FABRICATION OF ENVIRONMENTALLY BENIGN CHITOSAN/3-HYDROXYFLAVONE DUAL EMITTER COMPOSITE THIN FILMS FOR OLED APPLICATIONS

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ABSTRACT

Biopolymer chitosan composite films doped with dual emitter (DE) 3-hydoxyflavone were prepared by solvent intercalation method. The FTIR, SEM, PXRD and TGA techniques were used to characterize the films. The surface morphology, crystallinity and stability of the films improved as the dopant concentration increased. The UV absorbance maxima of the films found at 329nm and 418nm as dual absorption with a bathochromic shift with respect to dopant absorption maxima 305nm and 340nm. This was attributed to binding of 3-hydroxy flavone to the polymer matrix. Similarly, emission maxima were found at 472nm and 530nm, on shining them at 329nm. As a result, non-luminescent chitosan films changed to be effective photoluminescent material of dual emission with large stokes shift of 143 nm for band I and 112nm for band II. The relative quantum yield of doped composite films were found to be in the range of 30.15% to 37.05%. Hence, these films with blue and green emission would find use as white light emitting diode materials.

1 INTRODUCTION

Purely organic light-emitting compounds with an aromatic backbone have shown promise in optoelectronic and biomedical applications [1][2]. In turn, multicolor-emissive systems, particularly dual emitters (DEs), have a lot of potential for sensors, data encryption, anticounterfeiting, high-sensitivity bioimaging, and the production of low-cost white organic light emitting diodes(WOLED) [3].

Construction of WOLED generally requires the use of two (blue and yellow) or three (blue, green, and red) different colour emitters, covering the whole visible light range from 400 to 700 nm to achieve good colour rendering. This requirement often leads to complex device architectures, demanding fabrication processes and high cost in order to accommodate multiple emissive materials. In contrast to systems composed of several fluorescent molecules, single-molecular systems with white emission through DE have several advantages by avoiding phase separation, colour aging, and degradation. Moreover, they offer simpler devices with enhanced reproducibility and stability. Many organic compounds like azulene, 4-N, N-dimethylaminobenzonitrile (DMABN) exhibited phenomena of DE [4, 5]. Singlet DE can also result from the presence of dual CT states, excimer states, excited state intramolecular proton transfer (ESIPT), and structural changes in the emitter caused by UV light absorption. Of late widely distributed subgroup of flavonoids are 3-hydroxy favonols (3HF) have attracted much attention, due to unique and beneficial photophysical characteristics, and biocompatibility [4]. The ESIPT process of 3HF derivatives, could be influenced by solvents, metal ions, proteins rich in a-helix structures, or advanced DNA structures altering microenvironment, resulting in dual emission, with normal fluorescence emission around 400 nm and tautomeric emission at longer wavelengths [5].

So, in this work, 3HF a dual emitter was taken as a dopant to enhance fluorescence activity of biopolymer chitosan. One of the processes to make it fluorescent material is doping a luminescent dye into the polymer. Specifically, this work focused on the fabrication of dual emissive biopolymeric films.

2 METHOD

2.1 *General Procedure for the preparation of composite film [chitosan/3-hydoxy flavone* (3HF)]

The procedure followed here is solvent intercalation technique. Chitosan composites were prepared by dissolving 0.5 g of chitosan in 25 ml of 2% acetic acid, stirred in a magnetic stirrer for about one hour, the dopant 3-hydroxy flavone (0.01 g, 0.02g, 0.03 g), slurry in ethanol was added to chitosan solution and ultrasonicated for 3 hr. This was uniformly spread over Petri dish, annealed at a temperature of 50^{o}C for 24 hr. The films were cooled to room temperature, slowly peeled off from the Petri dish.

3 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

The surface morphology of the neat film and doped films are depicted in Figure.1.The analysis revealed that there was a distinct difference between the neat and doped chitosan films showing the uniform distribution of the dopant in the polymer matrix. This could be due to good adhesion and strong hydrogen bonding between the chitosan and the dopant.

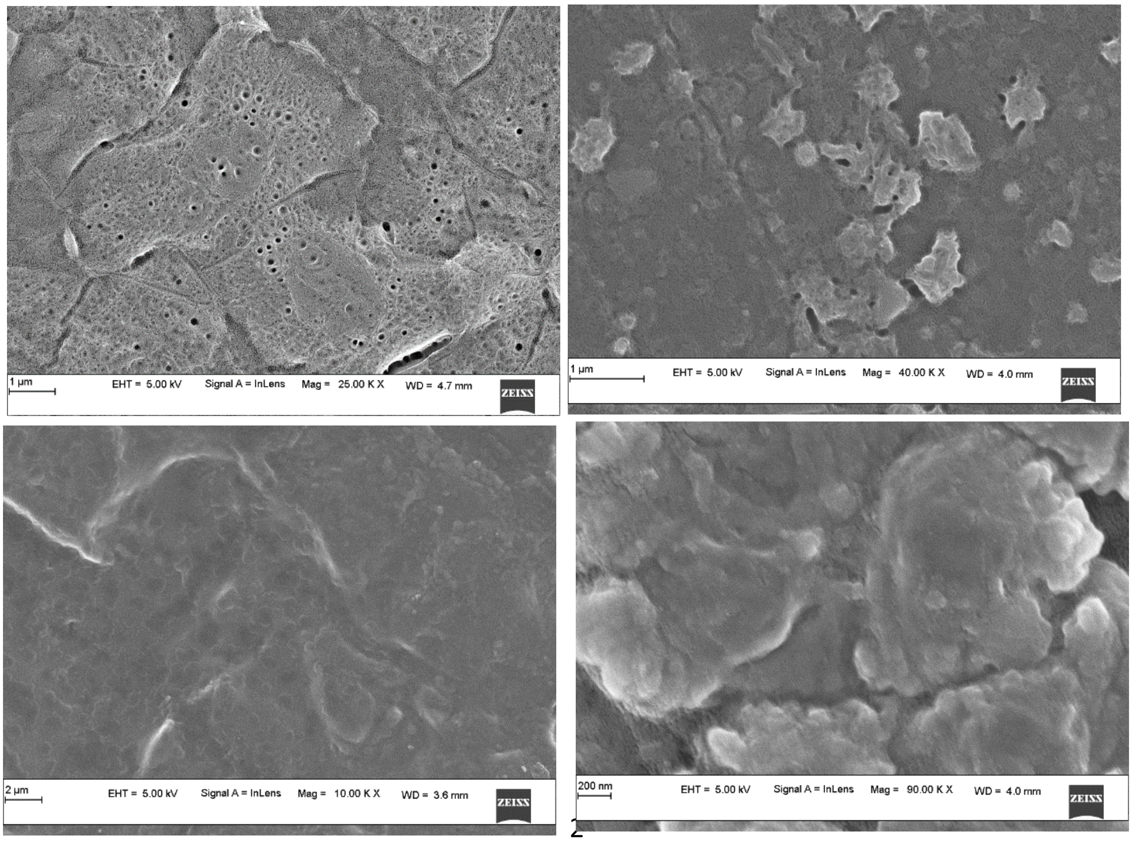

Figure.1. SEM image of (a) Pristine, (b) 2wt%3 HF, (c) 4wt% 3HF, (d) 6wt% 3HF

3.2 Powder XRD diffraction Pattern of 3HF doped chitosan films

The X-ray diffraction pattern of dopant 3HF, doped film and neat films are given in Figure .2. Polymers are prone to orientation because of their long chain structure. The primary tool for determining crystalline orientation is XRD. In some cases, polymer crystals have a disproportionately large number of defects. So, diffraction peak broadening takes place in some polymers. The weak and broadened diffraction peaks centred on 8^0 and 20^0 was accounted for semi crystalline nature of chitosan. The dopant 3HF showed peaks at 15.5^0, 12.1^0, 18.2^0. In 3HF doped films, one sharp diffraction peak observed at 15.03 which resembled the pattern of dopant 3HF confirming the presence of dopant in the chitosan matrix. Overall crystallinity of the doped films increased on doping.

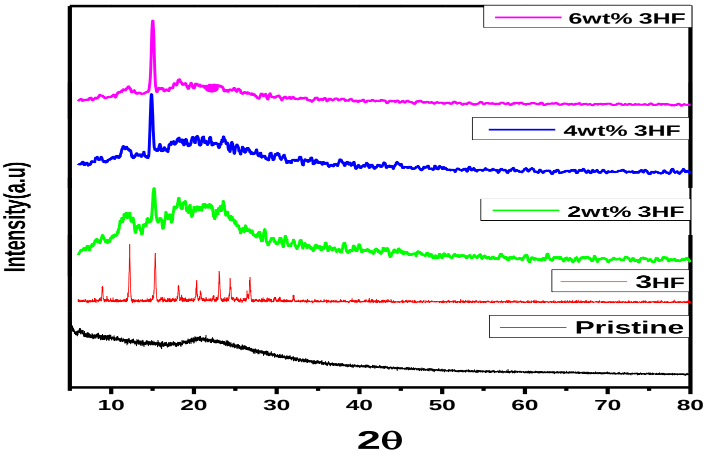

Figure .2. PXRD pattern of doped chitosan /-3-hydoxyflavone films.

3.3 Thermogravimetric Analysis (TGA)

The thermal properties of neat film and doped films were studied by TGA and depicted in Figure.3. From TGA, it was found that the first disintegration of pure chitosan film took place at the temperature of 27^0C-113^0C, with a weight loss of 15%. This stage could be assigned to the loss of residual water in a sample. The next two disintegrations took place at the temperature of 250^0C-322^0C and 503^0C-629^0C with the weight loss of 26.1% and 31.9% corresponding to the decomposition of an ether group and glucosamine residue [6]. The chitosan-HF (2w% and 4wt%) showed the first degradation at 27^0C-113 ^{0}C with the weight loss of 15% which was similar to that of pure chitosan; the next two degradations were taking place at the temperature range of 250^0C-322^0C and 503^0C-629^0C with the weight loss of 26% and 31.9%. For 3HF (6wt%) first degradation at 27^0C-97 ^{0}C with the weight loss of 14% which was similar to that of pure chitosan; the next two degradations were taking place at the temperature range of 245^0C-303^0C and 503^0C-629^0C with the weight loss of 21.9% and 22.1%. It can be observed that the second thermal degradation for the doped film (6wt%) is greater compared to the pure film because of the presence of a dopant in the film, suggesting that the doped film is thermally stable compared to the neat film

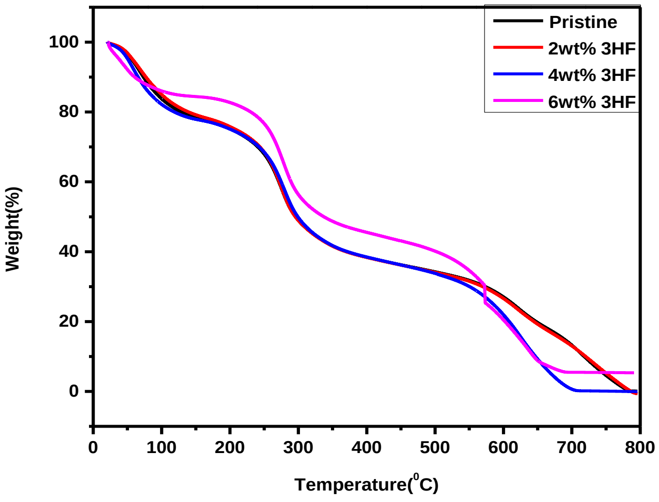

Figure.3. TGA thermograms of neat and 3HF doped films

3.4 *FTIR analysis*

In the IR spectrum of chitosan, absorption bands seen at 1560cm^{-1} due to primary amine bending vibration, whereas a broad band was observed at 3400cm^{-1} accounted for O-H as well as NH_2 stretches [7], a forked absorption band originated due to alkyl –C-H stretch was seen at 2800cm^{-1} [8]. The prominent absorption band seen at 1020cm^{-1} could be accounted for -C-O-C- of glycosidic linkage as well as ring -C-O-C- stretch [9]. In the IR spectra of 3HF doped chitosan films, the change in the region 3700cm^{-1}-2700cm^{-1} was observed. Generally, in case of polymer the changes in this region would define type of interaction of dopant with the matrix. The band was shifted to the higher wavenumber (3265cm^{-1}) compare to pristine (3200cm^{-1}) indicating dopant 3HF was linked to the matrix by physical forces.

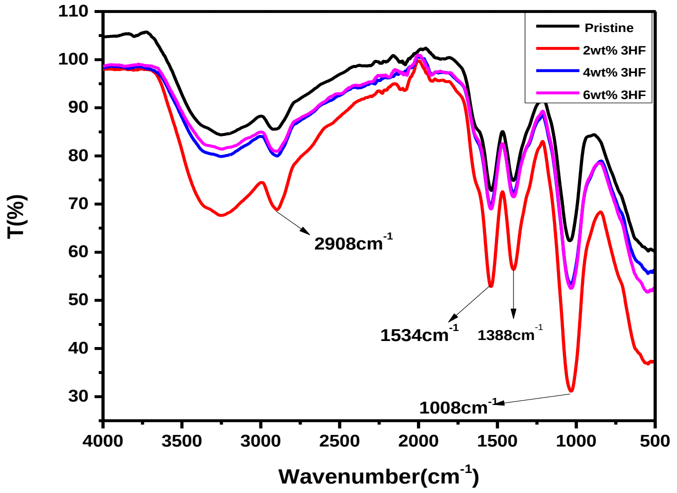

Figure.4. FTIR spectra of doped chitosan /-3-hydoxyflavone films

3.5 UV-Visible spectroscopy of chitosan /3-hydoxyflavone films

The UV visible spectroscopy of chitosan and 3-hydoxyflavone is depicted in Figure.5. One of the most fundamental processes in biology and chemistry is proton transfer. In any system, intermolecular proton transfer typically entails the transfer of protons from the donor to the acceptor, which necessitates the formation of a dimer or complex between the proton donor and acceptor. Intramolecular proton transfer, on the other hand, is the transfer of a proton within the same molecule. Among which excited-state intramolecular proton transfer (ESIPT) gaining popularity due to its large Stokes shift. Due to ESIPT process, 3HF produces normal (N*) and tautomer (T*) excited forms. Here, the 3-hydoxy flavone (3HF) exhibited two absorbance peaks at 305nm and 340nm. The doped films also exhibited two peaks at 329nm and 418nm. The bathochromic shift was observed after doping process. These changes in the absorbance after doping due to the changes in the microenvironment of the system due to binding of the dopant with active groups of matrix .

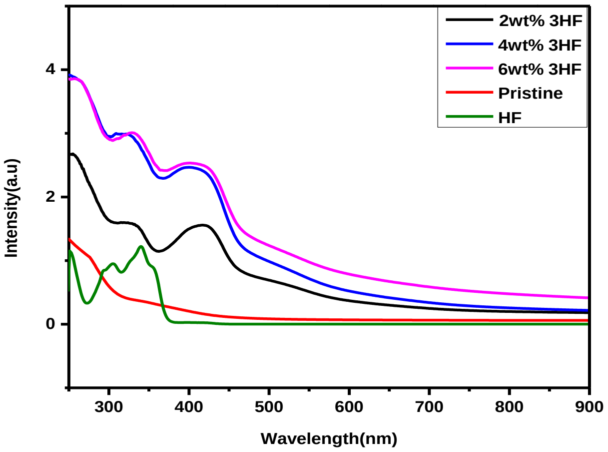

Figure.5. UV analysis of doped chitosan /-3-hydoxyflavone films

3.6 Tauc's Plots for 3-hydoxy flavone doped chitosan films

The important criteria for a compound to show photosensitizing activity is that the compound should possess minimum optical band gap energy. Optical band gap energy could be found out by calculating absorption coefficient of the films. The absorption coefficient of the films was calculated from the thickness of the film (t) and absorbance (A) using the equation,

$$\alpha = (2.303/t)\ A \qquad (1)$$

The plot of absorption coefficient (α) vs photon energy (eV) was depicted in Figure. 6(a). It was found that the absorption coefficient increases as the dopant concentration in the polymer matrix increases. On the other hand, the value of the absorption edge of films doped with respective dopants was determined by extrapolating linear portion of the line to the zero-absorption value. The absorption edge of undoped chitosan film was found to be 4.8eV. But for the films doped with HF, their positions were found to be shifted to the lower energy value, due the interaction of dopants with the polymer chain. Thus, shift of the absorption edge could be due to the change in the electron- hole framework in conduction and valance band [10].

The term optical energy gap is one of the fundamental quantity for determining semiconductor nature of the fabricated films, which was given by the Tauc's equation [11]

$$\alpha h\upsilon = B\,(h\upsilon - E_g)^n \qquad (2)$$

where E_g is the optical energy gap, B is the constant which depends on the probability of transition, n is the index which could be assumed to be ½ for allowed direct optical band gap, 2 for the allowed indirect optical band gap. From the Fig. 6(b &c), it can be seen that the linearity of the $(\alpha h\upsilon)^{1/2}$ vs hυ indicates the fabricated films are best fit for a direct allowed transition. The value of optical energy band gap for the pristine was 4.8eV. However, the introduction of dopant to the polymer matrix tends to gradual decrease in the band gap energy with an increase in wt% of dopant from 4.8eV to 3.34eV.

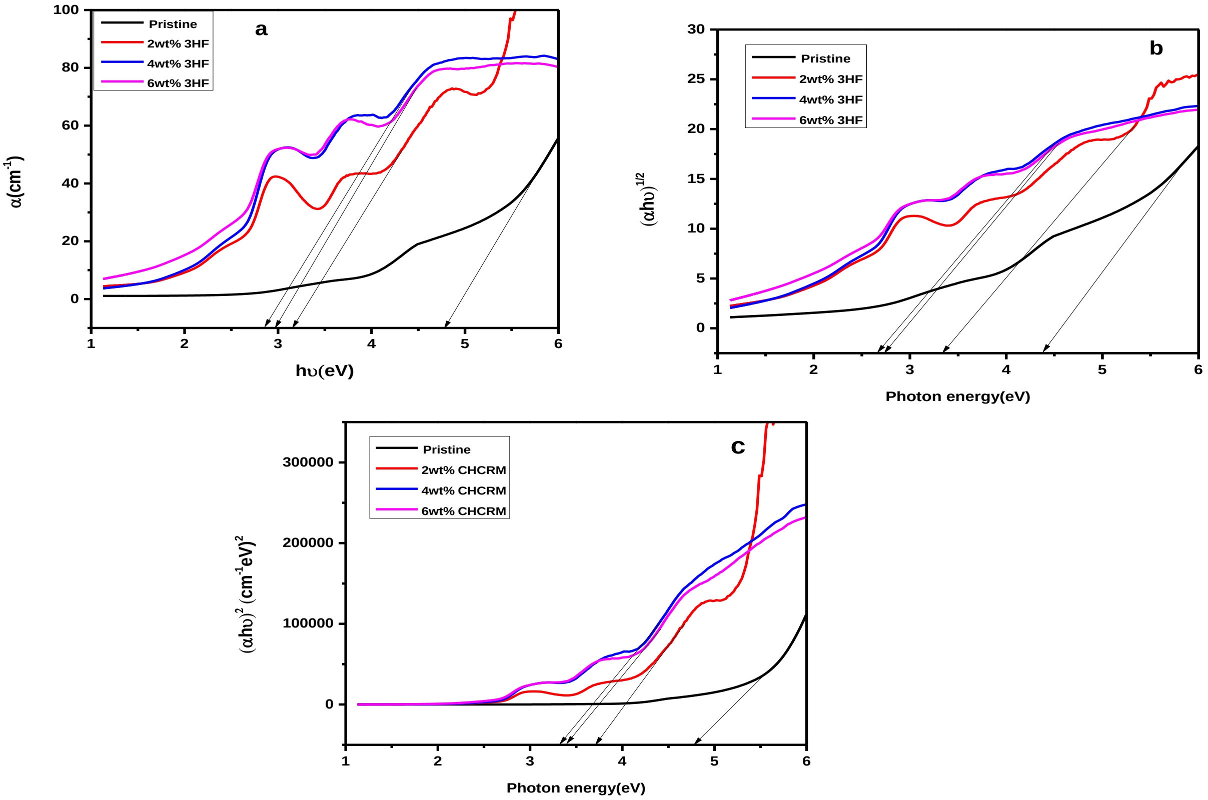

Figure. 6. a) Absorption coefficient of doped and undoped 3HF(b) Direct band gap of doped and undoped 3HF (c) Indirect band gap of doped and undoped 3HF.

3.7 Photoluminescence analysis of chitosan /3-hydoxyflavone films

The 3HF derivatives exhibit dual emission, with well-separated bands whose positions and intensities provide much information about the microenvironment [12][13]. The dopant molecule showed two emission peaks at 374nm and 530nm when excited at 305nm and 340nm. But after 3HF was doped into chitosan matrix, the emission peak observed at 472nm and 530nm. Generally, in 3-hydroxy flavone exists in tautomeric forms (keto and enol form). The emission of light by 3HF molecule depends on media in which it is present. The proton donor and acceptor of ESIPT molecules can form intermolecular hydrogen bonds with the solvent molecules in polar solvent, which prevents the formation of intramolecular hydrogen bonds in the ESIPT molecules. As a result, in polar or protic solvents, the normal enol form transforms into the solvated enol form, causing the N* (normal form) band to rise and the T* band to suppress (tautomer) Figure 7. Moreover, when 3HF was in polar solvent, it showed red shift. Similar kind of changes took place when 3HF bound to protein. Similarly, the changes in the emission peaks after doping resembled the changes of protein binding with 3-hydoxy flavone. Similarly the emissive peaks were found at 472nm and 530nm, upon shining at 329nm Figure.8. The hyperchromism was observed for first peak while hypochromism for second peak clearly indicated binding of chromophore into matrix through weak interaction of H-bonding with increased ratio of IN*/IT*. The large stokes shift of 143 nm for band I and 112nm for band II was observed for composite films. The relative quantum yield of doped films were found to be in the range of 30.15% to 37.05%.

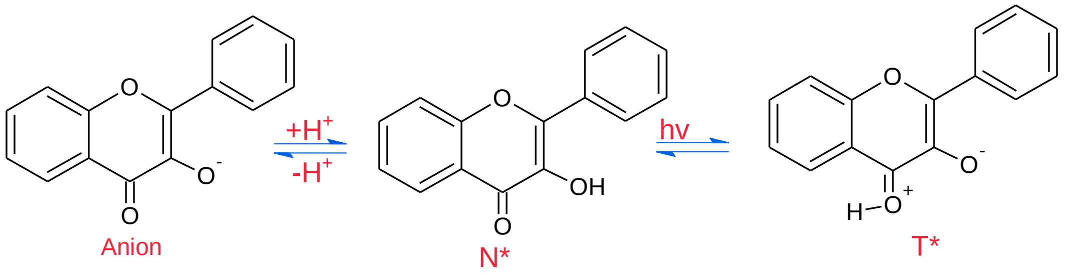

Figure.7. Normal (N*), Tautomeric (T*), and anionic forms (A) of 3HF

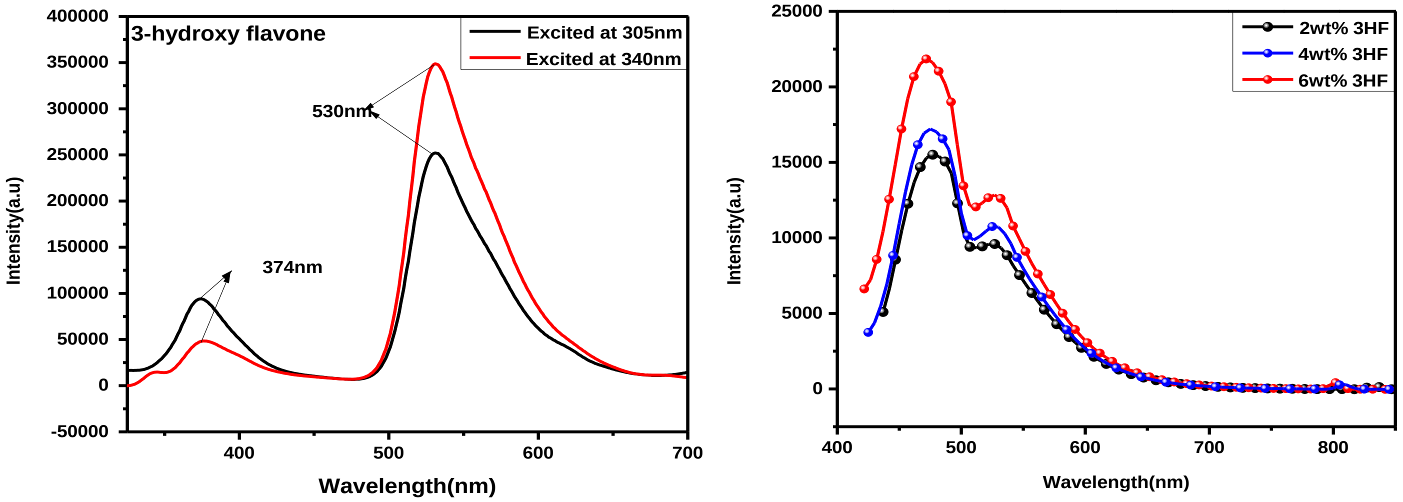

Figure.8. Photoluminescence spectra (a) 3HF and (b) Chitosan /3-hydoxyflavone films excited at 329nm

3.7 ***Dielectric and A.C. conductivity studies chitosan /3-hydoxyflavone films***

The ability of a material to exhibit charge separation under the influence of an applied field can be used to deduce dielectric properties. The dielectric constant of polymer matrix doped with 3HF exhibit a monotonic increase with the dosage amount (Figure.9a). AC conductivity occurs due to the motion of the charge carriers through the polymer matrix and dopant and is depicted in Figure. 9b. In doped films, at the lower frequency region, a greater volume of charges assemble between the dopant molecule - matrix interfaces causing a drop in conductivities. However, at higher frequencies, a strong frequency-dependent conductance was observed.

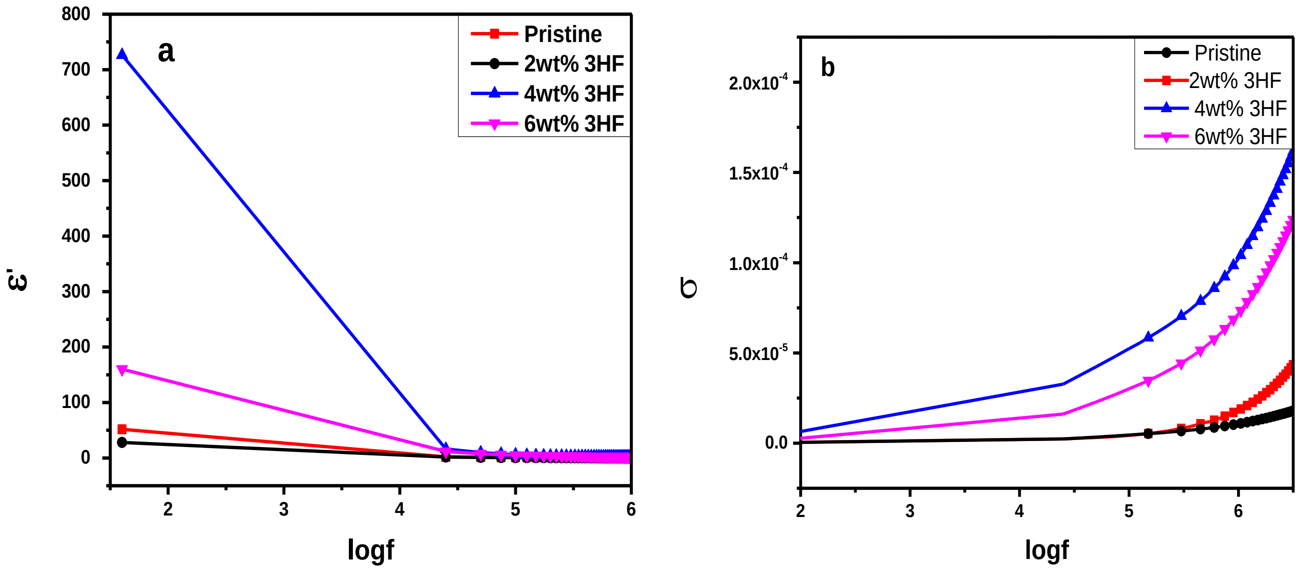

Figure.9. Dielectric and A.C. conductivity of chitosan /3-hydoxyflavone films excited at 329nm

4 CONCLUSION

Biopolymer chitosan films doped with 3HF (2%, 4%, 6%) were fabricated by solvent intercalation technique. The fabricated composite films were characterized which confirmed the successful doping.Upon determining the photoluminescence property of these films; exhibited dual emission with large stokes shift and increased quantum yield. So these blue (E_{max}, 472nm) and green (E_{max} 530nm) emissive films could find use in devising environment friendly WOLED.

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