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Tri-color emission and colorimetric recognition of acetate using semicarbazide and thio-semicarbazide derivatives: Experimental and computational studies

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ABSTRACT

Two new fluorescence probes having semicarbazide (**DSC**) and thio-semicarbazide (**DTSC**) units have been derived upon reaction with 2-hydroxy-5-methylbenzene-1,3-dialdehyde. Both the probes show excellent selectivity for acetate ion in DMSO medium whereby **DTSC** generates tricolor emission. The association constants of **DSC** and **DTSC** for acetate are 6.6×10^4 M^{-1} and 2×10^3 M^{-1} respectively with corresponding detection limits, 1.06×10^{-7}M and 2.5×10^{-6} M. Density functional theoretical (DFT) studies nicely demonstrate the interaction between the DTSC and acetate ion.

1. Introduction

The design of optical sensor for selective detection of anion has received considerable attention over the past few years. Anions are ubiquitous in biology, actively participate in enzyme activity, hormone transport, protein synthesis, and DNA regulation [1–4]. For example, the antibiotic ristocetin is known to efficiently and selectively bind amino acid carboxylates [5–6]. Acetate (AcO^-) is an important player in biochemistry, environmental, and pharmaceutical science [7–9]. It is considered as an indicator of organic decomposition in marine sediments [10]. Fluorescence, is already established as an efficient and sensitive technique [11] for anion recognition *via* significant change of emission color and/or intensity. Varieties of anion sensing mechanisms, *viz.* competitive binding, [12] photo-induced electron transfer (PET), [13] metal-to-ligand charge transfer (MLCT), [14] excimer/exciplex formation, [15] intra-molecular charge transfer (ICT), [16] excited-state intra-/inter-molecular proton transfer (ESIPT) [17] and H-bonding induced loop formation [18] *etc.* have been reported. Most of the reported AcO^-/carboxylate receptors [19–27] face interference from other basic anions like $H_2PO_4^-$ and F^-. Recognition of anions in biological systems is very often achieved *via* hydrogen bonding with highly pre-organized proteins having sterically well-defined complex sites in the interior of proteins [28–29]. Examples are also available where recognition and discrimination of different anions have been achieved *via* suitable receptor coordination sites [30–33]. Herein we describe synthesis, characterizations and photo-physical interaction of a probe (**DTSC**) derived from 2,6-diformyl-4-methylphenol (**DFP**) and thiosemicarbazide with AcO^-. **DTSC** has a unique tri-color emission in the presence of AcO^- in DMSO medium. A model semicarbazide derivative (**DSC**) of **DFP** fails to generate tri-color emission in the presence of AcO^- in DMSO medium.

2. Results and discussion

DTSC and **DSC** have been synthesized by a single step condensation reaction between **DFP** with thiosemicarbazide and semicarbazide in ethanol as a yellow precipitate with good yield (Scheme 1).The yellow solids are recrystallized from absolute ethanol to obtain pure **DTSC** and **DSC** as established from ^{1}H NMR, MS and FTIR spectra (Figs. S1–S6, ESI). The UV–vis. spectrum (Fig. 1) of the DMSO solution of **DTSC** shows two characteristic bands at 315 and 370nm along with a broad band centered at 450nm. Upon gradual addition (0.01 to 90μM)of AcO^-, the bands at 315 and 370nm decrease with the increase of the 450nm band. A clear isobestic point is observed at 400nm. Similarly for **DSC**, two bands *viz.* at 287 and 357nm decrease with the appearance

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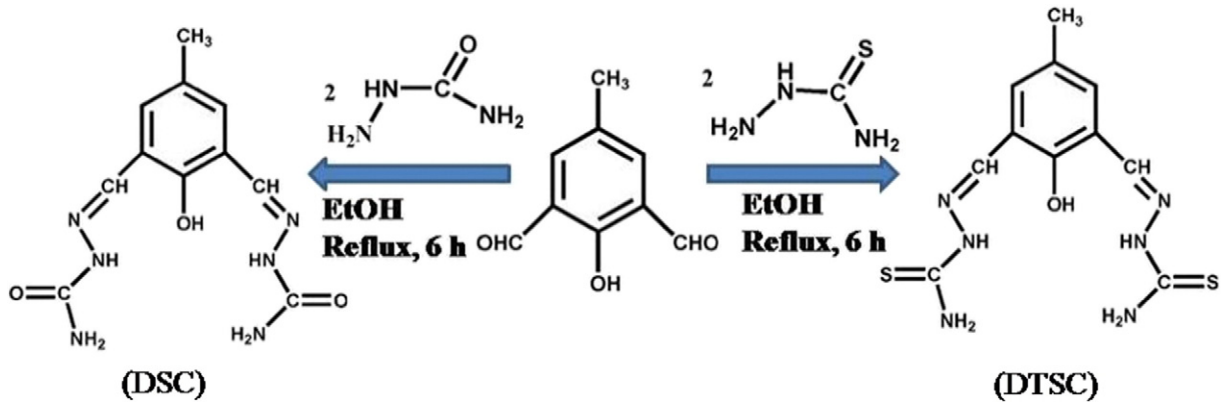

Scheme 1.

of a new band at 425nm which gradually enhances upon gradual addition (0.01 to 90μM) of AcO^-. Here too, an isobestic point at 382nm is observed (Fig. S7). The ratiometric change of absorbance along with the appearance of an isosbestic point indicates the formation of a new intermolecular charge transfer complex between the receptors (**DTSC** and **DSC**) and AcO^-, responsible for visible color change from colorless to yellow in case of **DSC**. Whereas, addition of AcO^- to **DTSC** develops an orange color which changes to yellow after 2h. Time dependent UV–vis. titration (Fig. 2) shows that addition of AcO^- to DMSO solution of **DTSC** develops a band centered at 500nm, responsible for the orange color. However, with time the absorbance of 500 nm band decreases with the enhancement of a new band at 450nm, responsible for yellow color, along with an isobestic point at 480 nm. Additionally, the band at

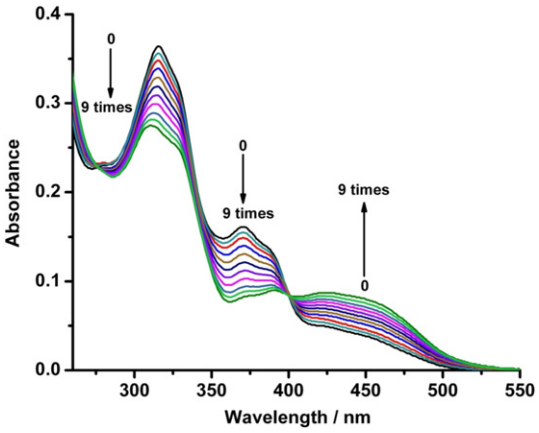

Fig. 1. Changes of absorbance of **DTSC** (10μM) upon addition of AcO^- (0.01, 0.05,0.1,0.5,1, 5, 10, 20, 30, 50, 60, 70 and 90μM) in DMSO.

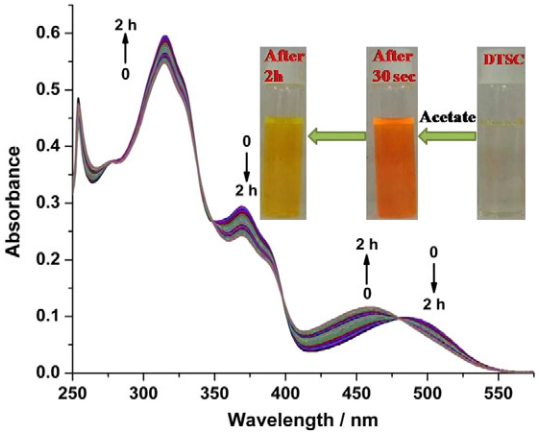

Fig. 2. Time dependent UV–vis. titration of **DTSC** with AcO^-, [**DTSC**]=10 μM, [AcO^-]=90μM.

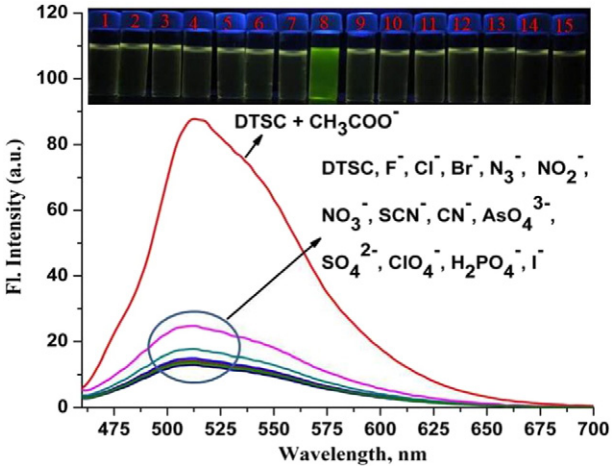

Fig. 3. Relative emission intensity of **DTSC** (10 μM) in the presence of different anions (100 μM) in DMSO (λ_{ex} = 515 nm).

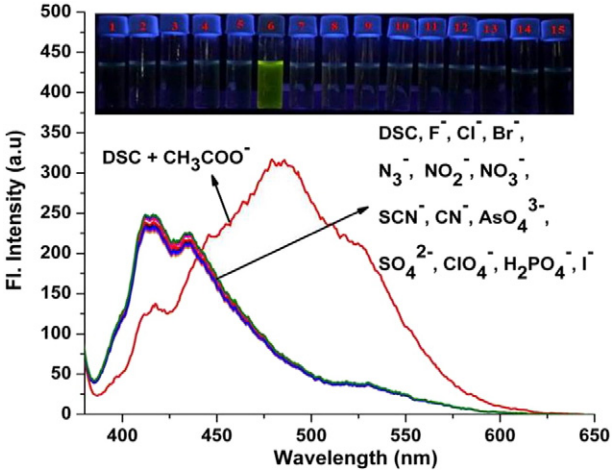

Fig. 4. Relative emission intensity of **DSC** (20 μM) in the presence of different anions (1000 μM) in DMSO (λ_{ex} = 482 nm).