

A Thiophene-Based Dicyanovinyl As an Anion Chemosensor [†]

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Abstract: In recent years, push-pull dicyanovinyl derivatives have been reported for several optical applications, including as fluorescent probes for cyanide ion detection. In presence of cyanide ions, this type of compound exhibits an ICT mechanism associated with the addition of the cyanide ion to the β -position of the dicyanovinyl group, due to the strong electron-withdrawing effect of the cyano groups. These structural changes caused by the addition reaction are accompanied by changes in the probe's absorption and emission. In this work, we report a thiophene-based dicyanovinyl derivative and its prospective application as an anion chemosensor. The photophysical characterization was carried out in acetonitrile and aqueous acetonitrile solutions. Preliminary sensing assays in the presence of various anions of biological, medicinal and environmental relevance were conducted and the interaction with CN^- was further explored through spectrophotometric titrations.

Keywords: thiophene; dicyanovinyl; chemosensor; anions

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1. Introduction

Anions are involved in several important biological processes playing numerous roles, as well as being involved in environmental and industrial applications. The development of small molecules for anion recognition is an area of research in constant development. The study of anion recognition in the 60's and 70's became a fundamental area of supramolecular chemistry with a wide range of applications [1–4].

The design of anion receptors is a challenge because anions have a small charge/radius ratio, are sensitive to pH, solvent and solvation [5].

Cyanide ion is a highly toxic substance for the environment and for mammals. Small amounts of cyanide can affect various functions in the human body, attacking the vascular, visual, central nervous, cardiac, endocrine and metabolic systems. The cyanide anion can be absorbed by the lungs, gastrointestinal tract and skin, causing vomiting, convulsions, unconsciousness and possibly leading to death. It is lethal to humans at concentrations in the range of 0.5–3.5 mg/kg body weight. In addition to being found in many foods and plants, cyanides are used industrially in the synthesis of organic chemicals, polymers, metallurgy, as well as in gold mining. Several strategies for colorimetric and fluorimetric detection of cyanide ion have been reported in recent years, involving various mechanisms such as coordination, CdSe quantum dots, displacement approach, deprotonation of hydrogen bond interactions and nucleophilic addition reactions [6,7].

Dicyanovinyl derivatives are widely used as colorimetric and fluorescent chemosensors. Based on the structural properties of this group, it is possible the occurrence of nucleophilic addition reactions, at the β position of this group, by chemical species with a high electron density. In the literature, the addition of cyanide ion to the β position of the

dicyanovinyl portion is widely reported, causing significant colorimetric and fluorimetric changes associated with intramolecular charge transfer (ICT) allowing its detection [8–12].

The use of five-membered rings such as thiophene allows the establishment of an electron donor-acceptor relationship with chromophores by increasing π -conjugated systems. In addition to providing thermal and chemical stability, these kinds of compounds also improve delocalization of electrons, revealing improved optical properties [13–16].

In this communication, we report a thiophene-based dicyanovinyl derivative and its prospective application as a cyanide chemosensor. The photophysical characterization was carried out in acetonitrile and aqueous acetonitrile solutions. Preliminary sensing assays in the presence of various anions of biological, medicinal and environmental relevance were undertaken, followed by spectrophotometric titrations with cyanide ion.

2. Experimental section

2.1. Methods and Materials

All reagents were purchased from Sigma-Aldrich, Acros, and Fluka and used as received. UV-visible absorption spectra were obtained using a Shimadzu UV/2501PC spectrophotometer. Fluorescence spectra were collected using a FluoroMax-4 spectrofluorometer. The relative fluorescence quantum yields were determined by using a quinine sulfate in 0.05 M H₂SO₄ as fluorescence standard. The synthesis of thiophene dicyanovinyl derivative **1** was reported elsewhere [15].

2.2. Photophysical Studies of Thiophene Dicyanovinyl Derivative **1**

Thiophene dicyanovinyl derivative **1** was studied in ACN solution with concentrations between 1.0×10^{-6} and 1.0×10^{-5} M. Quinine sulfate ($\Phi_F = 0.546$) in 0.05 M H₂SO₄ used as fluorescence standard with a concentration of 1.0×10^{-5} M. Compound **1** was excited at 421 nm, the same for the fluorescence standard solution. The cells were made of quartz and after the plot of each spectrum, the respective area was determined. The calculation of the relative quantum fluorescence yield of the dicyanovinyl derivative was performed using Equation (1).

$$\frac{\Phi_{\text{comp}}}{\Phi_{\text{stand}}} = \frac{A_{\text{stand}} \times F_{\text{comp}} \times n_{\text{stand}}^2}{A_{\text{comp}} \times F_{\text{stand}} \times n_{\text{comp}}^2} \quad (1)$$

where, A_{stand} and A_{comp} are the absorbances of the solutions at the excitation wavelengths of the standard and the compound under study, respectively; F_{stand} and F_{comp} are the areas under the fluorescence plot of the standard and the compound; n_{stand} and n_{comp} represent the refractive index value of the standard and the compound under analysis, respectively.

2.3. Preliminary Chemosensing Studies and Spectrophotometric Titrations

Evaluation of compound **1** as a colorimetric and fluorimetric chemosensor was carried out in the presence of several anions with environmental and biomedical relevance (H₂PO₄⁻, AcO⁻, NO₃⁻, ClO₄⁻, HSO₄⁻, BzO⁻, Br⁻, CN⁻, I⁻, F⁻) in the form of tetrabutylammonium salts in ACN solution (1.0×10^{-2} M). Solutions of compound **1** were prepared in ACN (1.0×10^{-5} M) and ACN/H₂O (8:2, 8.0×10^{-6} M). The solution of compound **1** in ACN/H₂O (8:2) was prepared by adding 1.6 mL of compound **1** in ACN (1.0×10^{-5} M) and 0.40 mL of distilled water directly to the vial.

The preliminary tests were carried out by addition 50 equivalents of each anion to the solution of compound **1** in ACN and ACN/H₂O (8:2).

As a result of the preliminary study, a spectrophotometric titration of dicyanovinyl derivative **1** was performed in the presence of CN⁻. The solution of the dicyanovinyl derivative (8.0×10^{-6} M) was prepared in ACN/H₂O (8:2) and the solution of the anion under study (1.0×10^{-2} M) was prepared in ACN. The spectrophotometric titration was performed by the sequential addition of CN⁻ solution to the dicyanovinyl derivative solution.

3. Results and Discussion

3.1. Photophysical Characterization of Thiophene Dicyanovinyl Derivative 1

The synthesis of thiophene dicyanovinyl derivative **1** (Figure 1) was achieved through a previously published procedure involving a Knoevenagel reaction of the corresponding aldehyde precursor and malononitrile, catalysed by piperidine in refluxing ethanol [15].

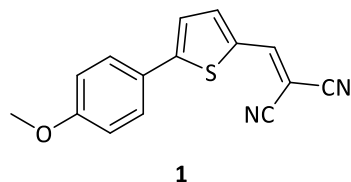


Figure 1. Thiophene dicyanovinyl derivative **1**.

The photophysical properties of the dicyanovinyl derivative were investigated in ACN solutions ($1.0 \times 10^{-5} \text{M}$). The compound showed an intense absorption band ($\log \epsilon = 4.42$) at 421 nm. Upon excitation at 421 nm, the compound showed an intense emission band at 519 nm (Figure 2), with a Stokes' shift of 98 nm. The relative fluorescence quantum yield, determined by using quinine sulfate as standard ($\Phi_F = 0.546$) in 0.05 M H_2SO_4 , was found to be low ($\Phi_F = 0.012$).

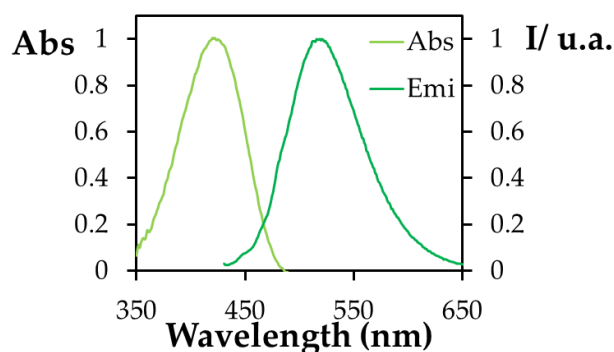


Figure 2. Normalized UV-visible absorption and emission spectra of the dicyanovinyl derivative **1** in ACN ($1.0 \times 10^{-5} \text{M}$, $\lambda_{\text{exc}} = 421 \text{nm}$).

3.2. Preliminary Optical Chemosensing Studies of Thiophene Dicyanovinyl Derivative 1

A preliminary chemosensing study of dicyanovinyl derivative **1** was performed in ACN ($1.0 \times 10^{-5} \text{M}$) and ACN/ H_2O (8:2, $8.0 \times 10^{-6} \text{M}$) solutions with various anions of interest, in ACN solution ($1.0 \times 10^{-2} \text{M}$). The study consisted in adding 50 equivalents of the solution of each anion to the compound's solution. It was observed that the compound's solution showed a loss of color intensity after interaction with the most basic anions CN^- and F^- in both situations, probably due to the addition of the anion to the double bond of the dicyanovinyl group. As for the fluorimetric behavior in ACN, compound **1** showed an enhancement of fluorescence in the presence of H_2PO_4^- , AcO^- , NO_3^- , BzO^- , I^- and F^- , while in ACN/ H_2O (8:2) showed a loss of fluorescence in the presence of HSO_4^- , BzO^- , Br^- , CN^- and I^- (Figure 3).

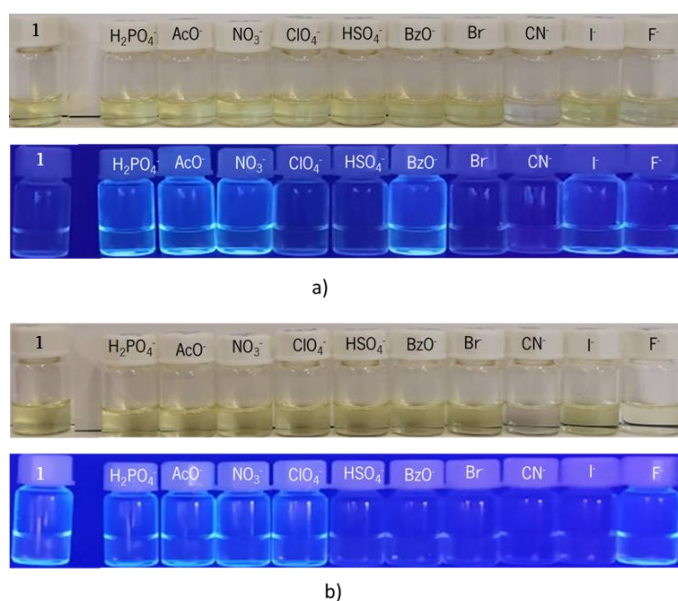


Figure 3. Dicyanovinyl derivative **1** solutions in the presence of various anions, (a) in ACN, under natural light (above) and UV radiation at $\lambda_{\max} = 365$ nm (below); (b) ACN/ H₂O (8:2) under natural light (above) and UV radiation at $\lambda_{\max} = 365$ nm (below).

3.3. Spectrophotometric Titration of Thiophene Dicyanovinyl Derivative with Cyanide

From the previous tests and considering the colorimetric and fluorimetric response of compound **1** to the presence of CN⁻, a spectrophotometric titration of dicyanovinyl derivative **1** with CN⁻ was performed in ACN/H₂O (8:2), which revealed a very sensitive colorimetric response towards this anion. The UV-visible spectra revealed that the intensity of the absorption band at 422 nm decreased rapidly and progressively upon the addition of the anion. The number of CN⁻ equivalents for total loss of absorbance was about 4 equivalents in ACN/H₂O (8:2) solution (Figure 4).

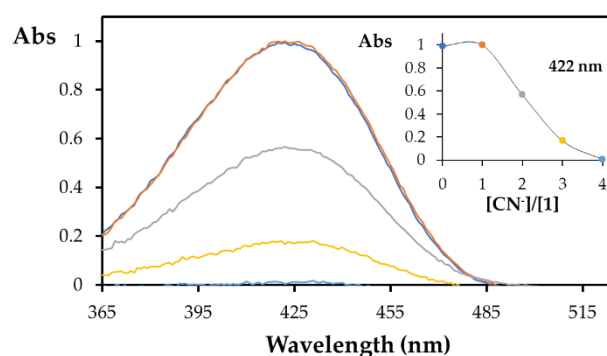


Figure 4. Spectrophotometric titration of dicyanovinyl derivative **1** with addition of increasing amounts of CN⁻ in ACN/ H₂O (8:2). The inset represents the normalized absorbance at 422 nm ($[1] = 8.0 \times 10^{-6}$ M).

A spectrofluorimetric titration of compound **1** was also performed in ACN/ H₂O (8:2) with CN⁻. The fluorescence spectra revealed that the intensity of the emission band at 521 nm decreased progressively upon the addition of the anion, in accordance with the results from the spectrophotometric titration. The number of CN⁻ equivalents to achieve an almost complete fluorescence quenching (>90%) was of about 5 equivalents in ACN/H₂O (8:2) (Figure 5).

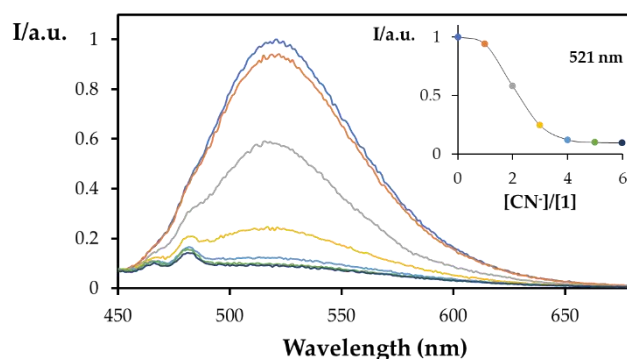


Figure 5. Spectrofluorimetric titration of dicyanovinyl derivative **1** with addition of increasing amounts of CN^- in ACN/ H_2O (8:2). The inset represents the normalized intensity at 521 nm ($[\text{1}] = 8.0 \times 10^{-6}$ M).

4. Conclusions

The thiophene dicyanovinyl derivative **1** was characterized by absorption and emission spectroscopies, establishing its photophysical properties. A preliminary chemosensory study in ACN and ACN/ H_2O (8:2) of dicyanovinyl derivative **1** in the presence of selected anions showed a colorimetric and fluorometric response of this compound in the presence of cyanide, through loss of color and fluorescence. Therefore, more detailed spectrophotometric and spectrofluorimetric titrations were conducted which revealed that the number of equivalents necessary for achieving a plateau was of 4 and 5 equivalents, respectively, which can be considered a very sensitive response. Based on the preliminary chemosensory studies and the spectrophotometric titrations, this novel thiophene dicyanovinyl derivative is a promising candidate as colorimetric and fluorimetric probe for cyanide ion recognition.

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