

# Highly Fluorescent Conducting Polymer Hybrid Materials Based on Polyaniline-Polyethylene Glycol-Arsenic Sulphide

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## Abstract

Highly fluorescent binary and ternary hybrid materials based on polyaniline, polyethylene glycol (PEG) and arsenic sulphide have been prepared via oxidative chemical polymerization and characterized by FT-IR and powder X-ray diffraction techniques. Thermogravimetric analysis showed that all the materials are thermally stable up to 250°C. The optical behaviour was investigated using UV-Vis. and fluorescence spectroscopy. Fluorescence spectra of polyaniline and its hybrids were found to be concentration dependent, and concentrations were optimized to achieve maximum intensity of emission. Aggregation caused quenching (ACQ) may be the possible reason for concentration dependent emission. Hybrids showed significantly enhanced fluorescence than polyaniline. The AC electrical conductivity was also measured and found to be better for hybrids than the polyaniline. In the PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrid, the conductivity was found to be  $9.57 \times 10^{-1}$  S/cm at 100 KHz. This valuable improvement in luminescent property and conducting behaviour may be useful in various optoelectronic and electronic applications.

## Keywords

Polyaniline Hybrids, Fluorescence, Aggregation Caused Quenching (ACQ), Electrical Conductivity, Opto-Electronic Applications

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## 1. Introduction

Conjugated conducting polymers have recently received special attention in nanoscience and nanotechnology

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because of their highly  $\pi$ -conjugated polymeric chains and metal like conductivity [1]-[4]. The optical properties of conducting polymers [5]-[7] are as important as electrical properties because they allow number of applications such as sensing [8]-[10], displays and other opto-electronic applications [11] [12]. Along with various advantages, these pristine conducting polymers have several drawbacks such as poor emission, processability and stability. However, these drawbacks could be overcome to a large extent by preparing their hybrids with inorganic semiconductors such as metal sulfides and oxides. In the past, hybrids of polyaniline with various micro/nano structural semiconductors such as ZnS, CdS, Bi<sub>2</sub>S<sub>3</sub> have been prepared and studied for their various properties [13]-[17]. The combinations of organic and inorganic species create new material for development of new multifunctional devices [18]-[20]. It improves mechanical, optical, electrical and other properties of material. In conducting polymer, polyaniline is cheap, easily synthesizable and has high environmental stability. So, polyaniline has been frequently used as a host material for hybrids with various metallic sulfides [21] [22].

The structural photoelectrical properties of PANi/Bi<sub>2</sub>S<sub>3</sub> composite thin film prepared by electrodeposition have been studied. It was found that with the increase in concentration of PANi in PANi/Bi<sub>2</sub>S<sub>3</sub> hybrid, conductivity increases [23]. NiS/PANi counter electrode showed excellent electro catalytic activity and low charge transfer resistance relative to that of a platinum counter electrode in sulfide/polysulfide (S<sup>2-</sup>/S<sup>3-</sup>) electrolyte [24]. The photoluminescence and Raman evidence for mechanic-chemical interaction of polyaniline-emeraldine base with ZnS in cubic and hexagonal phase have also been reported [25].

In present work, binary/ternary hybrids of polyaniline with PEG and As<sub>2</sub>S<sub>3</sub> were synthesized by *in situ* polymerization of aniline in acidic medium. All the materials were characterized for their spectral, thermal, optical and electrical properties. Luminescence behaviour of polyaniline and its hybrids were investigated at different concentration in dimethylsulphoxide (DMSO). To the best of our knowledge no reports have been found related to synthesis and optical properties of ternary hybrid of PANi with As<sub>2</sub>S<sub>3</sub>-PEG.

## 2. Experimental Section

### 2.1. Materials and Methods

Aniline (Merck, A.R. grade) was distilled twice at normal pressure before use. Polyethylene glycol 6000 (Average molecular weight 7000 - 9000, LOBA chemicals, A. R. grade); arsenic sulfide (Merck) and ammonium persulphate (Merck) were used as received. Triple distilled water was used in all the synthesis processes.

### 2.2. Synthesis

Polyaniline was prepared by standard procedure [13]. Syntheses of various hybrids are stated below:

#### 2.2.1. Synthesis of Polyaniline-Polyethylene Glycol (PANi-PEG) Hybrid

To the solution of aniline (3 g, 0.03 mol) dissolved in 60 mL 2N HCl, 1.0 g polyethylene glycol dissolved in 25 mL water solution was added, mixed thoroughly and cooled below 5°C in an ice bath. Ammonium persulfate 9.0 g (0.07 mol) dissolved in 60 mL water was added slowly in an hour along with continuous stirring. The green color precipitate was obtained, kept in freezer over night, filtered, washed and dried. Yield (in g) = 3.1 g.

#### 2.2.2. Synthesis of Polyaniline-Arsenic Sulfide (PANi-As<sub>2</sub>S<sub>3</sub>) Hybrid

Aniline, 3.0 g (0.03 mol) was dissolved in 60 mL 2N HCl and kept in ice bath. 2.0 g (0.05 mol) arsenic trioxide was dissolved in 200 mL 2N HCl and then H<sub>2</sub>S was passed for 15 minutes. A yellow colored colloidal As<sub>2</sub>S<sub>3</sub> solution was obtained which was cooled to the temperature of less than 5°C. A pre-cooled solution of 9.0 g (0.07 mol) of ammonium persulfate dissolved in 60 mL water was added slowly by burette in aniline hydrochloride and arsenic sulfide colloidal mixture with continuous stirring. After 30 minutes a green colored precipitate started to form indicating the initiation of the reaction. The reaction was allowed to proceed for an hour, and then the mixture was kept in freezer overnight. A bluish green color precipitate was obtained. The precipitate was filtered and washed with 2N HCl and thrice by triple distilled water in order to remove unreacted reagents. The precipitate was dried in an oven at 60°C - 70°C and then kept over anhydrous CaCl<sub>2</sub> in desiccator. Yield (in g) = 3.5 g.

#### 2.2.3. Polyaniline-Polyethylene Glycol-Arsenic Sulfide (PANi-PEG-As<sub>2</sub>S<sub>3</sub>) Hybrid

2.0 g (0.05 mol) arsenic trioxide dissolved in 200 mL 2N HCl and H<sub>2</sub>S was passed into the solution for 15 minutes.

To the resulting colloidal solution, aniline 3 g (0.03 mol) dissolved in 60 mL 2N HCl and 1.0 g polyethylene glycol dissolved in 25 mL water solution was added, mixed thoroughly and cooled below 5°C in an ice bath. Ammonium per sulfate 9.0 g (0.07 mol) dissolved in 60 mL water was added slowly in an hour along with continuous stirring. The green color precipitate was kept in freezer over night, filtered washed and dried. Yield (in g) = 4.5 g. There were no yellow colored particles of  $\text{As}_2\text{S}_3$  present in the prepared hybrid indicating good coating of  $\text{As}_2\text{S}_3$  nanoparticles by polyaniline. The overall synthesis process is shown in **Figure 1**.

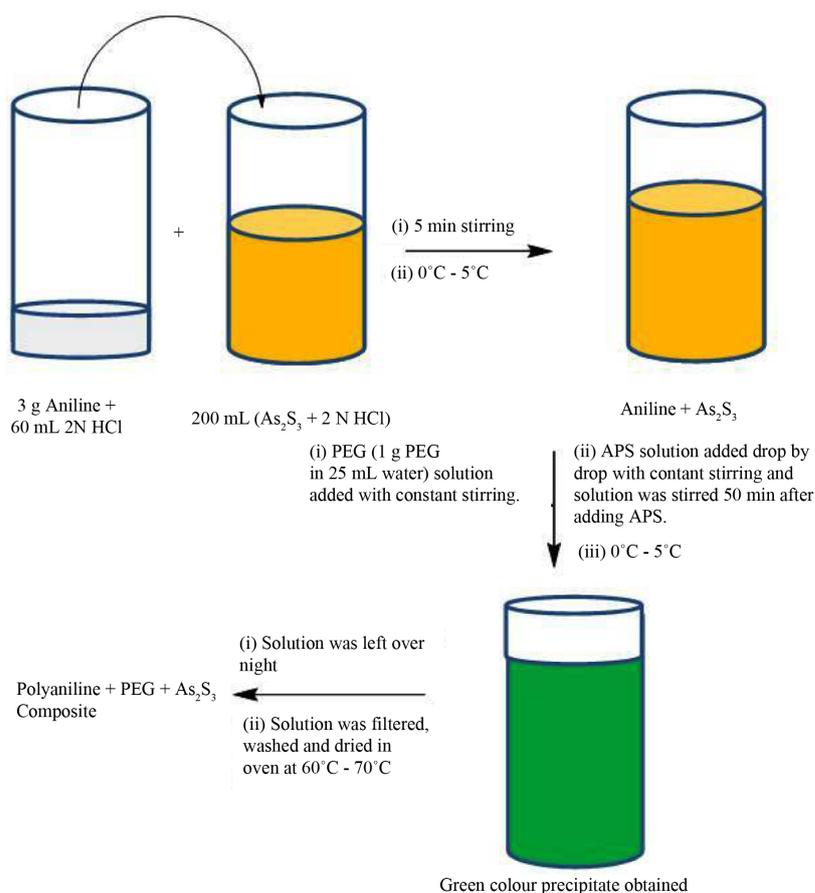
### 2.3. Measurements

IR spectra of the samples were recorded using PerkinElmer FTIR Spectrometer as KBr pellets. UV-Visible spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Fluorescence spectral measurements were carried out on a JY Horiba fluorescence spectrophotometer. The thermo gravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 600 at heating rate of 10°C per minute. AC impedance/conductance in the frequency range of 40 Hz to 100 KHz was made using a LCZ meter (Keithley 3330). The basic accuracy of the LCZ meter used for our measurements was 0.1% for the impedances in the range of 0.1 mΩ to 19.999 MΩ; capacitances in the range of 0.001 pF to 199.99 mF and for conductance in the range of 0.001 μS to 199.99 S.

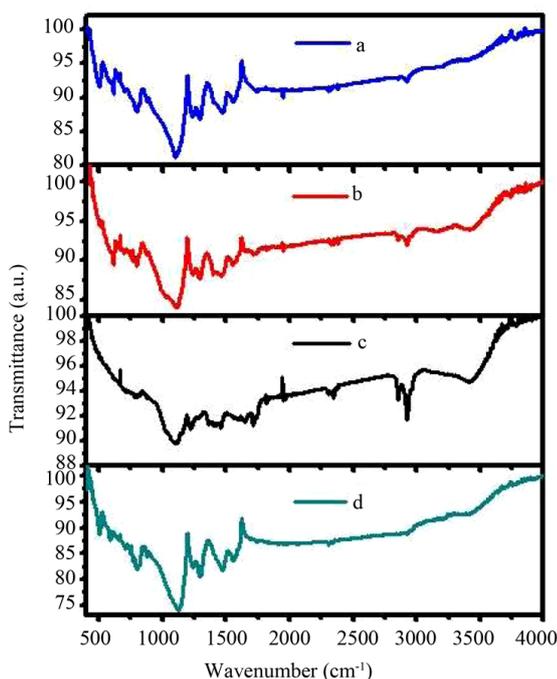
## 3. Results and Discussion

### 3.1. IR Spectroscopy

IR spectra of the samples were recorded in the range 400 - 4000  $\text{cm}^{-1}$  in KBr medium. The IR spectra of the hybrids and PANi have been shown in **Figure 2** and all the characteristic bands are tabulated in **Table 1**. A broad



**Figure 1.** Synthetic scheme for the preparation of Pani-PEG- $\text{As}_2\text{S}_3$ .



**Figure 2.** Infra-red spectra of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

**Table 1.** Characteristics of I. R. (in cm<sup>-1</sup>) of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

Sample	Quinoid	Benzenoid	(C-N) stret.	(C-C) stret.	(C-H) (op)
PAni	1555	1468	1292	1105	796
PAni-PEG	1556	1463	1293	1107	791
PAni-As <sub>2</sub> S <sub>3</sub>	1558	1451	1285	1100	795
PAni-PEG-As <sub>2</sub> S <sub>3</sub>	1558	1469	1296	1122	802

band comes at the region of 3415 - 3460 cm<sup>-1</sup> is due to  $\nu$  (N-H) stretching mode. The vibrational bands at 1563 cm<sup>-1</sup> correspond to stretching of  $\nu$  (N=Q=N) where Q refers to C<sub>6</sub>H<sub>4</sub> in quinoid form and the band at 1490 cm<sup>-1</sup>  $\nu$  (N-B-N) where B refers to C<sub>6</sub>H<sub>4</sub> in benzenoid form. The bands at 1300 cm<sup>-1</sup> are assigned to C-N stretching vibration in QBQ and QBC, QBB, BBQ and the band at 1240 cm<sup>-1</sup> is due to C-N stretching vibration of aromatic amine. In the region of 1020 - 1170 cm<sup>-1</sup> the aromatic C-H in plane bending while the bands at 803 cm<sup>-1</sup> is due to C-H out of plane bending of 1, 4 disubstituted benzene are observed. A strong band comes at 1140 cm<sup>-1</sup> due to electronic band or vibrational band at pure nitrogen quinone in polyaniline. A band at 703 cm<sup>-1</sup> is assigned to the ring C-C bending vibration, while the band at 590 cm<sup>-1</sup> is due to the ring in plane deformation. The C-H out of plane bending mode has been used as a key to identify the type of substituted benzene. A band at 500 cm<sup>-1</sup> is assigned to aromatic ring deformation.

A very good agreement between these spectra of PANi and hybrids, indicating that biomimetic synthesis leads to hybrid material based on these systems. The bands at 1468 cm<sup>-1</sup> were found to undergo a red shift to 1451 cm<sup>-1</sup> in presence of As<sub>2</sub>S<sub>3</sub> long with similar shifts from 1105 to 1000 cm<sup>-1</sup> and 796 to 795 cm<sup>-1</sup>. The interaction of cationic anilinium ions with anionic As<sub>2</sub>S<sub>3</sub> colloidal particle may be responsible for bringing As<sub>2</sub>S<sub>3</sub> particles close to the nitrogen sites which lead to weak interactions between the conjugated polyaniline shells with non-conducting As<sub>2</sub>S<sub>3</sub> core.

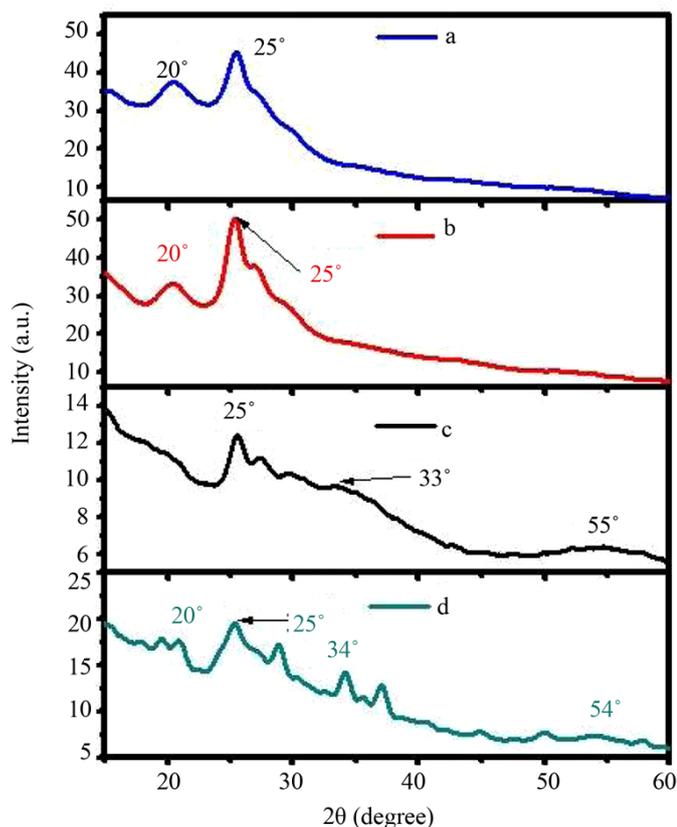
### 3.2. X-Ray Diffraction Studies

The powder X-ray diffraction is one of the best methods to find out incorporation of additive into the host material

*i.e.* in the case of binary and ternary hybrids. The X-Ray Diffraction pattern of PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub> are shown in **Figure 3**. It shows broad and well defined peaks, which indicate the semi crystalline nature of all the materials. The plains of benzenoid and quinoid rings of PANi chain are responsible for semi crystalline nature. As per various reports present in literature, As<sub>2</sub>S<sub>3</sub> exhibit peaks at about 33° and 54°. The similar peaks were observed in PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrids which clearly indicate the presence of As<sub>2</sub>S<sub>3</sub> in hybrids. It is also clear from the XRD patterns that crystallinity decreases from polyaniline to its hybrids as intensity of the peaks decreases. PANi encapsulates As<sub>2</sub>S<sub>3</sub> particles, interaction of PANi and As<sub>2</sub>S<sub>3</sub> weaken the interaction between two PANi chains and thus crystallinity of PANi is hampered and the degree of crystallinity decreases.

### 3.3. Thermogravimetric Analysis

Thermal degradation patterns of the PANi and various hybrids have been displayed in **Figure 4**. From the pattern it is clear that they follow a three-stage decomposition pattern. The first stage being weight loss, starting from room temperature to 100.0°C corresponds to loss of water molecules/moisture present in the polymer. The second stage loss from 100.0°C to 250.0°C is associated with a loss of dopant ion from the polymer matrix (dedoping). However, the weight loss after 250.0°C is due to degradation and decomposition of the polymer after the loss of dopant ion. PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub> exhibit weight loss 15%, 18%, 19% and 20%, respectively in the temperature range 100°C - 250°C. The total weight loss up to 800°C of PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub> are 54%, 56%, 66% and 69%, respectively. It indicates that up to 200.0°C As<sub>2</sub>S<sub>3</sub> hybrids have less weight loss than PANi and PANi-PEG but above 250°C hybrids have larger weight loss than PANi and PANi-PEG. The cause behind temperature drop in hybrid at higher temperature region could be attributed to a strong interaction at the interface of As<sub>2</sub>S<sub>3</sub> and PANi weaken the force of interaction of PANi interchains and enhance thermal decomposition of PANi in the hybrid.

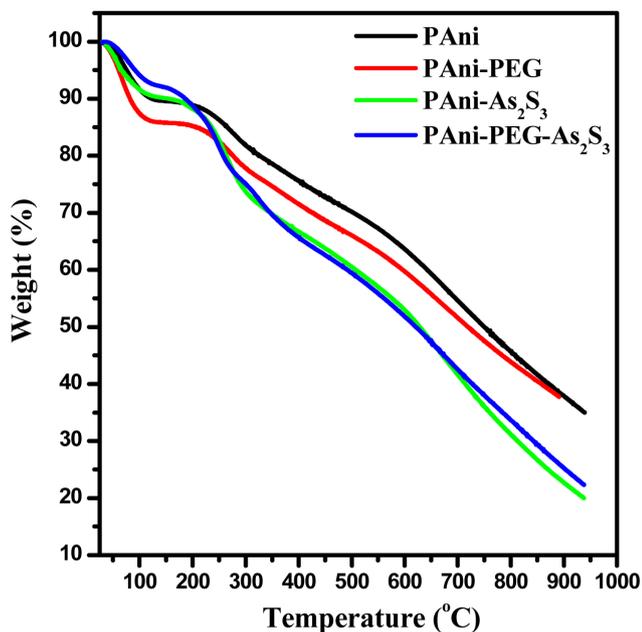


**Figure 3.** Powder X-ray diffraction patterns of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

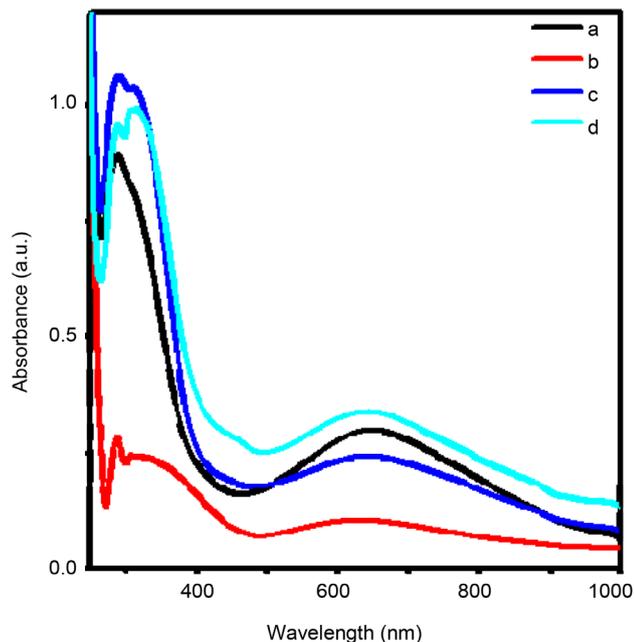
### 3.4. UV-Visible Spectra

The UV-Visible absorption spectra are helpful to identify extent of conjugation in conducting polymers and also in comparative study of conducting polymers with their hybrids. The absorption spectra of PANi and various hybrids were recorded in DMSO solution and given in **Figure 5**.

The absorption spectrum of PANi exhibits band at 645 nm, indicates high degree of conjugation. However, these bands have been found slightly blue shifted in the case of hybrids. The obtained values are tabulated in



**Figure 4.** TGA curves of PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub>.



**Figure 5.** UV-visible spectra of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

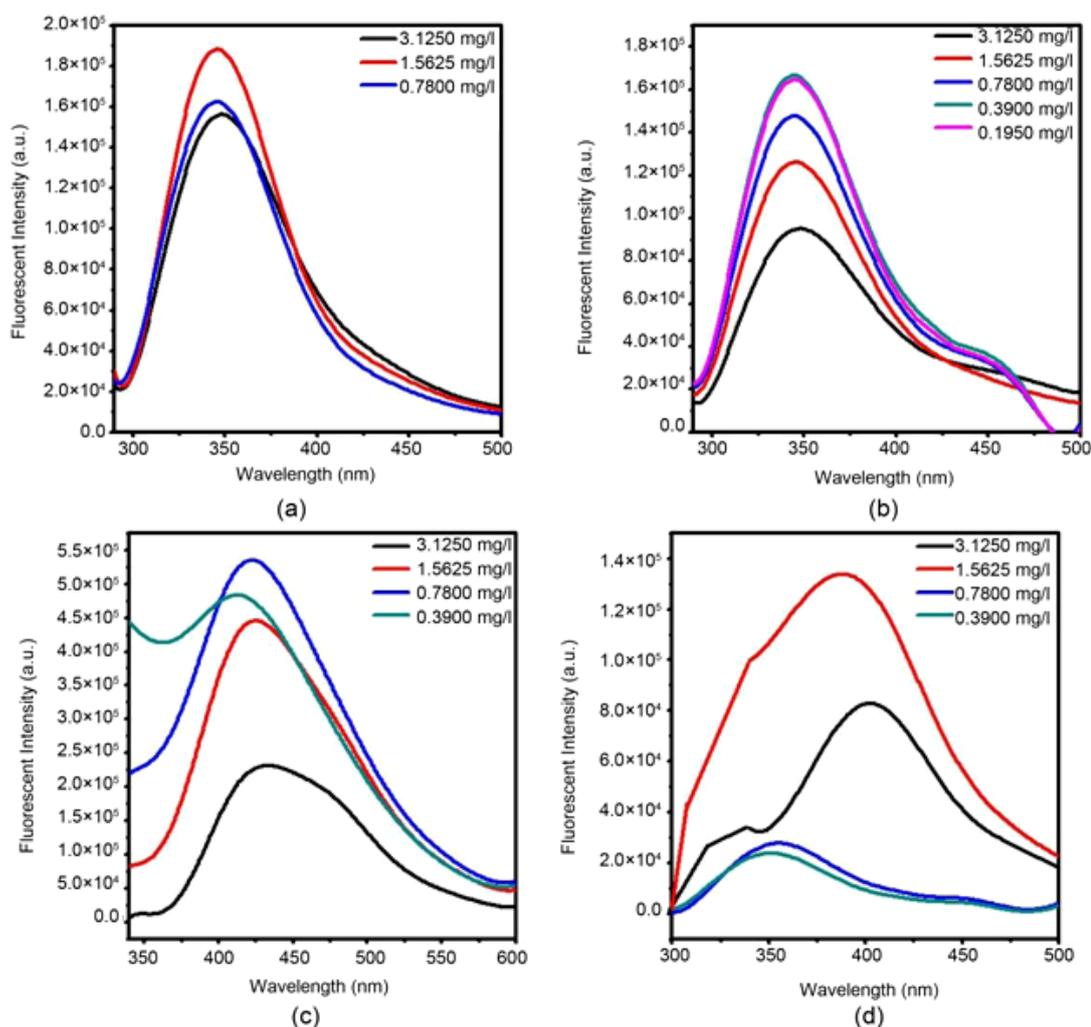
**Table 2.** The blue shifting in hybrids depend upon the amount of the PANi. Higher the amount of PANi lesser will be the shifting of these bands. In the absorption spectra of hybrids, the band appears at the lower wavelength region also suffer blue shift in respect to PANi. It may be due to the microstructural changes which depend on the synthetic conditions.

### 3.5. Fluorescence Studies

The fluorescence spectra of PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub> were recorded in DMSO. All the materials showed significant emission in the range of 300 - 550 nm. In order to achieve optimum concentration, the fluorescence spectra were recorded at different concentrations and are shown in **Figure 6**.

**Table 2.** UV-visible spectral bands of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

Samples	$\lambda^{abs}$ ( $\pi \rightarrow \pi^*$ band) (nm)	$\lambda^{abs}$ (Exciton band) (nm)	$\lambda^{emi}$ (nm)
PANi	292	645	345
PANi-PEG	287	630	343
PANi-As <sub>2</sub> S <sub>3</sub>	290	641	411
PANi-PEG-As <sub>2</sub> S <sub>3</sub>	289	641	392



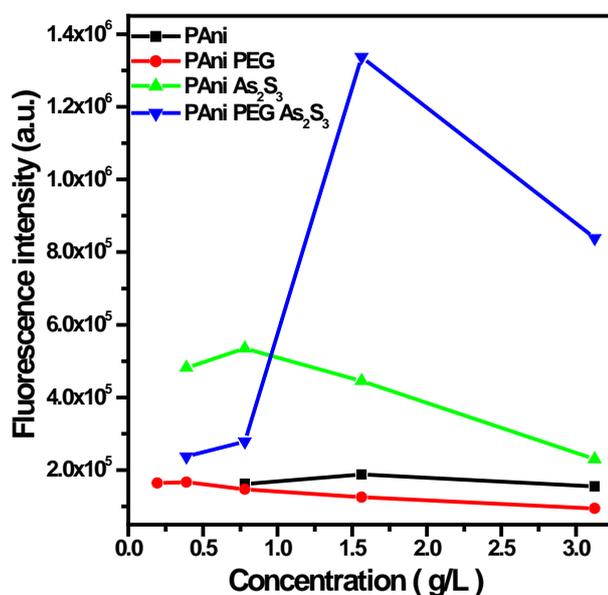
**Figure 6.** Fluorescence spectra of (a) PANi, (b) PANi-PEG, (c) PANi-As<sub>2</sub>S<sub>3</sub> and (d) PANi-PEG-As<sub>2</sub>S<sub>3</sub>.

Above optimum concentration, the fluorescence intensity decreases due to aggregation caused quenching (ACQ) and below optimum concentration it decreases due to much dilution. From concentration versus fluorescence intensity curve (**Figure 7**), it is clear that PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrid showed highest emission among all. Also, PANi exhibits weaker emission than hybrids, might be due to presence of additives may reduce the possibility of aggregation in PANi.

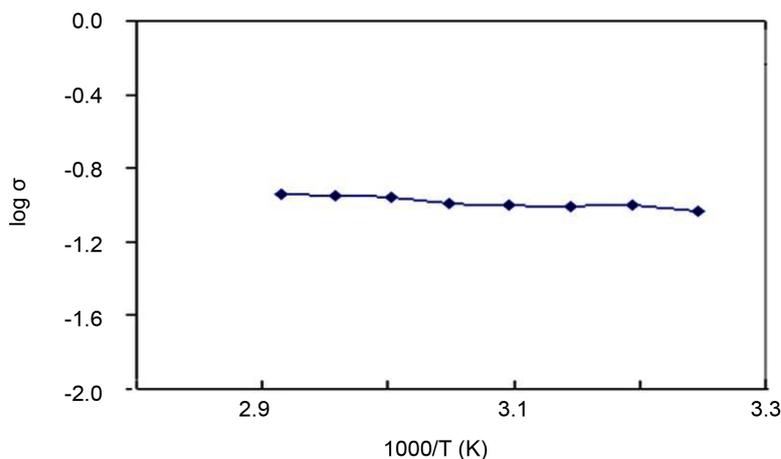
### 3.6. AC Electrical Conductivity Measurement

The AC electrical conductivity of PANi and various hybrids were measured at room temperature in the various frequency regions using platinum foils as contacts on pellets. The values are represented in **Table 3**. In all the cases, with increase in frequency conductivity of the materials increases.

At 100 Hz, the conductivity of polyaniline was found to be  $4.08 \times 10^{-1}$  S/cm. In the PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrid the conductivity was found to be  $9.53 \times 10^{-1}$  S/cm. The conductivity of PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrid is also measured as a function of temperature. It has been found that, an increase in temperature results into increase in conductivity and shows the semiconductor behavior of material. Arrhenius plot is shown in **Figure 8**.



**Figure 7.** Concentration vs. fluorescence intensity plots for PANi, PANi-PEG, PANi-As<sub>2</sub>S<sub>3</sub> and PANi-PEG-As<sub>2</sub>S<sub>3</sub>.



**Figure 8.** Arrhenius plot for PANi-PEG-As<sub>2</sub>S<sub>3</sub> hybrid.

**Table 3.** Conductivity data summary of polyaniline and hybrids.

Composition	$\sigma_{ac}$ (S/cm) 100 Hz	$\sigma_{ac}$ (S/cm) 1 KHz	$\sigma_{ac}$ (S/cm) 100 KHz
PAni	$4.08 \times 10^{-1}$	$4.40 \times 10^{-1}$	$4.42 \times 10^{-1}$
PAni-PEG	$3.98 \times 10^{-2}$	$4.28 \times 10^{-2}$	$4.39 \times 10^{-2}$
PAni-As <sub>2</sub> S <sub>3</sub>	$4.66 \times 10^{-2}$	$4.88 \times 10^{-2}$	$4.98 \times 10^{-2}$
PAni-PEG-As <sub>2</sub> S <sub>3</sub>	$9.18 \times 10^{-1}$	$9.53 \times 10^{-1}$	$9.57 \times 10^{-1}$

## 4. Conclusion

In conclusion, polyaniline based binary and ternary hybrids were prepared and exhibited better luminescent and conducting properties than polyaniline. Luminescent spectra of polyaniline and its hybrids were taken at different concentration in DMSO and found to be concentration dependent. Fluorescence signals of polyaniline and its hybrids were found to be aggregation caused quenching (ACQ) type. Powder X-ray diffraction pattern revealed that hybrids of PAni exhibit poor crystallinity than PAni. Ternary hybrid, PAni-PEG-As<sub>2</sub>S<sub>3</sub>, posses highest conductivity among all the materials. These materials may find potential application in electronic and opto-electronic devices.

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