Sensing of electron withdrawing group (-NO_2) in DNOC employing fluorescence of Camphorsulfonic acid doped Polyaniline (CSA-PANi) solution.

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ABSTRACT

This manuscript is an attempt to sense electron withdrawing group (-NO_2) employing fluorescence quenching study. The camphorsulfonic acid doped Polyaniline (CSA-PANi) is taken as a fluorophore and Dinitro-ortho-cresol (DNOC) is tested as a quencher. An organic nitro functional group is a key element in most of High Energy Materials (HEMs). We attempt to sense such nitro functional group using CSA-PANi. The straight line from the Stern-Volmer plot describes the static quenching in the system. A possible interaction between CSA-PANi and DNOC is given herewith in this manuscript.

Key words: *Fluorescence, Stern-Volmer plot, Static quenching, CSA-PANi, electron withdrawing group*.

1. INTRODUCTION

Sensing an electron withdrawing group, especially $-NO_2$ is of top priority now-a-days, because of its wide appearance in most of HEMs viz., TNT, RDX, PETN etc. Nitro group can withdraw the free electron in its vicinity. Lot of techniques such as spectroscopy, conductivity, gated mesoporous dyes etc. are adopted in signaling electron transfer [1-5], whereas the fluorescence quenching mechanism is a tool to signal accurately [6].

Earlier Swager [6-7], Trogler [8], Satish patil [9], and others [10-11] have employed same mechanism to sense the electron withdrawing groups. Many scientists have employed fluorophores that are hectic to synthesize or have restricted applicability of device manufacturing in sensing studies. Recent reports on sensing picric acid employing fluorescence quenching studies of CSA-PANi in solution [12-14] and PANi-PVA-IPN film [15] are the breakthroughs of adopting easily synthesizable polyaniline and its physical forms. One of the physical forms of PANi (films) is being used in devising semiconductors [16]. This will emphasize the applicability of doped PANi as fluorophores.

Polyaniline nanocomposites are employed in sensing of TNT through electrochemical and colorimetric processes [17]. Polyaniline is a conjugate conducting polymer which is reported to show fluorescence by doping it with sulfonic acids. There is a report on CSA-PANi fluorescence in sensing oxygen [18]. Coiled structure of undoped polyaniline has π stacking, whereas dopant uncoils the polymer chain, thereby allowing free flow of π electron throughout the length of the chain. This may allow the increased fluorescence performance for doped polyaniline.

The vacant orbital on nitro functional group of organic molecules induces more electron withdrawing character. An electron rich chemical compound gets influenced by nitro functionalized organic molecule in the vicinity. We are intended to signal the electron transfer from electron rich material to electron withdrawing nitro functionalized organic material. In this work we are intended to sense the same nitro group in DNOC which is a toxicant and may be used in pyrotechnic compositions.

2. Materials and Methods

CSA-PANi is synthesized adopting the procedure reported by C. Basavaraja et al. [19] 100mg of CSA-PANi polymer powder is dissolved in 100 ml of Dimethylformamide (DMF) for fluorescence studies. 100 ppm DNOC solution is procured from Premier Explosives Limited, Hyderabad for the study. Elico SL-174 spectrofluorometer is employed for fluorescence studies.

3. Results and discussion

5 ml of CSA-PANi solution per each analysis is used. The solution showed a pre emission at wavelength 470 nm with a pre excitation at 398 nm. The decrease in fluorescence intensity showed in figure 1 infers that the electron withdrawing group ($-NO_2$) is affecting the electronic configuration of polymer (CSA-PANi).

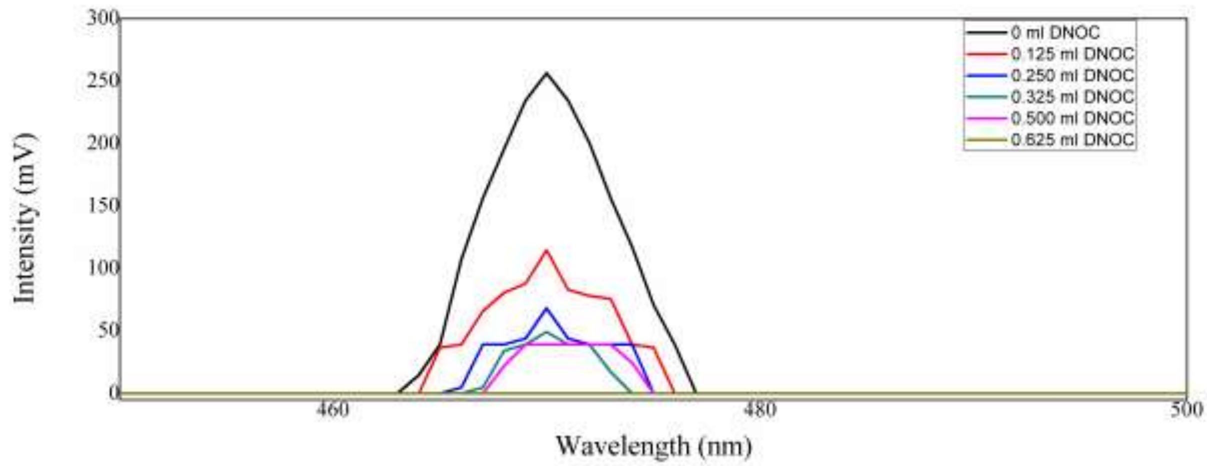

Figure 1: Fluorescence quenching of CSA-PANi with different concentrations of DNOC

The straight line in the Stern-Volmer plot shown in figure 2 denotes static quenching mechanism involved in this system.

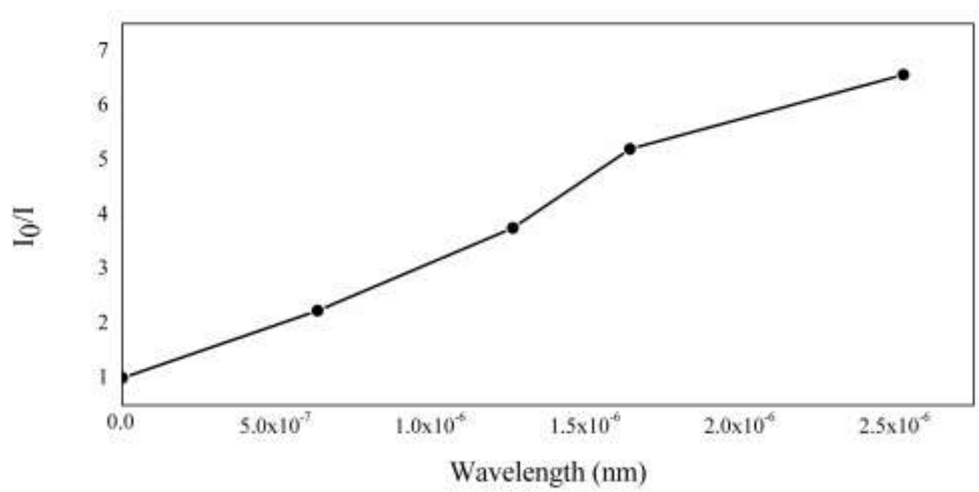

Figure 2: Stern-Volmer Plot for CSA-PANi and DNOC system

The expected interaction between CSA-PANi and DNOC is given in figure 3.

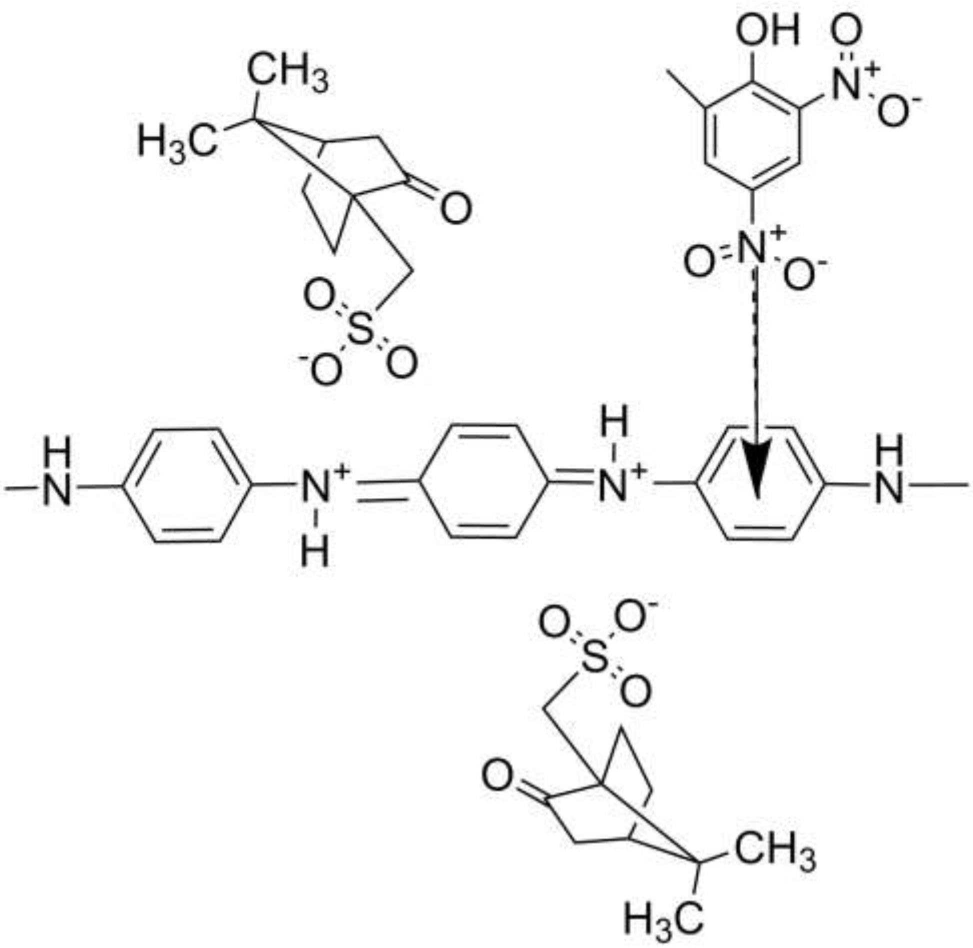

Figure 3: Possible interaction between CSA-PANi and DNOC

The interaction between π electrons of CSA-PANi and the vacant orbital of nitrogen in nitro group of DNOC may have arrested the π electron transition from benzenoid to quinoid, thereby causing reduction in the fluorescence intensity.

4. Conclusion

The CSA-PANi solution is a potential fluorophore in sensing nitro group of DNOC. The quantitative data allowed sensing DNOC in the minute concentrations (ppm). This study may become a tool in sensing explosives using doped PANi.

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