



A fluorescent coumarin-thiophene hybrid as a ratiometric chemosensor for anions: Synthesis, photophysics, anion sensing and orbital interactions



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ABSTRACT

A colorimetric and fluorimetric fluorescent chemosensor (**CT-2**), having a coumarin ring as a signaling unit and an acetamido thiophene ring as an H-donor receptor, has been synthesized from amino derivative (**CT-1**) of **CT-2** for the purpose of recognition of anions in DMSO. The absorption and emission maxima were both determined for the fluorescent dye in different solvents. Both hypsochromic shift at the absorption maximum, and quenching of fluorescence after interactions between the anions and the receptor part, were observed. This phenomenon was explained using orbital interactions based on quantum chemical calculations. The selectivity and sensitivity of **CT-2** for F^- , Cl^- , Br^- , I^- , AcO^- , CN^- , $H_2PO_4^-$, HSO_4^- and ClO_4^- anions were determined with spectrophotometric, fluorimetric and 1H NMR titration techniques and it was found that **CT-2** be utilized for the detection of CN^- , F^- and AcO^- in the presence of other ions as competitors. Color and fluorescence changes visible to the naked eye and under UV (365 nm) were observed upon addition of CN^- , F^- and AcO^- to the solution of chemosensor (**CT-2**) in DMSO. The sensor showed no colorimetric and fluorimetric response for the anions such as Cl^- , Br^- , I^- , $H_2PO_4^-$, HSO_4^- , and ClO_4^- . However, 1H NMR titration shows that the chemosensor was more sensitive to CN^- , than F^- and AcO^- at the stoichiometric ratio of 1:2.5 respectively. Additionally, the compounds **CT-1** and **CT-2** showed good thermal stability for practical applications.

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1. Introduction

Anions are important in clinical, environmental, chemical and industrial processes [1]. Drinking water is known to be the most important source of fluoride and so is important for both human body and bone growth [2]. Exposure to excess fluoride may cause collagen break down, bone disorder, thyroid activity, and depression. Fluoride deficiency causes gum disease and osteoporosis, while an excess (above 1.5 ppm) leads to fluorosis (fluoride poisoning) because of its nephrotoxic effect [3,4]. High chlorine concentration was determined in the sweat test used in the diagnosis of cystic fibrosis [5,6]. It is known that excess of bromide causes severe irritation of the respiratory tract. Iodide has an effect

on the functioning of the thyroid gland. Both excess and deficiency of this anion affects the operation of the thyroid gland and can cause serious illness [7,8]. Acetate anion plays a critical role in many metabolic processes, and exhibits specific biochemical behavior on antibodies and enzymes [9,10]. Cyanide ion is also vital as a raw material in industrial process and it is also highly toxic for the human body [11,12].

As a consequence, efforts have been made to determine fluoride, chloride, bromide, iodide and other ions such as acetate, chlorate, sulfate, phosphate and cyanide in real samples. The determination of anions can be achieved by several methods including spectroscopic, chromatographic, electrochemical and analytical techniques. However, the detection of anions with the use of simple preparation and minimal instrumental assistance is desirable toward practical applications. Colorimetric and fluorimetric chemosensors are important alternatives to the traditional methods for determination of anions. Therefore, synthesis of new additional chemosensor is still required.

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The sensor (**CT-2**) reported here contains coumarin and thiophene unit as the main core. The coumarin ring is commonly used as a fluorophore/chromophore in sensor systems because of its high fluorescence quantum efficiency, large Stokes shift, bright color under ambient light and ease of synthesis and derivatization [13,14]. Thiophene derivatives are also valuable compounds in heterocyclic chemistry due to its important optical properties.

In this work we chose coumarin as the fluorophore/chromophore for signaling, and thiophene at the 3-position of the coumarin ring to modify the fluorescence properties of the coumarin core, in order to form a receptor for anions via an acetamide functional group. We first studied the photophysical properties of the fluorescence chemosensor (**CT-2**) and its starting compound (**CT-1**). Afterwards, binding properties of the chemosensor toward specific anions such as F^- , Cl^- , Br^- , I^- , AcO^- , CN^- , $H_2PO_4^-$, HSO_4^- and ClO_4^- was also investigated. Additionally, the experimental results obtained were explained with theoretical calculations. Thermal properties of **CT-1** and **CT-2** for optical usage were also determined. **CT-2** showed remarkable selectivity toward CN^- , F^- and AcO^- over other anions at the stoichiometric ratio of 1:5 (**CT-2**:Anion) respectively. However, the chemosensor was more sensitive to CN^- , than F^- and AcO^- at the stoichiometric ratio of 1:2.5 respectively.

2. Experimental

2.1. Materials and instrumentations

All the chemicals used in the synthesis of the compounds were procured from Aldrich Chemical Company and were used without further purification. The solvents used were of spectroscopic grade. Thin-layer chromatography was carried out using precoated aluminium-backed plates (Merck Silica Gel 60 F254) and visualised under UV light ($\lambda = 254\text{--}365\text{ nm}$). FT-IR Spectra were recorded on a Mattson 1000 FT-IR spectrophotometer in KBr (ν are in cm^{-1}). NMR spectra were run on a Bruker Avance 300 MHz instrument. NMR samples were referenced against tetramethylsilane at 0.00 ppm for 1H . Coupling constants (J) are given in hertz (Hz). Signals are abbreviated as follows: singlet, s; doublet, d; doublet–doublet, dd;

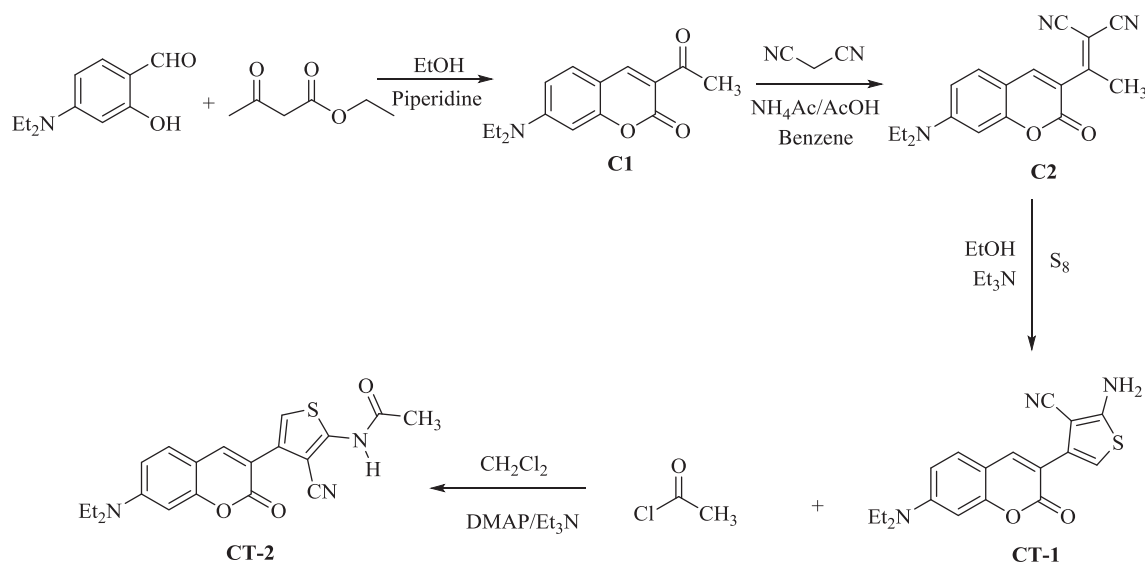
triplet, t; multiplet, m. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. J values are given in Hertz (Hz). High resolution mass spectra were recorded on a Waters-LCT-Premier-XE-LTOF (TOF-MS), mass spectrometer operated in Electronization (EI) mode in m/z (rel. %) (Gazi University Laboratories, Department of Pharmacological Sciences). The melting points were measured using Electrothermal IA9200 apparatus and were uncorrected. Thermal analyses were performed with a Shimadzu DTG-60H system, up to $600\text{ }^\circ C$ ($10\text{ }^\circ C\text{ min}^{-1}$) under a dynamic nitrogen atmosphere (15 mL min^{-1}).

2.2. Spectrophotometric measurements

Ultraviolet–visible (UV–vis) absorption spectra were recorded on Shimadzu Corporation, Kyoto Japan UV-1800 240 V spectrophotometer (Gazi University, Department of Chemistry, Turkey) at the wavelength of maximum absorption (λ_{max} , in nm). Fluorescence spectra were recorded on HITACHI F-7000 FL Spectrofluorophotometer. All spectrophotometric measurements were performed in thermostated quartz sample cells at $20\text{ }^\circ C$, using spectral grade solvents. The solution concentrations were $10\text{ }\mu M$ for absorption spectroscopy and $1.0\text{--}5.0\text{ }\mu M$ for fluorescence spectroscopy. Spectrophotometer slit widths were set to bandwidths of 5 nm for emission spectroscopy. The relative fluorescence quantum yields, Φ_{fl} , were determined by standard methods [15,16] with Coumarin 153 (laser grade, Acros Organics, $\Phi_{fl} = 0.38$ in ethanol) as a reference.

2.3. Synthesis of 2-amino-4-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)thiophene-3-carbonitrile (**CT-1**)

To a solution of **C2** (2-(1-(7-(*N,N*-diethylamino)-2-oxo-2H-chromen-3-yl)ethylidene)malononitrile) (10 mmol), elemental sulfur (12 mmol), and triethylamine (1 mmol) in 30 mL ethanol, were placed in a 100 mL round-bottom flask. The reaction mixture was heated under reflux with stirring for 4 h . The progress of the reaction was monitored by TLC (ethylacetate/n-hexane 1:1). After cooling, the orange precipitate was filtered and product was washed with hot ethanol and dried. The pure



Scheme 1. Synthetic pathway for **CT-1** and **CT-2**.

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