH_3CN–H_2O solvent system was used as the optimized condition for the titration experiments at room temperature. In the case of the reference compound **1**, addition of cyanide produced no obvious color changes even in a large excess, which can be ascribed to the

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† Electronic supplementary information (ESI) available: Synthesis, experimental details and characterization for **1** and **2**; crystallographic details, UV-vis titrations, and detection limit calculations. CCDC reference number 688682. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808589g

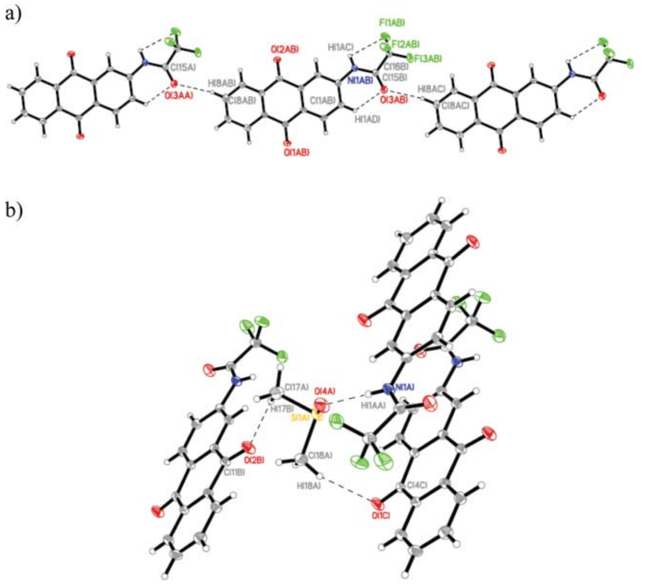


Fig. 2 a) One-dimensional chain formed through intermolecular C–H · · · O hydrogen bonds; b) DMSO-induced trimer of receptor **2**.

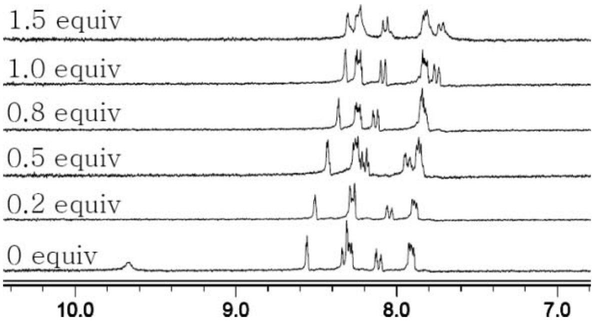
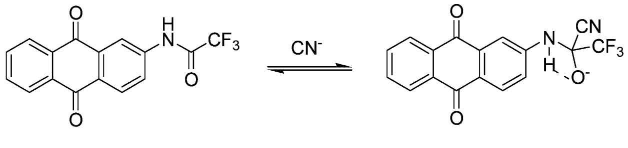


Fig. 3 ^{1}H NMR spectra of a solution of **2** in acetonitrile-d_3 upon the addition of Bu_4NCN.



Colorless

Yellow

Scheme 1 Suggested mechanism for off–on switching in the presence of CN^- anion.

strong intramolecular hydrogen bond between the NH and the anthraquinone oxygen forming a six-membered ring; hence the intermediate (cyanohydrin) can not be stabilized by the NH.[15]

To further investigate the selectivity of the sensor **2**, 12 anions of interest, namely, CN^-, F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_4^-, SCN^-, and N_3^- were added (as their tetrabutylammonium salts) to a solution of **2** in CH_3CN–H_2O (95 : 5, v/v) respectively. It can be seen that only CN^- induced a color change from colorless to yellow (Fig. 4a), and addition of other anions caused no obvious changes either in color or in the UV-vis spectra, even in a large excess (Fig. 4b). The resultant Job plot indicated a 1 : 1 receptor–cyanide binding stoichiometry (Fig. 4c).[16] The binding constants calculated from a 1 : 1 stoichiometry using nonlinear curve fitting analysis,[17] based on the absorption spectral changes at $\lambda_{max} = 429$ nm, yields $K = 7.7 \times 10^4$ M^{-1}. The response time upon exposure to cyanide is instantaneous, and the selectivity over F^- and AcO^- is high (Fig. 5). This is very important because F^- and AcO^- are the main interfering ions in cyanide sensing.

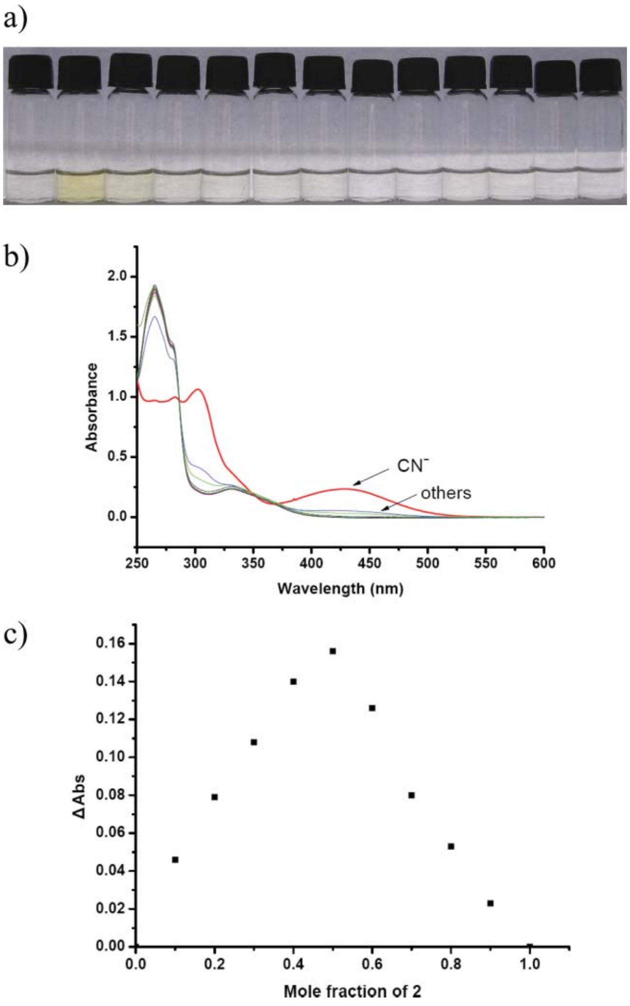


Fig. 4 a) The corresponding color changes and b) absorption spectra when 2-TFAQ **2** (50 μM) was treated with 2.0 equiv of various anions (vials from the left: **2** only, CN^-, F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_4^-, SCN^-, N_3^-) in CH_3CN–H_2O (95 : 5, v/v); c) Job plot of 2-TFAQ **2** with CN^-.

The detection limit of cyanide in aqueous environment was determined. Fig. S3† shows the plot of $A - A_0$ *versus* the cyanide concentration in CH_3CN–H_2O (95 : 5, v/v) solution. A linear response was observed in the 10–50 μM range. A detection limit as low as 0.51 μM was found, which makes sensor **2** a powerful tool for the detection of cyanide in water.

In summary, we have reported the use of 2-(trifluoroacetylamino)anthraquinone as a probe for the sensing of cyanide. Our method is safe, fast, simple to use and inexpensive. The probe is easy to synthesize and allows sensitive and highly selective detection of very low concentrations of cyanide in an aqueous environment.

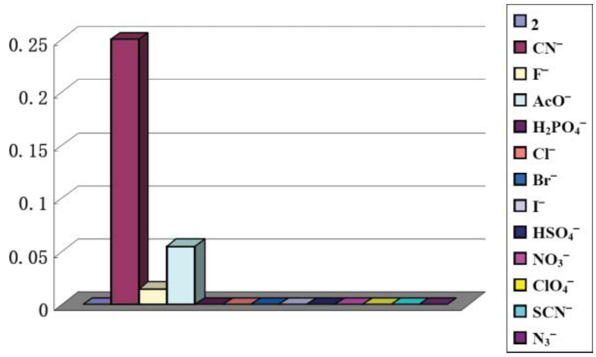


Fig. 5 Absorbance value changes ($A - A_0$) of **2** (50 μM) at 429 nm in the presence of 2.0 equiv of selected anions in $CH_3CN–H_2O$ (95 : 5, v/v) solution. From the left: **2** only, CN^-, F^-, AcO^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, ClO_4^-, SCN^-, N_3^-.

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