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Host-Guest Interaction of Anthraldehyde Dithiosemicarbazone and Construction of Molecular Logic Gates

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Abstract:
Novel anthraldehyde based dithiosemicarbazide chemosensor was synthesized and characterized for the selective optical and naked eye recognition of copper, fluoride and cyanide ions. The receptor shows fluorescence ON-OFF behaviour with Read-Erase-Write-Read property when an alternative addition of Cu^{2+} and F^-, which results the INHIBIT logic gate at the molecular level. While comparing the optical properties of the receptor with the presence of individual ions and a combination of the ions, the construction of molecular logic gates as a combination of AND, OR, NAND and XOR logic gates with the input of Cu^{2+}, CN^- and F^- ions.

Key words: Chemosensor, Molecular Logic Gate, Thiosemicarbazone, Fluorescence.

Introduction:

The design and development of selective optical sensors and receptors for anions and cations have gained considerable attentions, due to its essential role in many areas such as medicinal biological, environmental chemistry and catalysis. The recent discovery of anion π-interaction gives a new dimensions for the anion recognition and sensing. Fluoride, cyanide anions and copper cation detections have a special interest due to its application in industry, food and toxicity. Fluoride ion has great role in clinical treatments, fluorination in the water and nuclear warfare agents and its concentration in drinking water in excess can cause fluorosis, thyroid activity depression, dental caries and treating osteoporosis [1].

Large number of molecular logic gates were exploited after the introduction by Aviram et al., The fluorescent systems and their excited-state processes have been frequently employed in the rational design of molecular switches [2]. The logic gate at molecular level is illustrated by chemical and/or optical input and optical outputs.

The functional groups which have been explored as good receptors for fluoride ions are amides, pyrrole, urea/thiourea, imidazolium groups, phenyl hydrazones etc. But majority of them interfere with other anions as well. The current work pay attention towards the development of new fluorescent chemosensors to detect anions and cations selectively and sensitively. The study further extended to logic gate behavior of synthesized chemosensors towards F^-, CN^- and Cu^{2+} ions.

Experimental Section:

Synthesis of Anthraldehyde ethane-1,2-dithiosemicarbazone (AeDTSC):
The ethane-1,2-dithiosemicarbazide (TSC) was (0.208 g, 1 mmol) dissolved in DMF (20 ml) at 120 ^{0}C. Anthraldehyde (2 mmol) in DMF (5 ml) was then added dropwise. The mixture was stirred at 120^{0}C for 5 hour after which cold water was added to induce precipitation of the product. The product was filtered, washed and dried under vacuum.

Results and Discussions:

UV-Vis spectroscopic studies

The UV-Vis spectra of AeDTSC shows an absorbance at 298 and 310 nm, which attributed to π→π* and n→π* transitions respectively. The AeDTSC is made to interact with various anions and cations. The cyanide, fluoride and copper ions produced detectable change in the absorption spectra. Addition of other anions produced no significant change in the spectral pattern. UV-Vis spectra titration have been done in order to monitor the sensing ability of the compound towards fluoride anion. The clear isobestic point at 363 nm suggest that only one type of host-guest complex exists. The presence of aromatic ring enhanced the rate of

recognition of fluoride anion. Upon the addition of Cu^{2+}, a new absorption band at 400 nm was formed, this attributes the metal to ligand charge transition. The association constant is calculated using Benesi- Hildebrand equation [3],

$$\frac{1}{A-A_0}=\frac{1}{A_\infty-A_0}\frac{1}{K[C]}+\frac{1}{A_\infty-A_0}$$

Fluorescence Spectral Studies

Emission spectra studies were carried out to investigate the fluorescence behavior of AeDTSC in the presence and absence of ions. A high intense emission peak at 443 nm was observed for AeDTSC when it excited at 340 nm. The presence of F^-, CN^- and Cu^{2+} were show red shift of 15, 11 and 12 nm respectively, whereas, the addition of other ions didn't show any changes.

Logic gate behavior:

The absorption and emission spectra of the receptor are significantly affected by addition of Cu^{2+}, CN^-, F^- and combination of ions. The multiple ion detection of AeDTSC is used to describe the logic operations by considering the presence of CN^-, Cu^{2+} and F^- ions as inputs. Examining the changes of absorption and emission as outputs this molecule can operate functions of multiple logic gates including XNOR, NOR and OR when CN^-, Cu^{2+} (In1) and F^- (In2) are used as inputs. The circular diagram is as shown in the Figure 2.

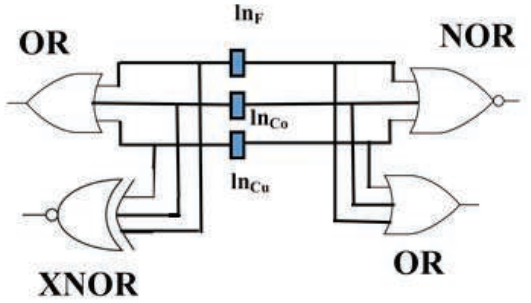

Fig.2. Combinatorial circuit diagram of AeDTSC with three input (F^-, CN^- and Cu^{2+} ions).

Conclusion:

The presence of CN^- and F^- result formation of new peaks at 382 and 422 nm. Interaction of hydrogen bond donors (N−H and O−H) of the AeDTSC with guest fluoride/cyanide ions are accompanied by intermolecular proton transfer. The presence of C=N chromophore is responsible for visible colorimetric change from colourless to yellow which is detectable with naked eye. The electron donating property of anthracene and the electron withdrawing property of the thioketone group in the receptors give a "push-pull" based excited state

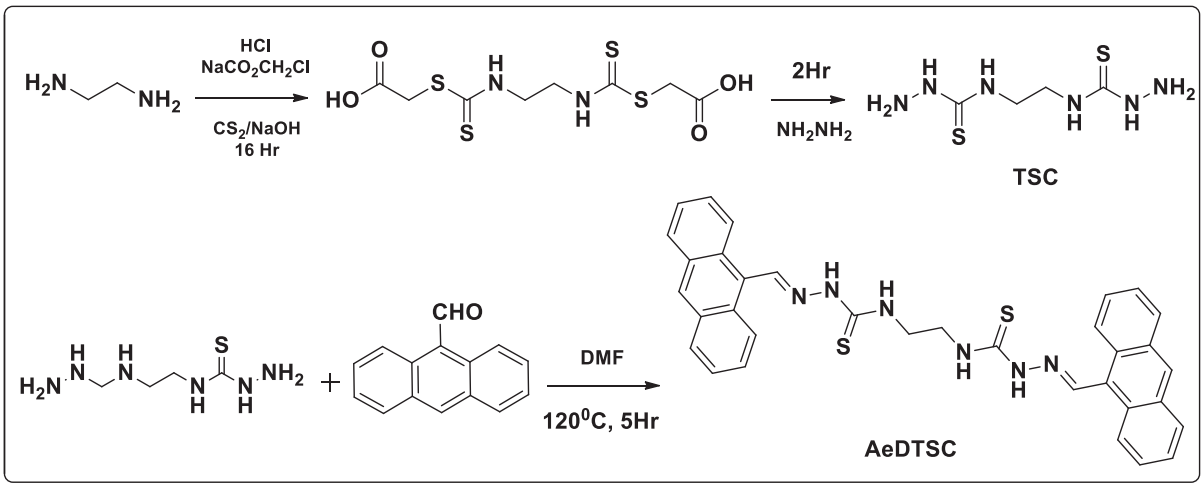

Fig.1. Synthesis of dithiosemicarbazone compound (SalTSC).

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