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H-bond stabilization of a tautomeric coumarin-pyrazole-pyridine triad generates a PET driven, reversible and reusable fluorescent chemosensor for anion detection

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ABSTRACT

A coumarin based anion sensor utilizing pyrazole both as an electron donor and hydroxyl H-bond donor and pyridine as a tautomer stabilizer is reported. The chemosensor exhibits ON-OFF-ON states and is more sensitive to F^- at the stoichiometric ratio of 1:1. The OFF state is due to PET and the role of pyrazole is two fold, both stabilization of the enol tautomer via H-bonding and hosting domain of electrons enabling PET. Moreover, the absorption and emission properties of chemosensor change drastically upon acidification.

1. Introduction

Anion sensing [1] has grown to be a major field in the last decades with particular emphasis on Fluoride [2] detection mainly due to its physiological [3] and environmental [4] significance. Fluoride is the smallest and most electronegative anion and is capable of forming very strong hydrogen bonds with receptoric part including −NH and −OH as hydrogen bond donor groups which are crucial for colorimetric and fluorimetric detection of fluoride. Numerous colorimetric and fluorometric F^- chemosensors utilizing various molecular design approaches are available in the literature [5]. Breaking an −NH···N/O intramolecular weak interaction via abstraction of the H-bonded proton by solvated F^- was proven to be a useful design strategy in operating F^- chemosensors [6]. These F^- chemosensors generally employed electrostatic interactions arising from urea/thiourea, hydrazone, amide, sulfonamide, indole, pyrrole or calixpyrrole units [7]. Remarkably, despite biological examples [8] exploiting the use of hydroxyl groups as H-bond donors, only a handful of F^- chemosensors operating on a −OH···N intramolecular interaction are reported to date [2]. These examples were based on an Excited State Intramolecular Proton Transfer (ESIPT) mechanism and utilized for naphthol and phenol derivatives [2,9]. Hence one naturally expects an ESIPT mechanism based on an −OH functional group in close proximity to an H-bond acceptor.

Moreover, coumarin is seldom used [10] in F^- sensing although methods [11] of synthetic derivatization for tuning the photophysical properties to achieve functional coumarin based devices are well established. Herein we report the synthesis and electronic structure details of a novel coumarin based tautomeric triad that operates as an anion sensor by virtue of exclusively existing in the enol form. We took advantage of three logical steps that enabled the design of the fluorescent sensor **1** as well as the efficient conversion of **1** to the OFF state, **2** (Scheme 1): (i) Coumarin is the signaling unit (fluorophore/chromophore); (ii) Pyrazole at the 3-position of the coumarin ring, partly tunes the luminescent properties of the coumarin core, possesses an acidic proton and hence serves as the receptor for anions. The −OH function also acts as the H-bond donor. Thus pyrazole is purposeful both structurally and

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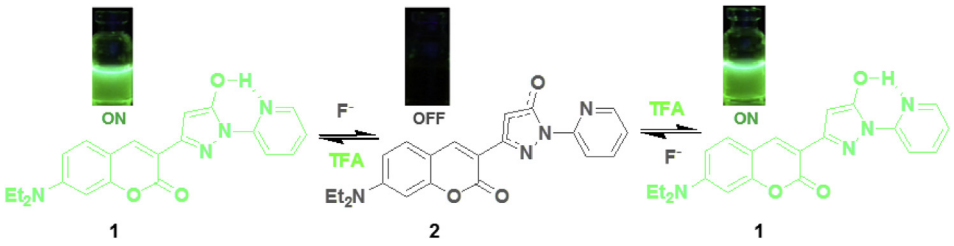


Scheme 1. Coumarin-pyrazole-pyridine (**1**) and deprotonated form (**2**).

electronically. (iii) Pyridine seems to take part in H-bonding only however, its absence favours the keto tautomer over the enol form (Scheme 2) by 7 kcal mol^{-1} (Supplementary data, Scheme S1) [7a]. Therefore pyridine is critical in accessing the functional tautomeric state.

2. Experimental

2.1. Materials and equipments

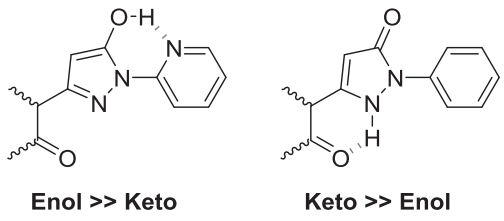
Reagents, anions and solvents used in all steps of synthesis and measurement were provided from Sigma Aldrich USA and used as commercial grade without further purification. Deuterated solvent (DMSO-d_6) for NMR studies were obtained from Merck Germany. Melting points were obtained from Electrothermal 9200 melting point apparatus. Nuclear magnetic resonance ($^1H/^{13}C$NMR/anion titrations) spectra were recorded on a Bruker Ultrashield 300 MHz NMR spectrometer. Mass spectra was recorded on a Waters LCT Premier XE (TOF MS) mass spectrometer. Ultraviolet–visible (UV–vis) absorption spectra were recorded on a Shimadzu UV-1800 UV-VIS Spectrophotometer. Fluorescence spectra were recorded on a HITACHI F-7000 FL Spectrofluorophotometer. Anions used for all measurements were obtained as tetrabutylammonium salts (F^-, Cl^-, Br^-, I^-, AcO^{--}, CN^-, $H_2PO_4^-$, HSO_4^- and ClO_4^-) and their solvents were prepared in DMSO as analytical grade. Thermal analysis was performed with a Shimadzu DTG-60H system, up to 500 °C (10 °C min^{-1}) under a dynamic nitrogen atmosphere (15 mL min^{-1}).

2.2. The synthesis of Methyl 3-(7-(diethylamino)-2-oxo-2H-chromen-3-yl)-3-oxopropanoate

It was synthesized by using our previous method [7a].

2.3. The synthesis of 7-(diethylamino)-3-(5-hydroxy-1-(pyridin-2-yl)-1H-pyrazol-3-yl)-2H-chromen-2-one (1) with conventional method

2-Hydrazinopyridine (0.109 g, 1×10^{-3} mol) was added to a stirred solution which was compound methyl 3-(7-(diethylamino)-2-oxo-*2H*-chromen-3-yl)-3-oxopropanoate (0.318 g, 1×10^{-3} M) in Acetic acid (20 mL), after stirred and refluxed for 4 h (the optimum time was determined by using TLC and found as 4 h). The mixture was cooled to room temperature, diluted with diethylether (10 mL) and stirred for 30 min in ice bath. At the end of the time, the mixture was filtred and acquired a yellow solid, then washed with cold diethylether (10 mL), and hot methanol to obtain pure compound **1**. (0.30 g, yield: 80%, mp = 193–195 °C). ^1H NMR (DMSO-d_6, 300 MHz): δ 12.39 (s, 1H); 8.49 (m, 2H); 8.12 (t, J = 7.6 Hz, 1H); 7.90 (d, J = 8.3 Hz, 1H); 7.6 (d, J = 8.9 Hz, 1H); 7.39 (t, J = 5.7 Hz, 1H); 6.75 (d, J = 8.1 Hz, 1H); 6.58 (s, 1H); 6.22 (s, 1H); 3.47 (q, J = 6.8 Hz, 4H); 1.15 (t, J = 8.9 Hz, 6H). ^{13}C NMR (DMSO-d_6, 75 MHz): δ 160.0; 156.6; 147.3; 147.1; 147.0; 130.6; 121.5; 110.0; 108.3; 96.6; 44.6; 12.8. HRMS (m/z) $(M-H)^+$ calculated for $C_{21}H_{21}N_4O_3$, 377.1614; found 377.1631.



Scheme 2. Favoured tautomers and intramolecular H-bonds.

2.4. MWI method for synthesis of 1

2-Hydrazinopyridine (0.109 g, 1×10^{-3} mol) and methyl 3-(7-(diethylamino)-2-oxo-*2H*-chromen-3-yl)-3-oxopropanoate (0.318 g, 1×10^{-3} mol), 1 mL Acetic acid were added in a microwave tube, then stirred 4 min at 270 W, 130 °C. The mixture was filtred and obtained as yellow solid which can be crystallization with methanol for further purification (0.24 g, yield: 65%).

2.5. UV–vis, fluorimetric and ^1H NMR titration measurements of 1 with all studied anions

2.5.1. For UV–vis and fluorimetric titration experiments

A stock solution (10 mL, 1×10^{-3} M) for **1** and stock solutions (1 mL, 1×10^{-2} M) of tetrabutylammonium (TBA) salts of each of the anions were prepared with DMSO. For UV–vis titration, the final solution containing 20 μL of **1** and 1980 μL of DMSO was prepared and transferred into a glass cell to obtain a final concentration of 1×10^{-5} M of **1**. (For fluorimetric titration, the stock solution of **1** was (10 mL, 1×10^{-5} M) and stock solutions of TBA salts were (1 ml, 1×10^{-4} M) and the final concentration was 1×10^{-7} M in DMSO in the same way). 2 mL-40 mL of the salts of TBA solution (1×10^{-2} M) were transferred to the solution of each chemosensor **1** (1×10^{-5} M) prepared above, into the glass cell. After mixing them for a few seconds, UV–vis absorption spectra were taken at room temperature (25 °C). TBA salts of F^-, Cl^-, Br^-, I^-, AcO^-, CN^-, $H_2PO_4^-$, HSO_4^-, and ClO_4^- (1×10^{-2} M) were dissolved in DMSO (1 mL). In all experiments, any changes in the UV–vis and emission spectra of **1** were recorded upon the addition of TBA salts while the ligand concentration was maintained at 1×10^{-5} M (for UV–vis titration) and 1×10^{-7} M (for fluorimetric titration).

2.5.2. For ^1H NMR titration experiment

For ^1H NMR titrations, two stock solutions were prepared in