STUDY OF EFFECT OF ELECTRON WITHDRAWING GROUPS ON FLUOROSCENCE QUENCHING OF FUNCTIONALISED POLYANILINE

Dr.Lakshmidevi V

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Department of Chemistry, Government First Grade College Ramaagara-565129
Karnataka, India.

Abstract:

In this paper synthesis of conducting polyaniline is carried out using camphor sulphonic acid and(CSA-PANi) and Dodecyl benzene sulphonic acid (DBSA-PANi) and its quenching studies with different quenchers containing varying deactivating groups(EWG) is reported. The fluorescence quenching experiments were performed in N-Methyl Pyrrolidone solvent with nitroaromatics. It is found that with the increase in the number of electron withdrawing or deactivating groups the fluorescence intensity of emission of functionalised polyaniline is decreased.

Key words: CSA-PANi, DBSA-PANi, deactivating groups, fluorescence quenching, Signal Amplification, Exciplex complex.

1. 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.

Detection of DNT (a NAC) by fluorescence quenching phenomenon using poly(acrylic acid)poly(pyrene methanol) (PAA−PM) as a fluorophore was reported by A.Samuelson et al.[1] Other exotic conducting polymers have been reported for the detection of NACs through fluorescence quenching.Trogler′s group has reported the synthesis of polysiloles and their sensing applications for the detection of nitroaromatic explosives[2]

Polyaniline is one of the most promising conjugated conducting polymers which have attracted more attention because of its low cost, superior electrochemical performance, mechanical flexibility and relative ease 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[3]. Because of this extended conjugation intermolecular hydrogen bonds are formed between the amine and imine group of the adjacent chain and π stacking occurs. The polymer chain becomes rigid which 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[4]. P.K. Kaholet al.[5] has shown that the dopants have no much effect on the electron localization length.

Polyaniline shows fluorescence characteristics due to the extended π conjugation and were used as selective fluorescent sensors for the detection of electron deficient nitroaromatics[6] (NACs). Nitroaromatics are the prominent high energy materials which are being 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[7,8,9]. The concept of amplifying signal in conjugated polymers was first described by Swager and co-workers in 1995[10]. Several sophisticated techniques using 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. Detection limit in parts per billion and parts per trillion are achieved through photo induced electron transfer mechanism (Fluorescence). Yolanda et al. have reported an innovative sensing mechanism of nitroaromatic explosives using silica gated mesoporous hybridmaterials[11]. The authors[11] opined the basic principle of their work is electron rich Tetrathiafulvalenes (TTF) rupture caused due to an interaction with the electron deficient nitroaromatics (explosives) releases the entrapper 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 Birlic Demirelet al.[12]. The authors have sensed the NACs using polymer films.

In this paper, the sensing ability CSA and DBSA doped polyaniline with nitro aromatics containing varying deactivating groups and its effect on fluorescence quenching employing NMP as solvent is reported. The fluorescence of doped PANi has been quenched and quenching is in accordance with S-V relation.

Experimental

2.1 Materials and Methods:

The CSA and DBSA doped PANi is synthesised by chemical oxidation method employing ammonium persulphate as the oxidising agent. The quenchers like PA, DNB, PNT, PNBA and NB and solvent NMP were of analytical grade and were used as received.

2.2 Instruments

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.

The fluoroscence quenching of CSA and DBSA doped polyaniline with nitroaromatics containing different number of deactivating groups or electron withdrawing groups using Nmethy pyrrolidone as the solvent in which it is more soluble is studied. A dilute solution of CSA and DBSA doped polyaniline is prepared and its fluoroscence quenching with different nitroaromatics are recorded. The fluoroscence spectrum of CSA and DBSA doped Polyaniline in the absence and in the presence of different nitroaromatics are shown in the Figure-1 and Figure-2.

The fluorescence intensity of the CSA and DBSA doped PANi solution decreased on reacting with electron deficient nitro aromaticsl[12]. There is a decrease in the fluoroscence intensity due to π-π interactions between the π-electron rich polymer backbone and the π-electron poor nitro aromatics. Chen et al explained the fluoroscence of conjugated polymer by using semiconductor band theory[13]

2.3 Fluoroscence Studies of Polyaniline doped With CSA and DBSA

Fluorescence Measurements

Fluorescence of CSA-PANi with different nitroaromatics like PA, DNB, PNT, PNBA and NB is carried out using 100 ppm solution as shown in the Figure-1. The emission wavelength and intensities are shown in the Table-1.

Table-1 The emission wavelength and intensities of CSA-PANi with different NACs

Excitation wavelength- 352 nm Emission wavelength 439 nm

Nitroaromatic	Intensity (cps)
Picric acid(PA)	99743
1,3- Dinitrobenzene (DNB)	74473
Para –Nitro benzoic acid (PNBA)	74083
Para-Nitro toluene (PNT)	68088
Nitrobenzene (NB)	7565

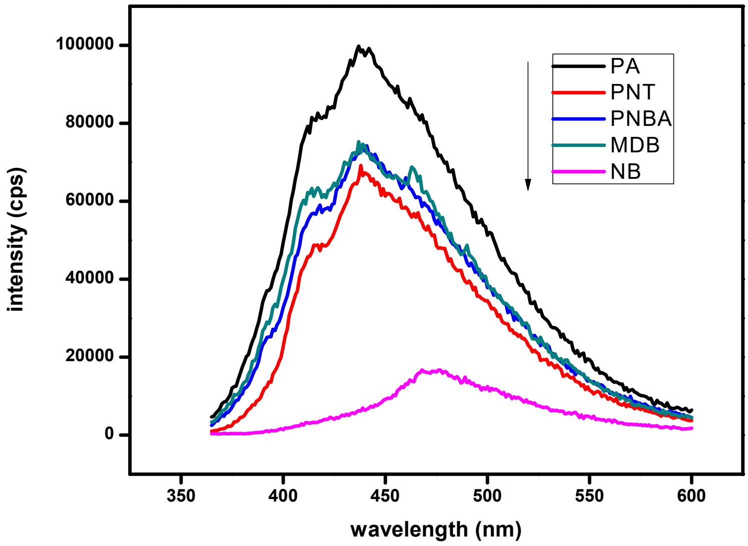


Figure -1 Fluorescence of CSA-PANi with different nitroaromatics

Similarly fluorescence of DBSA-PANi with nitroaromatics like picric acid (PA), 1, 3-Dinitrobenzene (DNB) and nitrobenzene (NB) is carried out using 100 ppm solution as shown in the Figure-2. The emission wavelength and intensities are shown in the Table-2

Table- 2 The emission wavelength and intensities of DBSA-PANi with different NACs

Excitation wavelength- 407 nm Emission wavelength 470 nm

Nitroaromatic	Intensity (cps)
Picric acid(PA)	590742
1,3- Dinitrobenzene (DNB)	336892
Para-Nitro toluene (PNT)	662834
Nitrobenzene (NB)	37602

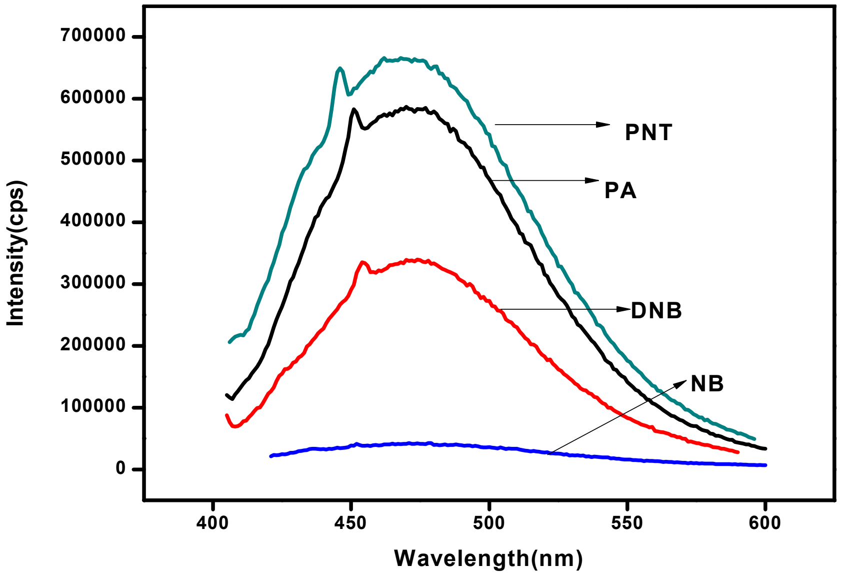


Figure -.2 Fluorescence of DBSA-PANi with different nitroaromatics

3. Results and discussion,

Figures- 1 and 2 shows the fluorescence quenching of CSA-PANi and DBSA-PANi with different nitroaromatics. From the figure it is observed that the fluorescence intensity of the fluorophore (CSA-PANi and DBSA-PANi) decreased regularly as the number of deactivating groups in the quencher increased but no change in the emission wavelength of fluorophore observed. This is due to quenching of the doped PANi by nitroaromatics.

From the fluorescence spectra, it was observed that all the NACs do not quench the fluorescence intensity of doped PANI equally. The differences in the quenching efficiency and response of the polyaniline to different NACs depends on the vapour pressure of the nitroaromatic, redox potential of NACs, number of nitro groups and the concentration of the quencher[14] and the exergonicity of electron transfer between excited polymer and nitroaromatic compounds and also their binding strength to the polymer affect quenching performance of NACs[15].It was observed that PA is more efficient in fluorescence quenching of doped polyaniline than other DNB and NB can be explained using vapour pressure and redox potential of quencher. The quenching constant is higher for PA and it is a better quencher due to its more electron deficient nature because of the strong electron-withdrawing effect of $–NO_2$ groups whereas NB and DNB exhibits only moderate quenching. PA (5.80×10^{-9} mm of Hg) even though has low vapour pressure compare to NB (1.8×10^{-1}mm of Hg) and DNB ($8.9 \text{ X } 10^{-4}$mm of Hg) [16] its binding affinity to the polymer is high due to its high polarisibility. PA contain acidic phenolic –OH which ionises to picrate ion, the negatively charged picrate ion interacts strongly with polymer and facilitates the electron transfer process compared to nonphenolic analytes. The NB and DNB are less effective in quenching even though their LUMO energy levels lie below the polymer. NB has high vapour pressure and low LUMO level energies; its quenching efficiency is less due to their weak interaction with sensing material[17]. Also as the number of electron withdrawing group increases, the transfer of electrons from polymer to NAC's becomes thermodynamically more feasible or the redox potential (oxidative properties) of nitro aromatics are enhanced and the energy of LUMO decreases and electron accepting capability of nito compound increases which is confirmed by cyclic voltametric studies. PA has three nitro substituents on the aromatic ring which account for their higher oxidizing potential relative to DNB, which has only two nitro groups. Reduction potential of 1, 3-dinitrobenzene (-0.345V) is higher compared to PA (-0.39 V)[18] indicating that MDB is better electron acceptor compared to PA and NB. But PA(5.80×10^{-9}mm of Hg at 25°C)[19] has higher vapor pressure than MDB and it can quench fluorescence of sensing molecules more efficiently compared to MDB. Hence picric acid is a better electron acceptor compared to dinitrobenzene [20].

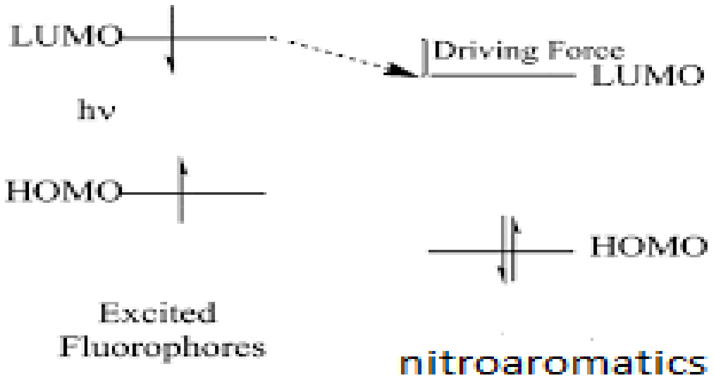
The redox potential of PA, MDB, NB and DBSA- PANi are -3.89, -3.45, --0.486 and -3.6eV respectively[21]. Evidence for electron transfer mechanism is further proved by cyclic voltametric measurements. The HOMO and LUMO levels of the polymers were calculated from the CV plots and that for PA and other analytes were taken from literature[22].There is a slight shift in the oxidation and reduction potentials of the polymers after the addition of PA. The thermodynamic feasibility of the quenching mechanism can be better explained using band gap of the polymers in absence and in presence of PA are provided in Table- 1

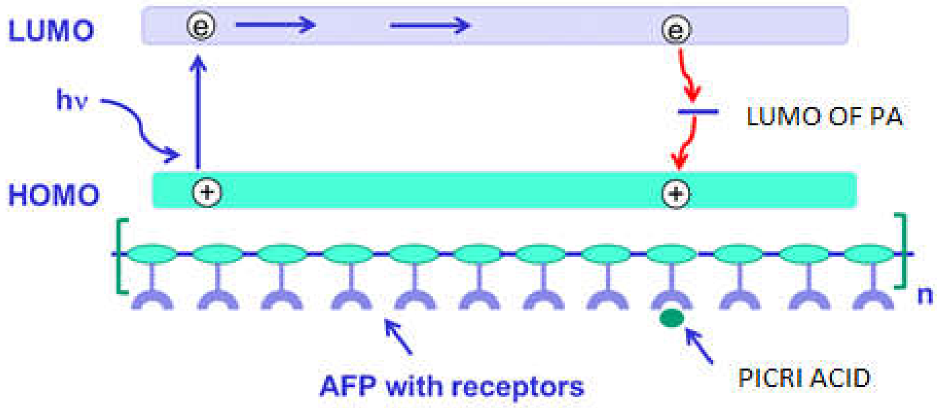
Table-1 HOMO and LUMO energy levels and the band gap calculated from CV and UV absorption

SAMPLE	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	HOMO(eV)	LUMO(eV)	Band Gap(eV) from CV	Optical band gap(eV)
DBSA-PANi	1.129	-0.89	-5.829	-3.61	2.219	1.6342
DBSA-PANi-PA	1.29	0.7996	-5.99	-3.9004	2.0485	1.5721
CSA-PANi	1.13	-0.886	-5.94	-3.814	2.126	1.688
CSA-PANi-PA	1.32	-.72	-6.02	-3.98	2.04	1.55

Sensing Mechanism

The band diagram (figure-2) shows how the conducting polymers amplify their signal





In polyaniline the repeating units are electronically coupled to form extended pi conjugation, the interaction between the orbitals creates a semiconductor band structure having valence and conduction band[8]. On photo excitation of a conjugated polymer, the electrons from the valence band (LUMO) are excited to the conduction band (HOMO) and leave a hole in the valence band. The hole electron pair is called exciton which migrates along the polymers backbone freely over several repeat units and creates molecular wire effect[23] and comes back to ground state with the emission of radiation as fluorescence. But in the presence of quencher (nitroaromatic) in solution, the quencher and the polymer form a weak excimer complex. This static association prevents the transfer of electron on the conjugated chain, and electrons are transferred to LUMO of quencher (nitroaromatic) which is less energetic than the ground state of polymer and lies in between HOMO and LUMO of polyaniline. The electrons come back to ground state with the non radioactive process resulting in decreased fluorescent intensity of conjugated polymer[24]. The fluorescence of each repeating unit is quenched resulting in the amplification of signal.

Conclusions

CSA and DBSA doped PANi was synthesized by chemical oxidation method. The synthesized PANi was used as a fluorophore for detecting nitroaromatic compounds such as PA, DNB, and DNB in this study. The mechanism and efficiency of quenching were deduced from the studies. Fluorescence quenching studies show the formation of the exciplex complex formed between the PANi with PA which shows the dynamic quenching on the interaction with PA following the PET mechanism. This study helps us to comprehensively understand the quenching effect of nitro groups and will thus provide a guideline for the development of light-up probes with nitro groups as quenching groups.

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