

Fluorescence quenching studies of camphorsulphonic acid doped polyaniline with picric acid

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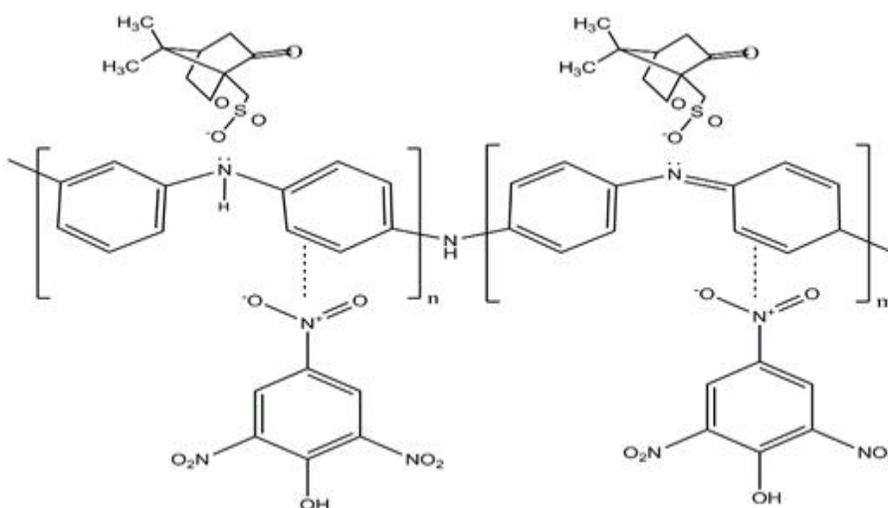
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• **Novelty and Highlights:**

1. The method of detection of electron withdrawing group employing quenching studies of HCl doped Polyaniline fluorescence is a new method.
2. The results obtained in this procedure are in correspondence with the S-V plot.
3. The estimated exciplex formation is given.

Graphical Abstract:



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Abstract:

In this study, we articulate the synthesis of camphorsulphonic acid doped conducting polyaniline (CSA-PANi) for the detection of typical nitroaromatic (NAC) (picric acid, PA). The synthesised CSA-PANi is characterised by its structure and thermal behaviour. The detection of PA is studied through the observed intense quenching of fluorescence signals in the emission spectra of the CSA-PANi solution. The detection limit employing S-V equation is found to be 5ppm in a 5ppm solution of CSA-PANi solution. The mechanism of quenching through the formation of exciplex complex formation is reported in the present study.

Key words: CSA-PANi, picric acid, fluorescence quenching, Stern-Volmer Equation, Exciplex complex.

Introduction

Conducting polymers play an important role in optoelectronics because of the delocalized electrons possessed by them provide a variety of useful properties including strong optical absorption and emission of electromagnetic radiation, photovoltaic response, reversible electrochemical switching and as efficient charge and exciton transporters.

Polyaniline is one of the most promising conjugated conducting polymers which have attracted more attention because of its ease of synthesis, good electrochemical performance, mechanical flexibility and relative reduced the cost of processing. Hence Polyaniline and its analogues find use in the field of sensor and actuators, super capacitors, electromagnetic shielding, corrosion protection, as well as electronic, electroluminescence and electro chromic devices [1]. Because of this extended conjugation, intermolecular hydrogen bonds have formed between the amine and imine group of the adjacent chain and π stacking, which makes the polymer chain rigid and induces insolubility in most dynamic solvents. The processability of PANi can be improved by using functionalized dopants like Camphorsulfonic acid (CSA) or Dodecyl Benzene Sulphonic Acid (DBSA) etc. The bulky dopants will reduce the mutual aggregation by increasing the solubility of PANi salt in non-polar and weakly polar solvents [2]. P.K. Kahol *et al.* [3] have shown that the dopants have no much effect on the

electron localisation length.

Detection of DNT (NAC) by fluorescence quenching phenomenon using poly(acrylic acid)-poly(pyrene methanol) (PAA-PM) as a fluorophore was reported by A.Samuels *et al.* [4]. Other exotic conducting polymers have been reported for the detection of NACs through fluorescence quenching.

The charge transfer complex formation between the π -electron rich donors (fluorophore) and electron deficient acceptors (quencher) via π - π interactions is the basic principle of the fluorescence quenching. Fluorescence intensity changes acutely in fluorescent conjugated polymers, because of their amplification effect. When NAC explosives contact with the conjugated polymers, charge transfer will occur between the electron-rich polymers and the electron-poor NAC quenchers. After the binding sites in conjugated polymers are occupied by NAC explosive molecules, the electrons do not transfer anymore, so the fluorescence intensity of the system decreases sharply [5].

Polyaniline shows fluorescence characteristics due to the extended π conjugation and was used as selective fluorescent sensors for the detection of electron deficient NACs [6]. NACs are the prominent high energy materials which are used as explosives and detonators etc. Due to extended π conjugation polymer backbone acts as a molecular wire and enables the rapid long-range

exciton migration along the polymer backbone contributing to the increased sensitivity and amplified quenching which aids in improving the detection limit as well as the response time [7-9]. The concept of the amplifying signal in conjugated polymers was first described by Swager and co-workers in 1995 [10]. Several sophisticated techniques using a metal detector, ion mobility spectrometry (IMS) and X-ray diffraction are being currently used for NACs detection. Very recently fluorescence quenching based detection has attracted much attention due to their high sensitivity and selectivity. The detection limit in parts per billion and parts per trillion are achieved through photoinduced electron transfer mechanism (Fluorescence). Yolanda et al. have reported an innovative sensing mechanism of NACs employing silica gated mesoporous hybrid materials [11]. The authors¹¹ opined the basic principle of their work is electron rich Tetrathiafulvalenes (TTF) rupture caused due to an interaction with the electron deficient NACs releases the entrapped dye thereby detecting through chromo fluorescence sensing.

The π - π stacking in polymers which is responsible for sensitive fluorescence quenching is clearly explained by Gokcen *et al.* [5]. The authors have sensed the NACs using polymer films. In this paper, we have reported the study on the effect of concentration of quencher (PA) on the fluorescence intensity of CSA-PANi in N-methyl pyrrolidone (NMP) solvent, and the study was carried out at room temperature. The fluorescence of CSA-PANi is quenched and quenching complies with S-V relation.

Experimental

Materials and Methods: The CSA doped PANi is synthesised by chemical oxidation method employing ammonium persulphate as the oxidising agent. The quencher PA and solvent NMP were of analytical grade and were used as received.

Preparation of Sample solutions: Very dilute solution of CSA- PANi in NMP are prepared to make the effect of self-absorption lesser and the quencher concentrations are varied. A 5 ppm CSA-PANi in NMP solution is prepared by diluting the stock solution of 100 ppm, which is a fluorophore and the 5.0 ppm PA in NMP is used as the quencher.

Instrument Fluorescence measurements are performed by employing Elico SL174 Spectrophotometer equipped with a Xenon arc lamp. The slit width for excitation and

emission were fixed at 5 nm. All measurements were made using 1 cm Quartz Cuvette at room temperature.

Quenching Experiments: The concentration of CSA-PANi was kept constant and the concentration of PA has varied is given in the table 1.

Table 1

S.No.	Volume of CSA-PANi in cm ³	Volume of PA in cm ³	Concentration of PA [m.mol]	Intensity(a.u.)	I ₀ /I
1	10	0.0	0	735.34 (I ₀)	-
2	10	0.1	0.022	532.57	1.38
3	10	0.2	0.044	398.20	1.85
4	10	0.3	0.066	312.71	2.35
5	10	0.4	0.087	200.32	3.67
6	10	0.5	0.102	197.88	3.72
7	10	0.6	0.131	156.30	4.70
8	10	0.7	0.153	78.0	9.43

For 5.0 ppm CSA-PANi and 5.0 ppm PA Excitation-331 nm, Emission- 371 nm. The polymer solution showed a maximum excitation wavelength at (λ_{ex}) 331nm and the emission wavelength was observed at (λ_{em}) 371nm. The fluorescence intensity 'I₀' was measured without adding the quencher and then the fluorescence intensity 'I' was measured at varied quencher concentrations for the fixed polymer concentration. The fluorescence emission spectra of CSA-PANi with different PA concentration are as shown in figure 1. A plot of I₀/I versus concentration of PA is as shown in figure 2.

Results and discussion

Fluorescence quenching studies Figures 1 shows the fluorescence quenching of CSA-PANi with PA. From the figure, it is detected that the fluorescence intensity of the fluorophore (CSA-PANi) decreased consistently with increasing concentration of quencher (PA) but no change in the emission wavelength of CSA-PANi is observed. This is due to quenching of the CSA-PANi by PA. The degree of quenching depends on the amount of quencher in a homogeneous solution [12]. This indicates that the non-radiative energy transfer between the excited donor (fluorophore) and the acceptor (quencher) [4].

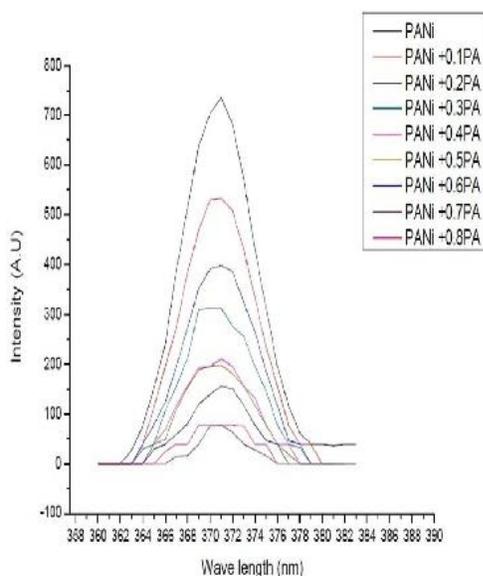


Figure 1: Fluorescence emission spectrum 5.0 ppm CSA-PANi with 5.0 ppm PA.

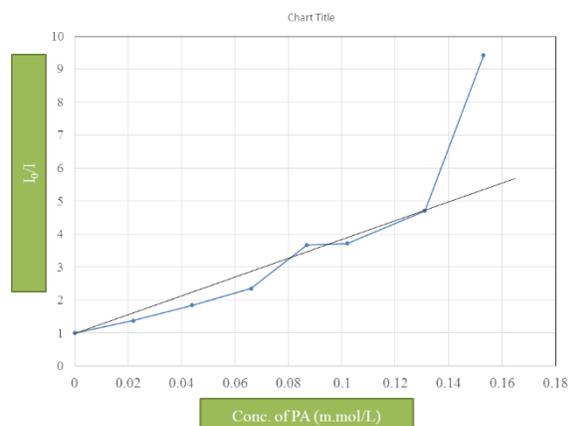


Figure 2: S-V plot between CSA-PANi with varying concentration of PA

The kinetics of the quenching of polyaniline was studied by using S-V relation.

$$I_0/I = 1 + K_{sv} [Q]$$

Where I_0 and I are the fluorescence intensity in the absence and presence of quencher, $[Q]$ is the concentration of quencher and K_{sv} is the Stern-Volmer constant. The plot of I_0/I versus the quencher

concentration is called Stern-Volmer plot and is shown in figure 2. The efficiency of the quencher is given by the slope of the Stern-Volmer plot. S-V constants are calculated from the trending line of the quenching curve for low quencher concentration [13]. In figure 2 we observe a linear increase in the S-V plot up to 0.6 ml (30×10^{-4} mg) of the quencher, there after the intensity increases exponentially. The value of the slope is calculated for the best fit to be $52.21 \times 10^3 \text{ M}^{-1}$.

S-V plot for a conjugated polymer shows a positive deviation from linearity with the increase in concentrations of quencher due to aggregation of the polymer [12]. Aggregation can enhance quenching both by extending the exciton path, so that it can sample more binding sites and by static and self-quenching of polymer chains [12]. The non-linearity in S-V plot, represents that quenching mechanism is collisional because conjugated polymers do not have excited states with sufficiently long lifetime [12]. But quenching occurs by the formation of a non-fluorescent complex between fluorophore and quencher in the ground state [14]. The estimated exciplex complex is shown in figure 3.

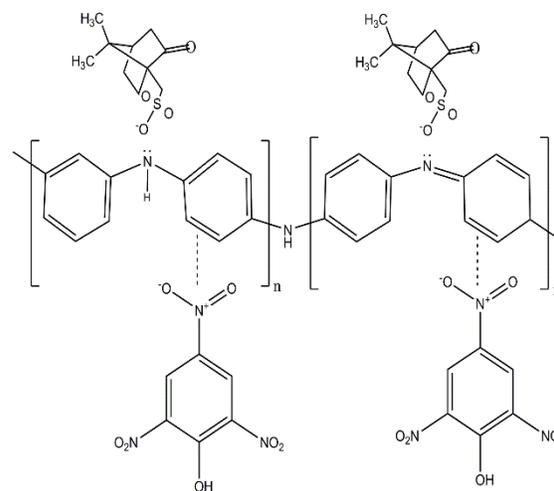


Figure 3: Estimated Exciplex formation.

Sensing mechanism the fluorophore and the analyte interactions may be explained in two ways, namely static and dynamic quenching. The excited state life time is unaltered in static whereas the change is observed in the dynamic [6]. In static quenching, complexation occurs between the excited fluorophore and the ground state of the quenching species. In this mechanism, quenching of the excited fluorophore by the complex quencher occurs upon irradiation. Due to the short lifetimes, they only exhibit static quenching.

Conclusions

The Stern-Volmer plot has clearly given the information about the static quenching of CSA doped Polyaniline with PA. The applicability of CSA-PANi in fabricating electronic devices may be given a glance in devising sensors to detect High Energy Materials (HEMs) with nitro functional groups.

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