FLUORESCENCE STUDIES ON ORGANIC ACIDS DOPED PANI-PVA THIN FILMS AND QUENCHING WITH PICRIC ACID

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Abstract

The polyaniline/poly (vinyl alcohol) (PANI/PVA) thin films were prepared by the chemical oxidative dispersion polymerization of aniline monomer in 0.2 M HCl aqueous media with the poly (vinyl alcohol) (PVA) and p-Toluenesulfonic acid (PTSA) as the stabilizer and dopant respectively. The PANI/PVA thin films were characterized by Fourier transform infrared spectroscopy (FTIR), Thermal gravimetric analysis (TGA), Scanning Electron microscopy (SEM). Fluorescence emission spectra of PTSA doped PANI/PVA thin films were investigated in different doping ratio of 0.1, 0.3 and 0.5. The present works the importance of fluorescence of p-Toluenesulfonic acid (PTSA) doped PANI /PVA thin films and the quenching phenomenon of the electron withdrawing groups such as nitro functionalized high energy materials called as nitroaromatics. The present report is on the fluorescence quenching study of picric acid.

Keywords: Fluorescence quenching, PTSA doped Polyaniline salt, Stern-Volmer plot.

INTRODUCTION

Polyaniline is the most of the intensively studied conductive polymers which have been exposed for use in electronic and optical application. Polyaniline have been intensively studied of their potential for commercial applications seen as pole injection layers for flexible light emitting diodes (16) electromagnetic interface shielding (17) corrosion protection (18) etc. The protonation PANI emeraldine base (PANI –EB) or its

derivatives with organic acids can be used for the protonation of electrically conducting polymers with improved process ability (1-5). 5

In this study, we investigated the effects of the dopant and the solvent on the change transport properties in polyaniline systems for dopants we used BSA, TSA, CSA, PTSA, NSA. The emeraldine base for of polyaniline along with the dopant is dissolved in solvent like chloroform, BEOH, DMF, NMF, DMSO. In PANI extended conjugation intermolecular hydrogen bonds are formed between the amine and imine group of the adjacent chain and stacking.

Polyaniline shows fluorescence characteristics due to the extended conjugation and were used as selective fluorescence for the detection of electron deficient nitroaromatics (NACS)5 Nitroaromatic are the prominent high energy materials which are being used as explosives and detonators etc. the present studies are employed by doping PANI with PTSA different concentrations dissolving DMF solvent before going for fluorescence studies. The H^+ ions were added upon protonation so that imine groups at the quinoid ring at as a charge delocalization of holes in the valence bond.

The electron withdrawing group ($-NO_2$) of picric acid quenches the fluorescence showed by the PTSA doped polyaniline base. The electron transitions are transfer from PTSA doped polyaniline base to electron withdrawing group of picric Acids. Quenching takes place and it is attracted much attention due to their high sensitivity and selectivity. The stacking in polymers which is responsible for sensitive fluorescence quenching is explained (8). The nitroaromatics are also in polymers films.

In this paper, we have reported the study on the effect of concentration of picric acid on the fluorescence intensity of PTSA-PANI employee DMF as a solvent and the study was carried out 0-50*C. the fluorescence of PTSA-PANI in difference concentrations has been quenched and quenching is in accordance with S-V relation. The S-V constant was obtained.

EXPERIMENTAL

Materials and Methods

Aniline ($C_6H_5NH_2$), ammonium persulfate ($(NH_4)_2S_2O_8$), p-Toluenesulfonic acid ($CH_3C_6H_4SO_3H$), Poly (vinyl alcohol) $[CH_2CH(OH)]_n$, Hydrochloric acid (HCl), Dimethylformamide (C_3H_7NO), methanol (CH_3OH) and acetone (C_3H_6O). All the

chemicals purchased were used as received and analytical reagent grade. Double distilled water was used in the experiment.

Synthesis of emeraldine salt

15 ml of concentrated HCl (0.2M) and 12 ml of aniline (0.2M) was taken in a round bottom flask. 180 ml of distilled water (covered with ice cubes salt mixtures in maintain low polymerization temperature) equipped with electromagnetic stirrer. Then 13 gram (0.08M) ammonium persulfate in 100ml 0.2M HCl was abruptly added into the above solution. The polymerization temperature maintained for 2 hours to complete the reaction.

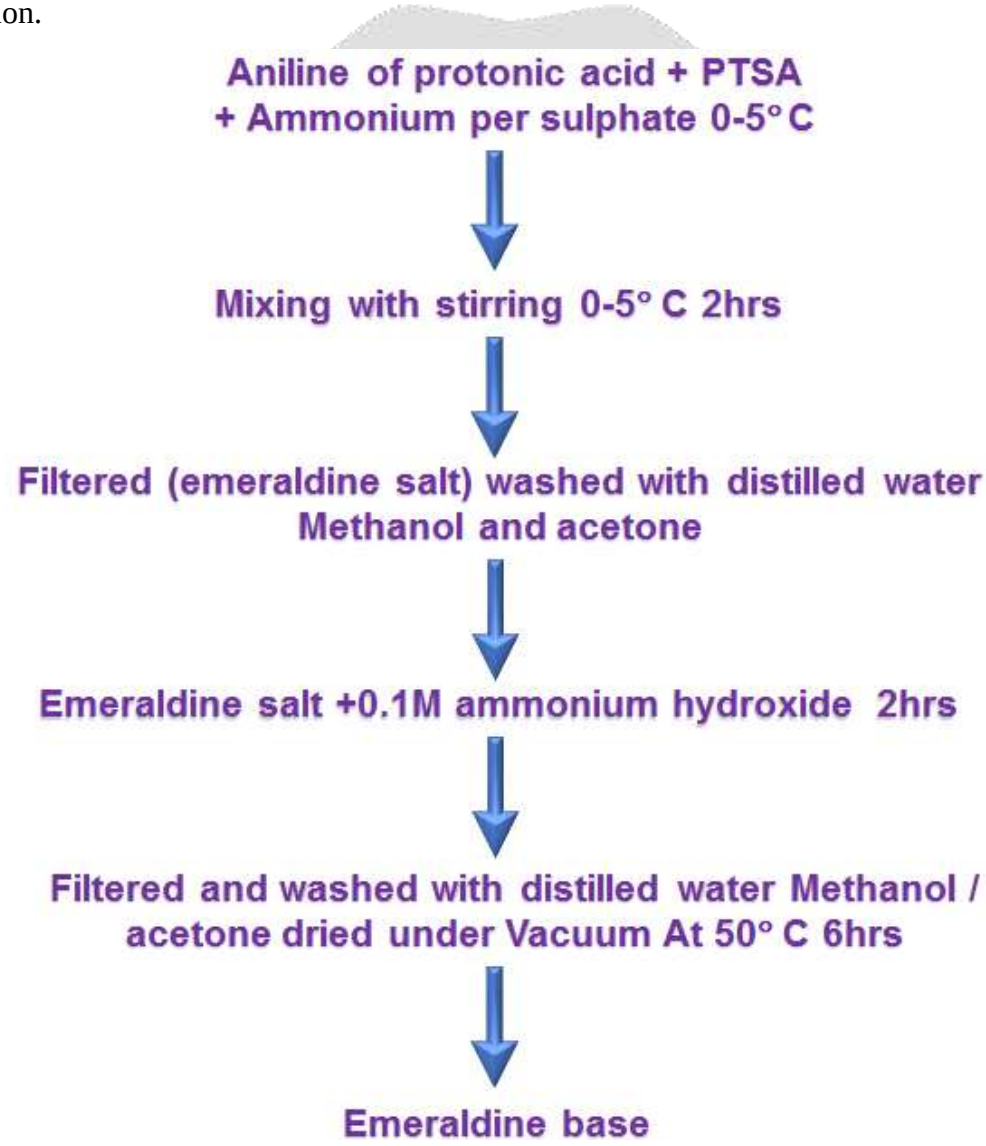

Figure 1. Flow chart of the preparation of emeraldine base

The precipitate emeraldine salt is filtered and washed with distilled water until the filtered is color less. It is then washed with methanol to remove oligomeric impurities. Finally, it is washed with acetone to remove water content and kept overnight for filtering.

The precipitated is collected in picker and dried under vacuum at 50°C for 6 hours then it is crushed into fine powder to get emeraldine salt. The emeraldine salt was taken in a round bottle flask contained 20ml of ammonia solution and 80ml of water stirred continuously for 24 hrs. The precipitate (blue emeraldine base) is filtered and washed with distilled water and finally with acetone. After keeping overnight, filtering the precipitate is then crushed into fine powder to get.

Preparation of PTSA doped PANI

PANI (EB) was synthesized by solid state reaction using experimental procedure reported by ***Raghu et. Al.*** [12]. PANI-PTSA was prepared by mixing 0.006M of emeraldine base with 0.0006M of PTSA using agate Mortar and pestle. Similarly, 0.006M of emeraldine base with 0.0018M of PTSA using agate Mortar and pestle. 0.006M of emeraldine base with 0.003M of PTSA using agate Mortar and pestle.

Preparation of sample solutions

Different concentration of dilute solution of PTSA-PANI in DMF are prepared to avoid absorption effects and the quencher concentration been varied. The 10 ppm PTSA doped polyaniline in DMF solution is prepared. The 5ppm of picric acid in DMF used as quencher.

Preparation of polymer films

The films of different doped polyaniline prepared by following procedure. A 0.07grm sample of doped PANI was mixed with 0.02 gram of PVA in 10ml of DMF and the solution was stirred for 12 hrs. Then 0.16ml each of the various doped polyaniline solution was cost on a glass slide and dried in a vacuum over at 50-60°C for 12 hrs.

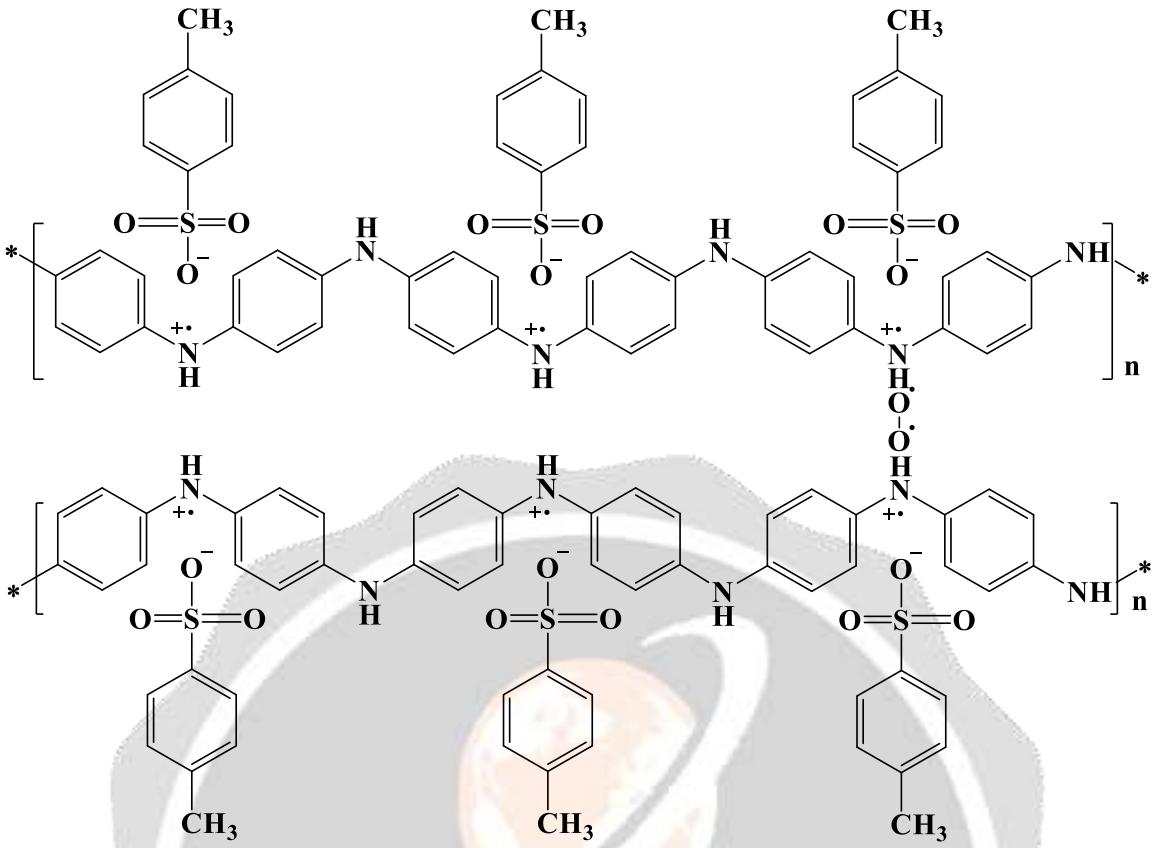

Figure 2. Chemical structure of emeraldine salt of PTSA doped PANI.

Characterizations

Fourier Transform Infra-Red spectrometer (FTIR): The FTIR spectra of the polymers were recorded on a Thermo Nicolet, Avatar 370 instrument in the range 4000–400 cm^1 at a resolution of 4 cm1 by making KBr pellets. Scanning Electron Microscope (SEM:) The morphologies of the polymers were studied by using coupling JEOL Model JSM - 6390LV scanning electron microscope. The electron microscope was operated at 20 kV. Thermal Gravimetric analysis: The thermogravimetric analysis (TGA) measurements were made using a Perkin Elmer, Diamond System at a heating rate of 10°C per min under nitrogen atmosphere. Fluorescence Spectrophotometer: Fluorescence measurements are performed by employing ELICO-SL174 spectrophotometers 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 emission spectra of PTSA-PANI are measured by fluorescence spectrophotometer. Studied spectroscopic data such as absorption and emission wavelength, fluorescence intensity and stokes shift. The concentration of PTSA –PANI

was kept constant and the concentration of P1 (0.1), P2 (0.3) and P3 (0.5). the quencher picric acid (PA) is take different concentration. The polymer solution showed a maximum excitation wavelength at different excitation and different emission wavelength was observed in P1 (0.1), P2 (0.3) and P3 (0.5) (λ_{ex})

Results and discussion

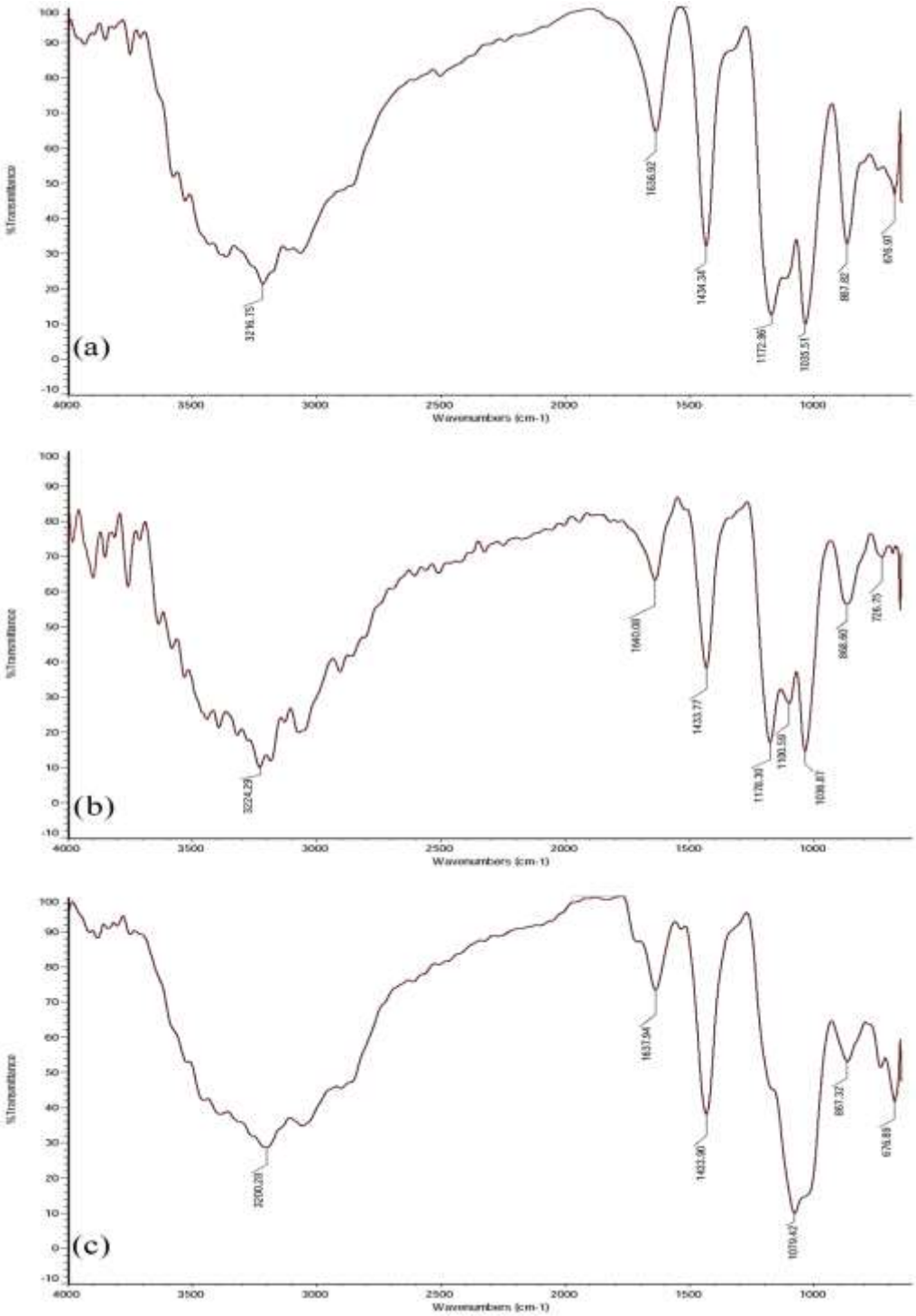

Figure 3. a) P1, b) P2 and c) P3 FTIR Spectra of PTSA doped PANI

FTIR Spectra

The FTIR spectrum of PTSA doped different concentrations P 0.1, 0.3,0.5 are shown in figure 3 (a), 3 (b) and 3 (c) respectively. The peaks at 1560.30 cm^{-1} in all the three peaks shows the quinoid. The peaks at 1693 cm^{-1}, 1636 cm^{-1}, 1640 cm^{-1}shows the Benzenoid ring respectively as shows the oxidation state of emeraldine salt of PANI.

A strong bond observed in 1931cm^{-1}, 1434 cm^{-1}, 1433 cm^{-1} in fig 3 (a, b, and c) described as the electronic light band. All the three spectra peak at about 1171 cm^{-1}, is due to C-N stretching mode peaks about 1172 cm^{-1}, 1178 cm^{-1} and 667 cm^{-1} is usually assigned to the C-N stretch of secondary aromatic amine the peak at 726 cm^{-1}, 1419.59 cm^{-1} in 4 and 5 figure are assigned to the aromatic C-H in plane bending modes. The peak at 565.1 cm^{-1}, 567.03 cm^{-1},568.96 cm^{-1}, are usually assigned to an out of plane bending deformation of C-H. The peaks at 798.47 cm^{-1}, 800.4 cm^{-1} in 3 and 4 usually assigned to para di substituted aromatic ring indication polymer formation. The peaks at 1034 cm^{-1}, 1035 cm^{-1},1036 cm^{-1}, is assigned to SO_3-group of the dopant and PTSA.

SEM Images

The SEM images powder displays highly agglomerated morphology made up of the petals like particle with 20 to 30 µm in diameter and 20µm in length these particles are formed during low temperature in situ polymerization of aniline and maintain their morphology even after re doping with PTSA but agglomeration appeared due to string intra and intermolecular ionic interactions between chains triggered by proto generated charge carried (i.e. polarons and bipolarons) in shown in figure 4(a). In figure 4(b) the images of PTSA doped PANI shows that high grown in hexagonal structure in the morphology all the crystal aligned in the same direction and the sulfonate groups in present in thickness the particle size 40 to 60 µm diameter and 100-200 µm in length the vender walls interaction between the phenyl ring PTSA and solvent descried Lennard potential. This molecular interaction known to cause crystal and growth of PTSA.

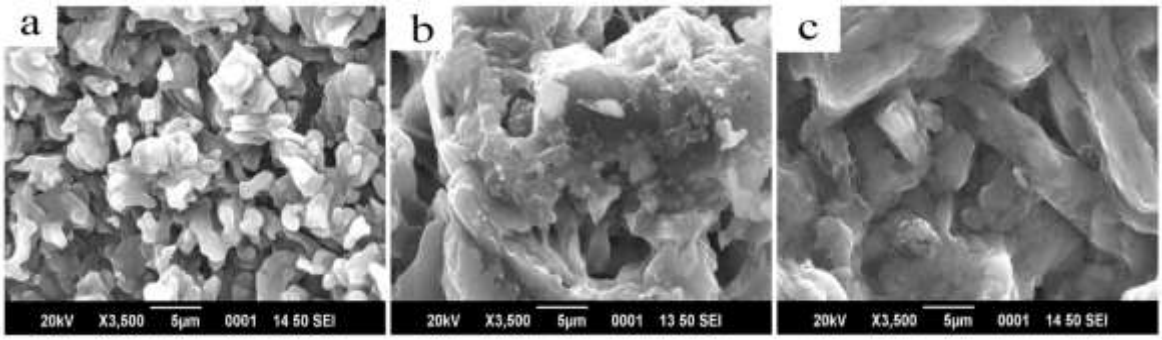

Figure 4. a) P1, b) P2 and c) P3 SEM images of PTSA doped PANI

In figure 4 (c) shows that the images of cotton like structure and the particle size 80 to 90 µm diameter and 200 to 300 µm in length the fibers of particle size present sulfonate groups are very thickness and agglomerates deformation resulting in increasing adjacent the rigs due to PTSA ion bulky molecule and steric hindrance by electro static reparation between doping ion and hydrogen of the imine sites.

Thermal Analysis

Figure 5 (a) shows that thermal behavior of PTSA doped PANI is illustrated by DTG curve the weight loss in the first 15.2% attributed to the description superficial water molecular associated with the doped PANI~1.62 first stage. Figure 5(b) shows PTSA doped PANI than remains stable ~98°C the second step extending up to 200°C with weight loss of 56.7% indicates the loss of PTSA and the polymer is completely dedoped at ~300°C

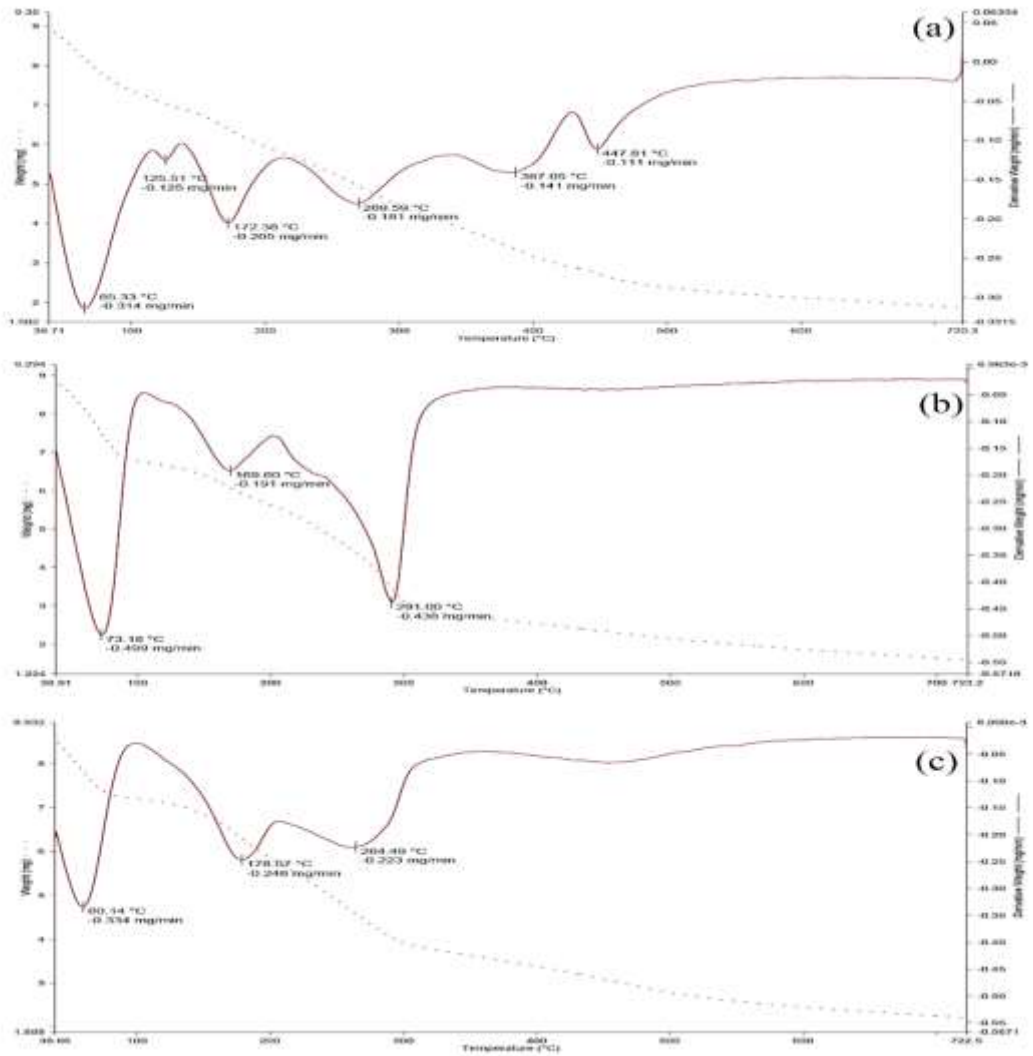

Figure 5. a) P1, b) P2 and c) P3 Thermal analysis of PTSA doped PANI

Figure 5(c) shows that stage extending up to 720°C in this stage sulphonate ions, were readily detached from the polymer backbone. The polymer backbone the polymer degradation stated. Move interestingly at 300°C. the acid was completely dedoped from the polymer and the total weight loss was found about ~6.08% at higher temperature, it shows full scale polymer degradation. Conclusion PTSA doped PANI was successfully obtained via the in situ oxidative polymerization of aniline with doping level is determined. Spectroscopic and thermal properties of the polymers are found to be affected by the type of the dopant used. Fluorescent characteristic of polymer solution/ film upon exposure to a good potential to be exploited as sensing material for detection. A good repeatability and reproducibility of measurement were obtained. A complete regeneration cycle took about 13 minutes and 4 complete cycle were observed in 60 minutes of testing.

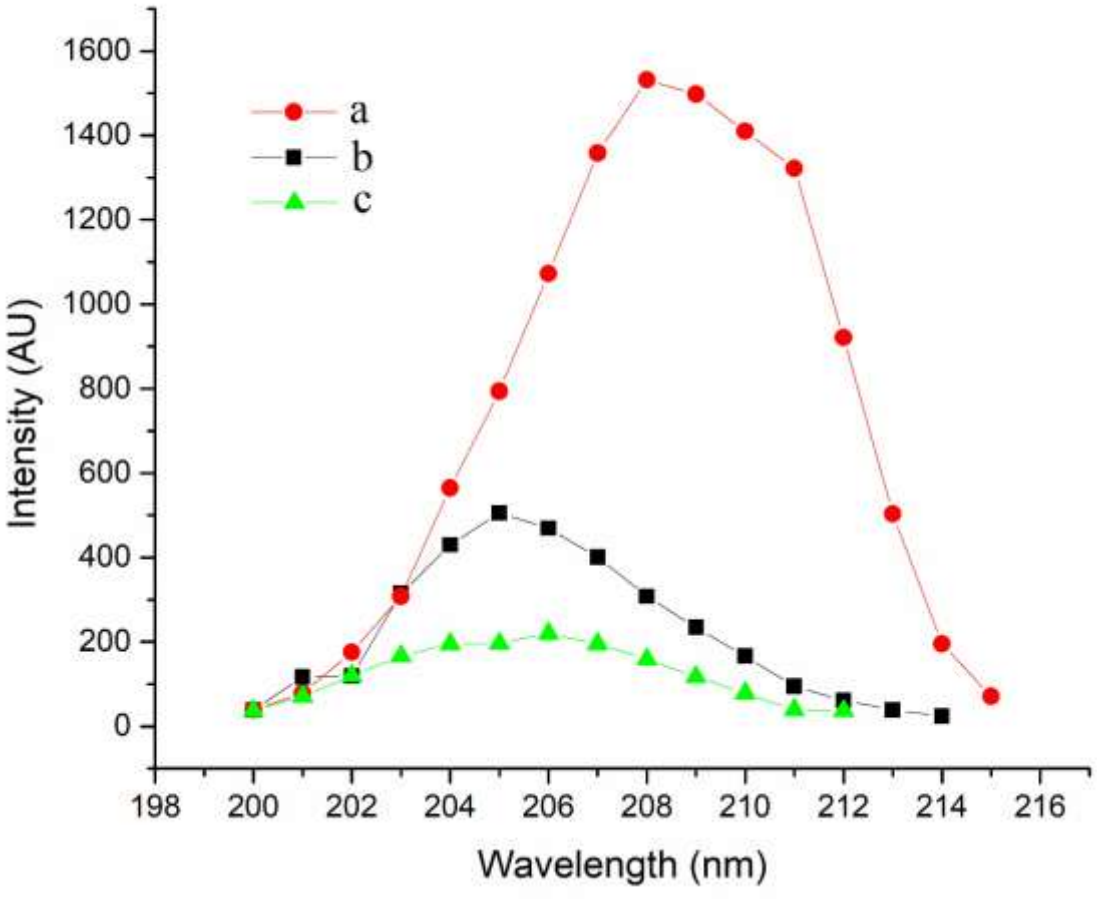

Figure 6. a) P1, b) P2 and c) P3 Fluorescence emission spectrum of PTSA doped PANI

Quenching studies

The self-quenching mechanism Covalently fluorophore pairs factors influencing efficiency of self-quenching are disassembled into four components as shown in figure 7 Quenching

of a fluorophore is significantly influenced by the molecular structure of the quencher. [17] in this study quenching by nitroaromatic compounds was evaluated to assist the molecular interaction between nitroaromatic molecules. Figure 6. a) P1, b) P2 and c) P3 shows the Fluorescence emission spectrum of PTSA doped PANI

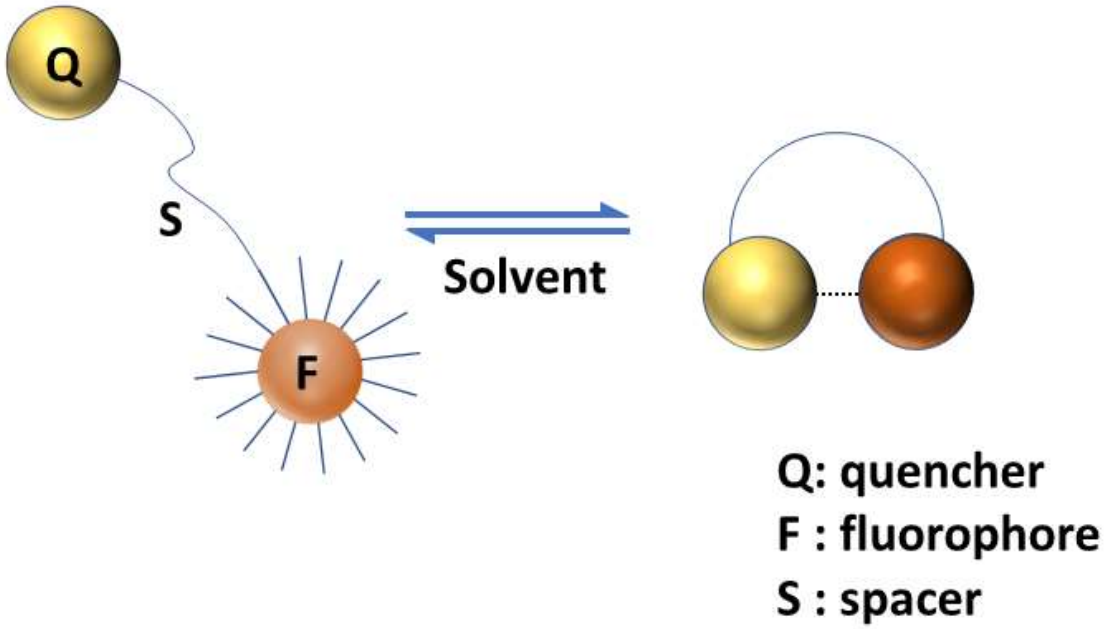

Figure 7. Quenching mechanism

The fluorophore interaction can be identified by examining the emission spectra using solvents. The emission spectra of PTSA doped PANI are measured. The spectroscopic data such as absorption and emission wavelength fluorescence intensity noted PANI is conjugated fluorescent polymer which exhibits π to π* and n to π* transitions. The emission spectra of Polymer solutions are mirror images of the excitation spectra upon photo excitation of a conjugated polymer. The electrons from the valance band are excited to the conduction band and then migrated along the polymer backbone

Conclusion

The fluorescence data of PTSA-PANI reveal that the nature and amount of shifts depend on the polarity of the solvents. It is concluded from the data that as the polarity of the solvent increases, PTSA-PANI shows a bathochromic shift for n-π and π-π* transitions. Knowledge about the excited electronic state dipole moments of the solute molecules is quite useful in designing nonlinear materials and in elucidation of the nature of the excited state.

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