

## **Multi-Color Fluorescence of Copolymer of Diphenylamine and M-Chloroaniline and their Hybrids with TiO<sub>2</sub> and ZnO**

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**Abstract:** Poly(*m*-chloroaniline) (3clp), polydiphenylamine (dpa), copolymer of diphenylamine and *m*-chloroaniline (3clpdpa), composite of copolymer with TiO<sub>2</sub> (3clpdpat), and composite of copolymer with ZnO (3clpdpaz) have been chemically prepared by oxidative polymerization of polymer and copolymer with TiO<sub>2</sub>, ZnO. These were characterized by FTIR, UV-visible, Fluorescence spectra, Atomic force microscopy and TGA. Fluorescence of polymers, copolymer and its composites were aggregation caused quenching type and were concentration dependent. Fluorescence intensity of composites of copolymer was found to be more than the polymer and its copolymer. Multicolor fluorescence was observed in polymers and its copolymer when excited by different laser light. These materials are being used as cell imaging agent.

**Keywords:** Aggregation-caused quenching, multicolor fluorescence, polymer composites.

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### **1. INTRODUCTION**

Optical properties of conjugated polyaniline are as important as their electrical properties as they, not only, display a variety of colors depending on the form but also yield a variety of fluorescence [1-4]. Such properties are useful in biological cell imaging.

Polyaniline [5] and substituted polyaniline are one of the most promising conducting polymers with luminescent property because of their low cost, easy preparation, unique properties which are easily controlled by oxidation and protonation, excellent environmental stability [6] and potential application in electronic devices [7]. In spite of various advantages, polyaniline has certain limitations when it comes to its applications as it is neither soluble in organic solvents as well as water nor fusible for thermosetting. In order to overcome such disadvantages, attempts have been made by use of molecular design, modification of monomer structure, use of functionalized acid dopants, formation of blends/composites and copolymerization. The synthesis of different homopolymers and copolymers derived from anilines with electron withdrawing groups has been reported [8-9]. Several polymers of alkoxy and chloro derivatives of aniline and copolymer of its derivative were synthesized to obtain varied optical property [10].

The copolymer of aniline and *m*-chloroaniline was found copolymer exhibits excellent solubility in DMF, DMSO and THF [11]. The copolymer of chloroaniline and aniline was found enhanced solubility with colorful solvatochromism [12]. Frenando V. Monali electrocopolymerised the *m*-chloroaniline and aniline and found the copolymers exhibit decreasing quenching as chloroaniline content increases [13]. To improve the optical property of substituted polyaniline, we prepared copolymer and composite of copolymer of *m*-chloroaniline and diphenylamine with TiO<sub>2</sub> and ZnO. However, systematic investigation on the synthesis and characterization of pure copolymer from *m*-chloroaniline and diphenylamine has not been studied until now.

The aim of this article is to investigate the oxidative copolymerization of *m*-chloroaniline and diphenylamine to get copolymer and its composite with TiO<sub>2</sub> and ZnO improved optical property. The resulting polymers and copolymers were characterized by FT-IR, UV-visible. Thermal stability was studied by Thermal gravity analysis (TGA).

### **2. EXPERIMENT SECTION**

#### **2.1 Materials**

Aniline, *m*-chloroaniline, diphenylamine and ammonium persulphate (APS) were purchased from S D Fine-chemical limited. Aniline and *m*-chloroaniline were purified by double distillations before used. All the other reagents were of analytical grade and used as received.

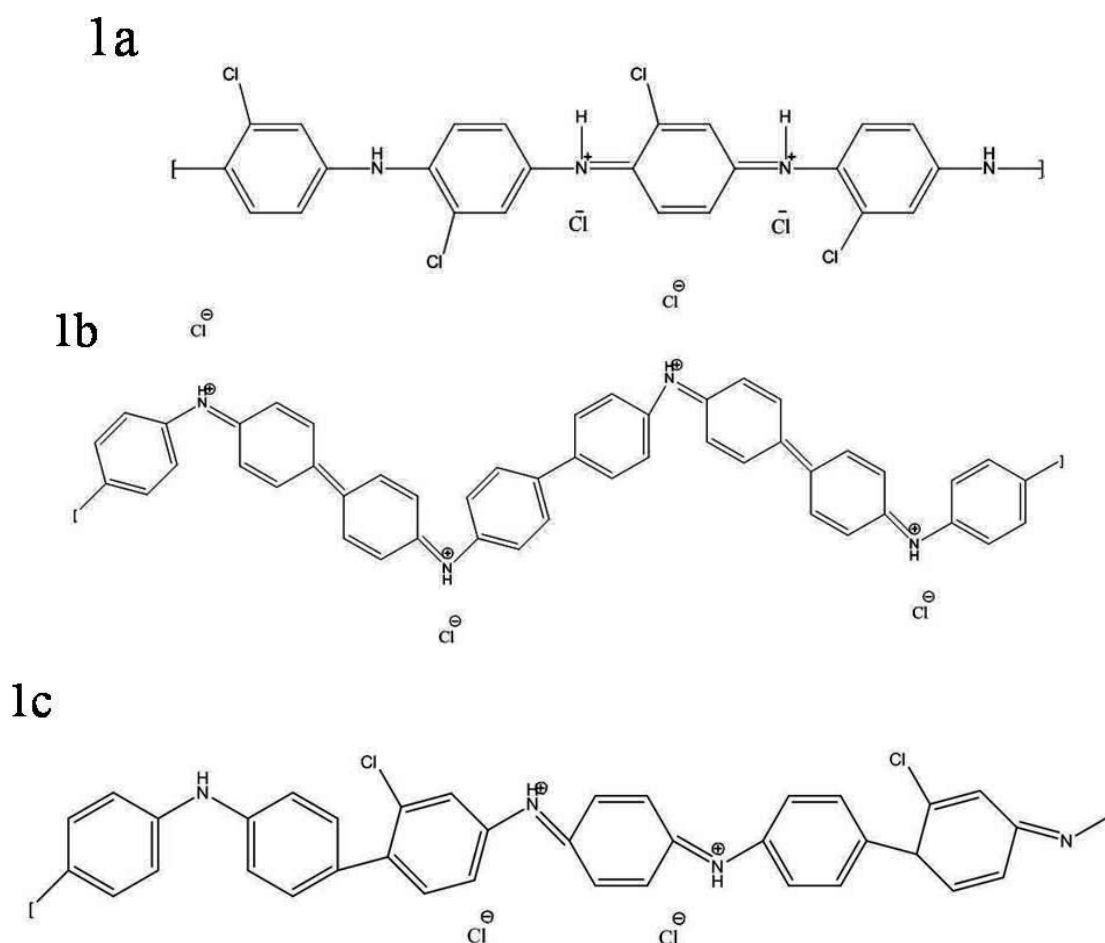
## 2.2. Measurements

The Ultraviolet-Visible absorption spectra of polymers, copolymer and its composites were recorded on Shimadzu UV-1700 model, The IR Spectra were recorded on PerkinElmer Spectrum two model, FTIR Spectrometer. The thermo gravimetric analysis (TGA) measurements were performed on Perkin Elmer STA 600 at heating rate of 10<sup>0</sup>C per minute. Fluorescence spectra measurements were carried out by JY Horiba fluorescence spectrophotometer.

## 2.3. Synthesis

### Synthesis of Poly(m-chloroaniline) and Polydiphenylamine

3.19 g (0.025 mole) m-chloroaniline and 4.23 g (0.025 mole) diphenylamine were added separately in 100 ml 0.5 N HCl with continuous stirring. After 5 minutes continuous stirring, ammonium persulphate solution (7 g APS dissolved in 50 ml 0.05 N HCl) was added in each solution with continuous stirring at low temperature (5-10 <sup>0</sup>C). Each reaction was stirred continuously 4 hours and kept whole night for complete polymerization. Orange and bluish green color solid were obtained in m-chloroaniline and diphenylamine solution, respectively. Each solution was filtered and washed with distilled water and dried in oven at 60 <sup>0</sup>C for 24 hours. The yields of polymers of diphenylamine and m-chloroaniline solution were 2.51 g and 1.51 g, respectively. Predicted structure of poly(m-chloroaniline) and polydiphenylamine are shown in Fig. 1a and Fig. 1b.



**Fig. 1** Structure of (1a) poly(m-chloroaniline), (1b) polydiphenylamine and (1c) copolymer of aniline and m-chloroaniline.

### Synthesis of copolymer of m-chloroaniline and diphenylamine (3clpdpa), 3clpdpa/TiO<sub>2</sub> composite, 3clpdpa/ZnO hybrid

m-chloroaniline, 3.19 g (0.025mole) and diphenylamine, 4.23 g (0.025mole) were added in 100 mL 0.5 N HCl with continuous stirring. A precooled solution of 14.0 g ammonium persulphate dissolved in 50 mL 0.05 N HCl was added. The reaction was allowed to proceed for 4 hours and the mixture was kept at room temperature over night. A bluish green solid was obtained. The solution was filtered

and washed with distilled water. The precipitate was dried in an oven at 60 °C for 24 hours. Composite of 0.2g of TiO<sub>2</sub>/ZnO with copolymer were prepared with same procedure as copolymer was prepared. The yields of 3clpdpa, 3clpdpa/TiO<sub>2</sub> hybrid, 3clpdpa/ZnO hybrid were 4.2 g, 4.32 g and 4.31 g, respectively. Predicted structure of copolymer of diphenylamine and m-chloroaniline is shown in Fig. 1c.

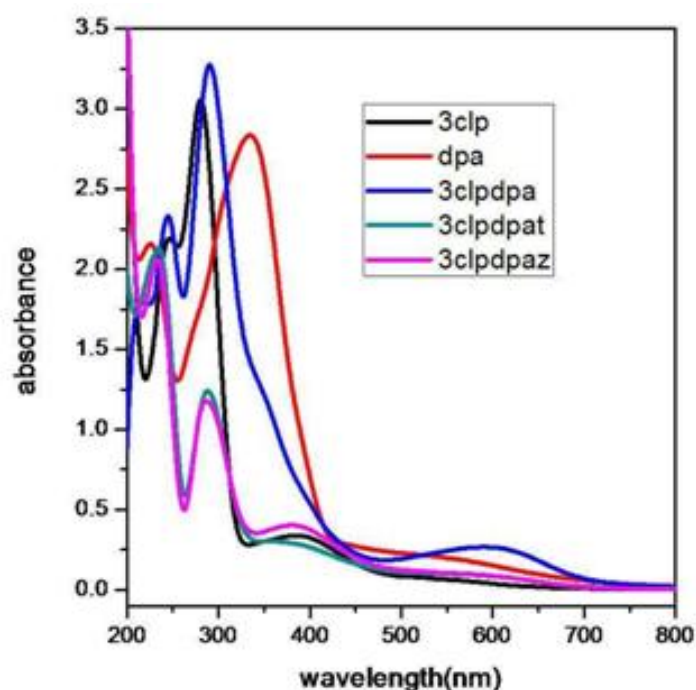
### 3. RESULT AND DISCUSSION

#### 3.1. IR spectroscopy

When ammonium persulphate is added to the reaction system, polymerization proceeds initially on the surface of TiO<sub>2</sub>/ZnO particles. The characteristics bands around 3200 cm<sup>-1</sup> to 3400 cm<sup>-1</sup> is due to  $\mu$  (N-H) stretching. The bands around 1575 cm<sup>-1</sup> were the characteristic bands of nitrogen quinone (Q) structure, the bands around 1500 cm<sup>-1</sup> related to benzene ring (B). The bands around 1300 cm<sup>-1</sup> was assigned to C-N stretching vibration. The spectra of copolymer and its composites exhibit a fairly intense absorption at 772 cm<sup>-1</sup> to 775 cm<sup>-1</sup> due to characteristic C-Cl stretching, it occurs as a strong absorption at 7.76 cm<sup>-1</sup> in the monomer and indicate the presence of chloroaniline units in the in copolymer and its composites. The intense C-H out of plane bending vibration of the 1,3,4-trisubstituted benzene rings appear around 8.30 cm<sup>-1</sup> and 8.75 cm<sup>-1</sup> indicates that the monomers in the copolymers in the copolymers were bonded head to tail in a agreement with expected structure.

#### 3.2. UV-Visible Spectroscopy

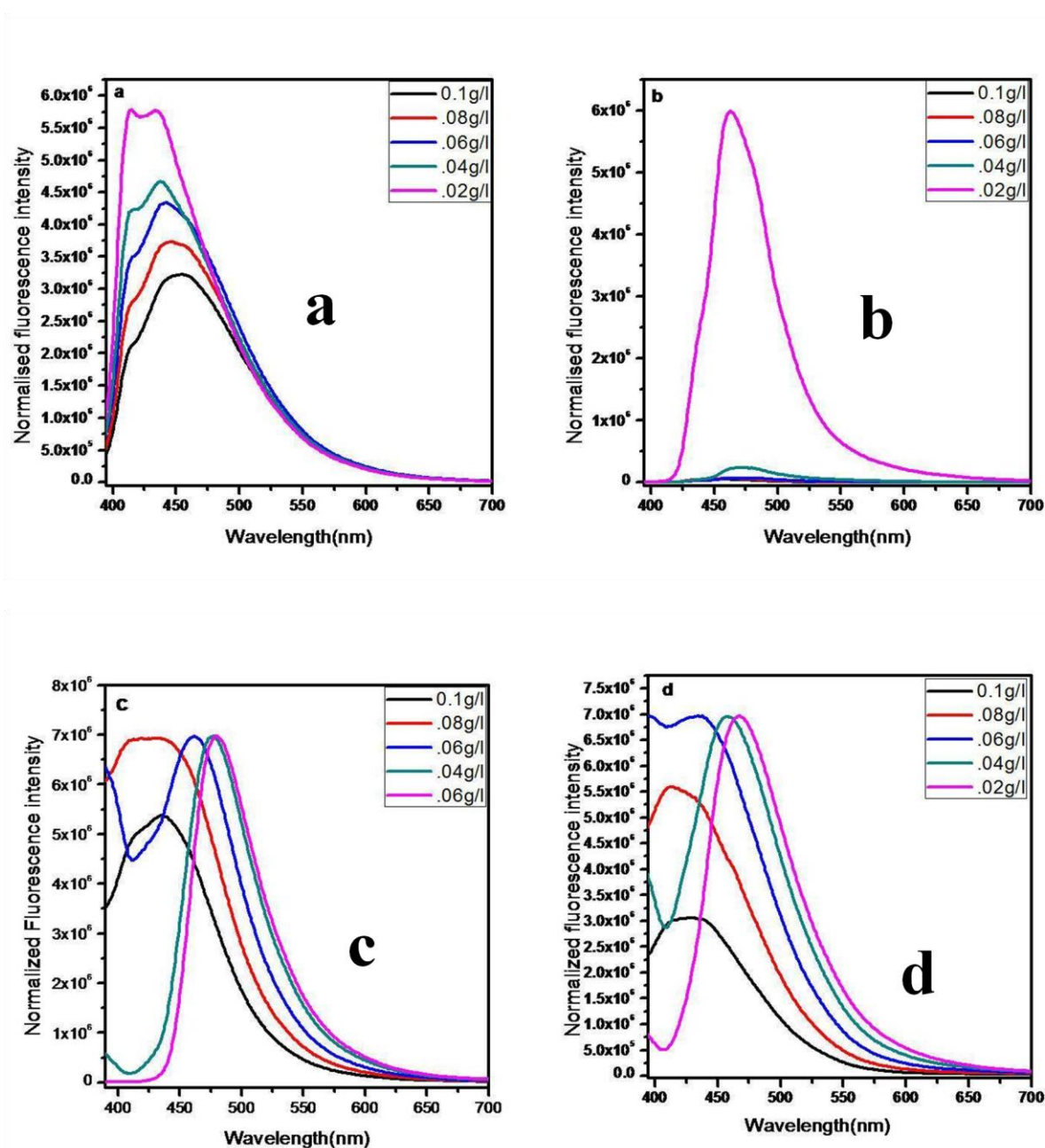
UV-Visible are helpful not only in identifying the nanomaterials but also the extent of conjugation in conducting polymers. Electronic spectra of 3clp, dpa, copolymer of diphenylamine and m-chloroaniline and composite of copolymer have taken in DMSO. UV-visible spectra of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpaz are shown in Fig. 2. The polymers and composites of their copolymer show two absorption bands. The intensities of both band of all samples decreases with decreasing concentration of solution. The first absorption band of  $\pi \rightarrow \pi^*$  transition has appeared at 242-349 nm, is assigned to the  $\pi \rightarrow \pi^*$  transition of the benzenoid ring and it is related to the extent of conjugation between the adjacent phenyl rings in the polymer/copolymer chain. The absorption band located at 539-596 nm is attributed to the quinoid ring [9,12]. It is sensitive to overall oxidation state of polymer. The intensity ratio of weak band ( $n \rightarrow \pi^*$ ) relative to strong band  $\pi \rightarrow \pi^*$  increases from copolymer to its composite. The lamda max. value of intense band ( $\pi \rightarrow \pi^*$ ) at (283 nm) of copolymer is in between the lamda max. value of 3clp (242 nm) and dpa (349 nm). It indicates that copolymer is more conjugated than 3clp and less conjugated than dpa.



**Fig. 2** UV-visible spectra of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpaz

### 3.3. Fluorescence studies

The fluorescence spectra of 3clp, dpa, 3clpdp, 3clpdpat and 3clpdpaz on different concentration are shown in Fig. 3. In Fig. 3 the intensity of fluorescence is plotted against wavelength for various polymer concentrations from Fig. (a-e) and the intensity of absorbance is also plotted against wavelength for same compound at various concentration from Fig. (f-j). Plots (a-e) are families of curves of fluorescence of 3clp, dpa, 3clpdp, 3clpdpat and 3clpdpaz, respectively. Plots (f-j) are families of curves of UV-visible spectra of 3clp, dpa, 3clpdp, 3clpdpat and 3clpdpaz respectively. Fig. 3 shows fluorescence of polymers, copolymer and hybrids of copolymer. Plots of fluorescence intensity verses concentration of 3clp, dpa, 3clpdp, 3clpdpat and 3clpdpaz (a-e) respectively are shown in Fig. 4. Composites of copolymer have enhanced fluorescence intensity. Fig. 5 (a-c) show the greenish blue and yellow color fluorescence of poly(m-chloroaniline), when excited by violet and blue laser light, respectively. Fig. 5 (d, e) show the greenish blue and light yellow color fluorescence of polydiphenylamine, when excited by violet and blue laser light, respectively. Fig. 5 (f) show the greenish blue color fluorescence of poly(m-chloroaniline), when excited by violet laser light. Fig. 5 (g, h) show the orange and yellow color fluorescence of poly(m-chloroaniline) in when excited by violet laser light at different concentration.



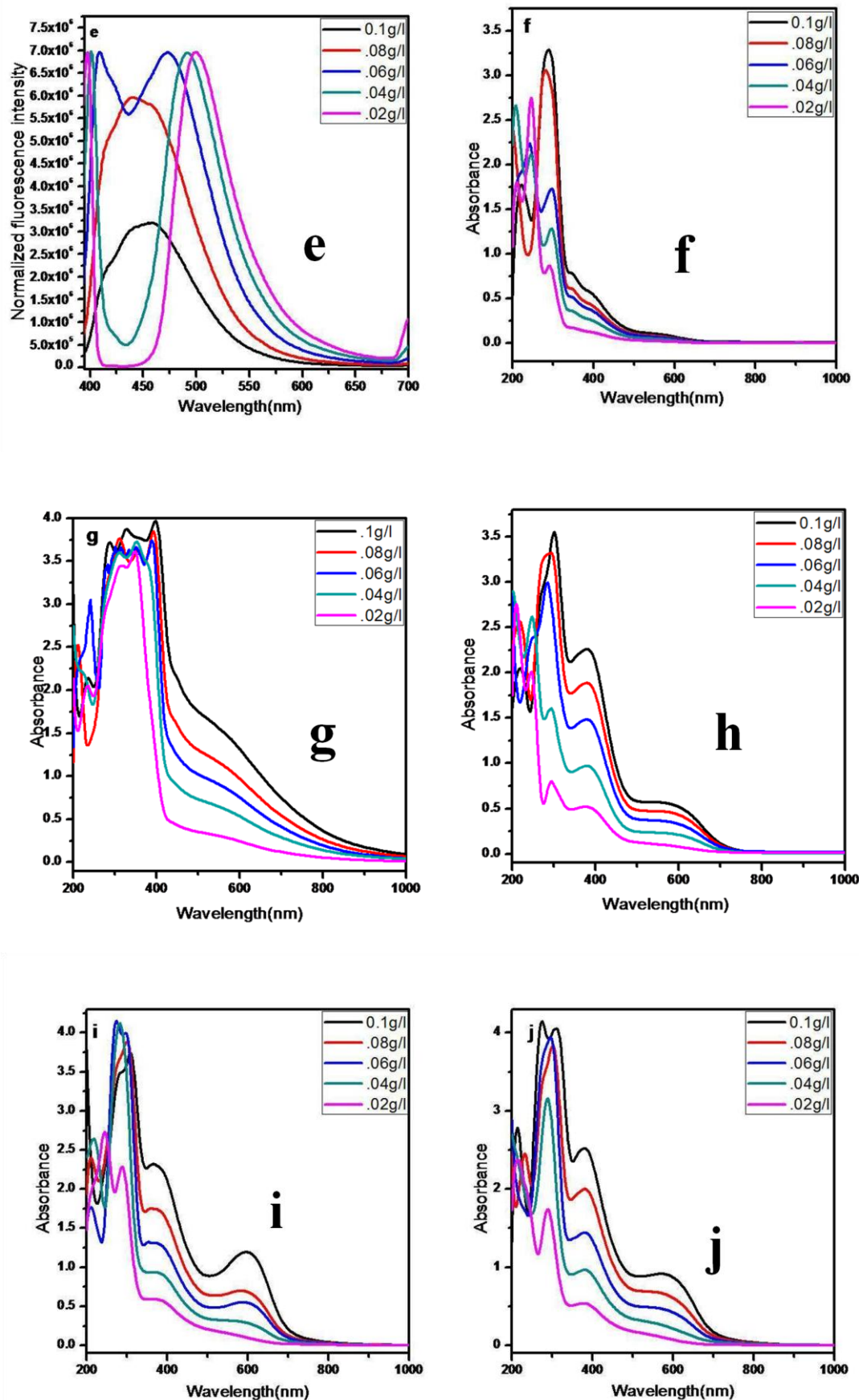
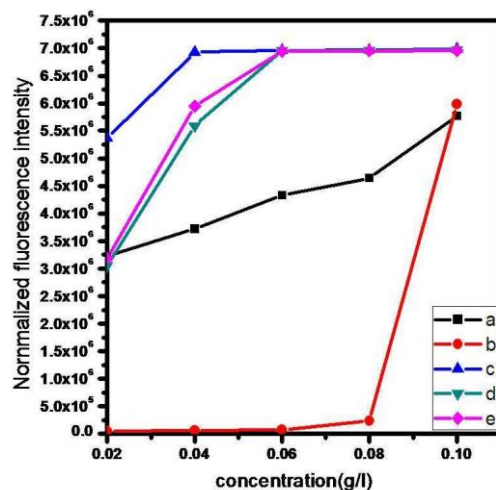
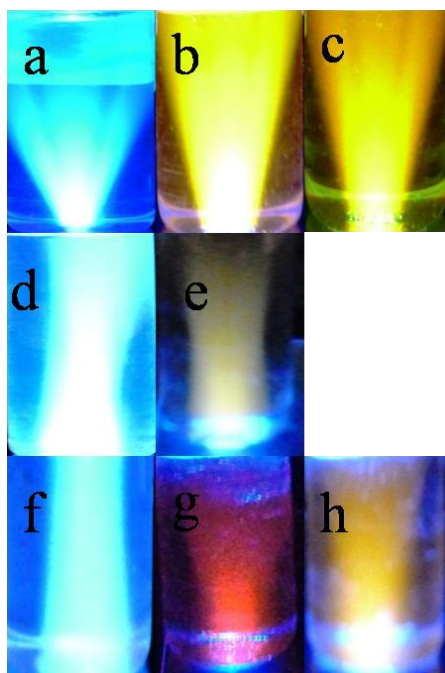


Fig. 3 Emission spectra (a to e) and Uv-visible (f to j) spectra of 3clp, dpa, 3clpdp, 3clpdpat and 3clpdpaz respectively for various concentrations.



**Fig. 4** Plot of fluorescence intensity versus concentration of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpez (a to e) respectively



**Fig. 5** (a-c) show fluorescence of poly(m-chloroaniline), (d-e) show fluorescence of polydiphenylamine and (g-h) show fluorescence of copolymer of m-chloroaniline and diphenylamine in different laser light.

### 3.4. Thermogravimetric analysis

Thermal degradation patterns of the poly(m-chloroaniline), Polydiphenylamine, copolymer of m-chloroaniline and diphenylamine and composites of copolymer with  $\text{TiO}_2$  and  $\text{ZnO}$  have been displayed in Fig. 6. 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpez could undergo a three-stage decomposition pattern. The first stage being weight loss, starting from room temperature to  $100^\circ\text{C}$  corresponds to a loss of water molecules/moisture present in the polymer. The second stage loss from  $100$  to  $350^\circ\text{C}$  is associated with a loss of dopant ion from the polymer matrix (dedoping). However, the weight loss after  $350^\circ\text{C}$  is due to degradation and decomposition of the polymer after the loss of dopant ion. 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpez shows weight loss 21%, 9%, 24%, 25%, 35% respectively from  $100^\circ\text{C}$  to  $350^\circ\text{C}$ . The total weight loss upto  $600^\circ\text{C}$  of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpez are 49%, 37%, 46%, 47%, 53% respectively. It indicates that thermal stability of copolymer (3clpdpa) is less than of that dpa and more than 3clp. Thermal stability of copolymer decreases from copolymer to its composites. The reason of temperature drop would be explained by the fact a strong interaction at the interface of nano- $\text{TiO}_2/\text{ZnO}$  and 3clpdpa weakens the interaction force of 3clpdpa interchains and helps thermal decomposition of 3clpdpa in the composite [14].

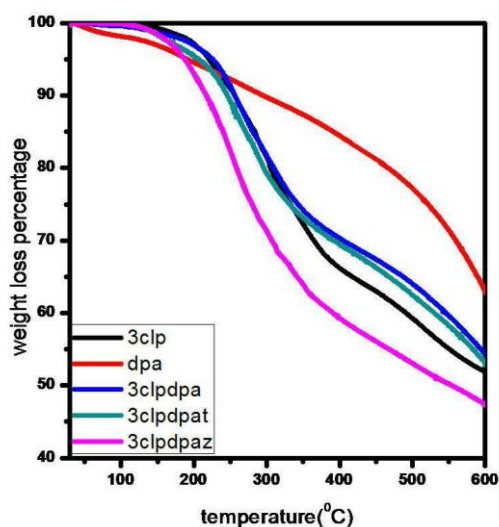
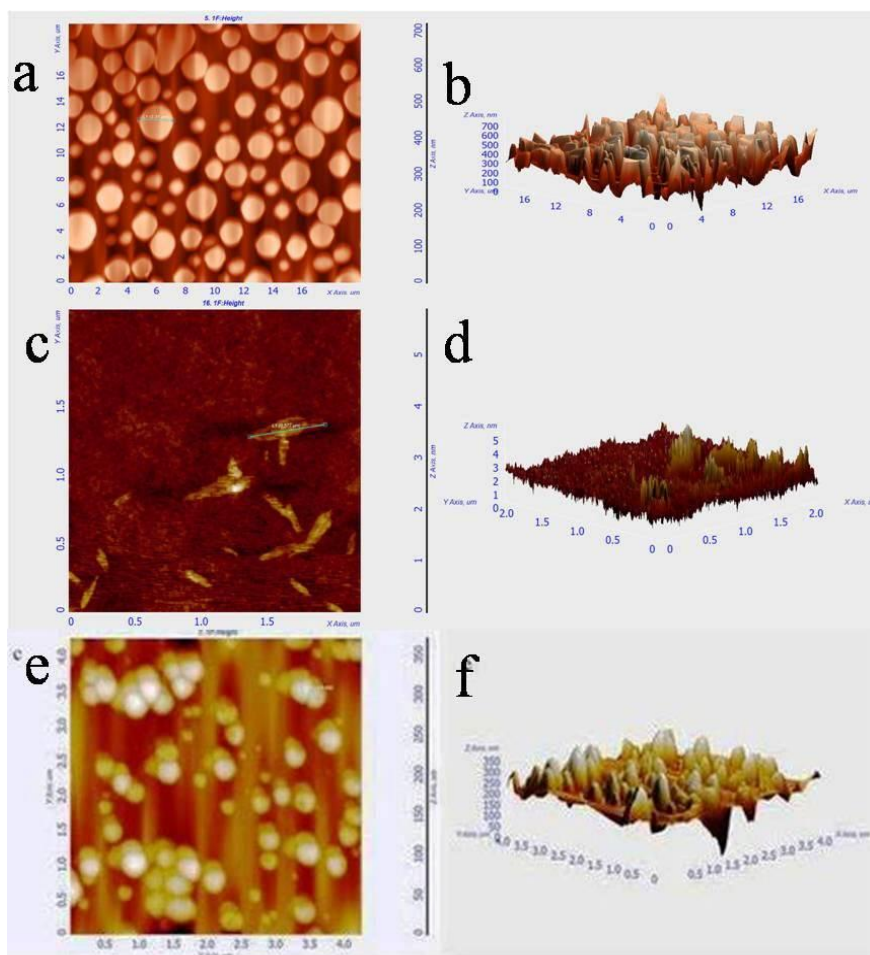
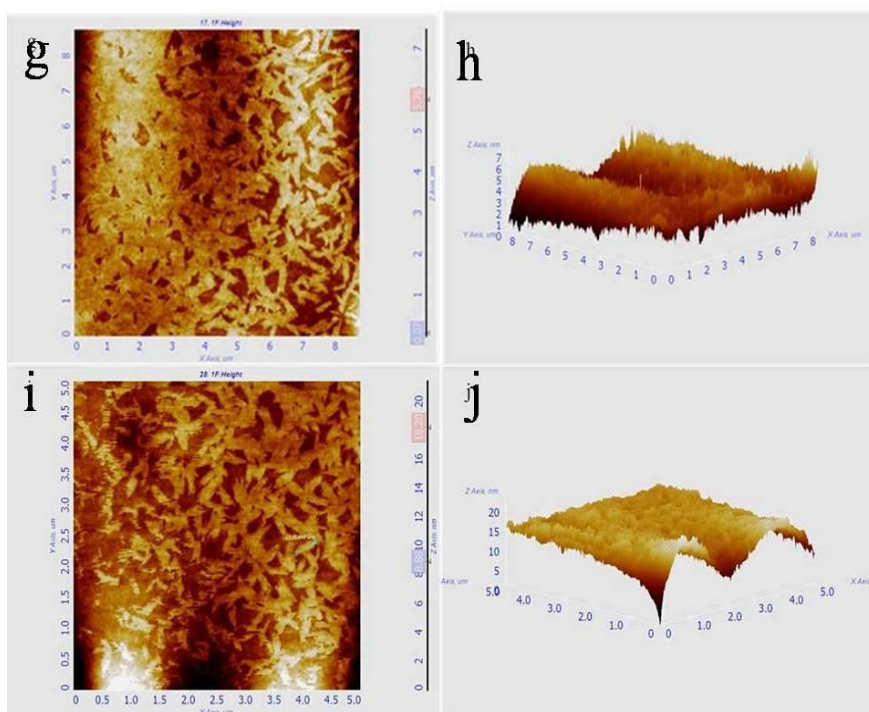


Fig. 6 TGA curves of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpaz

### 3.5. Atomic force microscopy (AFM)

The average size, average diameter, RMS roughness, peak to peak roughness and roughness average value of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpaz are given in table 1. The 2D and 3D images of 3clp, dpa, 3clpdpa, 3clpdpat and 3clpdpaz are given below. The average size from copolymer to composite increases due to formation of core shell structure. Fig. 7 shows that 2D image of 3clp has spherical shape particles, 2D image of dpa has angular leaf shape particles, 2D image of 3clpdpa has heart shape particles, 3clpdpat and 3clpdpaz have leaf shape.





**Fig. 7** (a, b) shows the 2D and 3D image of 3clp, (c, d) shows the 2D and 3D image of dpa, (e, f) shows the 2D and 3D image of 3clpdpa, (g, h) shows the 2D and 3D image of 3clpdpat, (i, j) shows the 2D and 3D image of 3clpdpaz.

**Table 1.** Table present RMS Roughness, peak to peak roughness, roughness average, average diameter and average size of 3clp, dpa, 3clpdpa, 3clpdpat, 3clpdpaz.

Sample characteristics	3clp (nm)	3clpdpa (nm)	3clpdpa (nm)	3clpdpat (nm)	3clpdpaz (nm)
RMS Roughness	120	0.483	40	0.83	1.48
Peak to peak roughness	706	5.8	369	7.46	21
Roughness average	105	0.339	29	0.66	1.08
Average diameter	2828	271	778	1212	1362
Average size	1605	128	433	482	566

#### 4. CONCLUSIONS

Polymers, copolymer and its composites have been synthesized, characterized, thermal, morphological and optical properties have been studied. The fluorescence spectra of polymers, copolymer and its composites were determined. The emission were related to their concentration and found to be aggregation caused quenching type fluorescence. The designed copolymer and composites of copolymer have enhanced fluorescence. The increased enhanced fluorescence may due to chloro atom present on chain in copolymer and its composites. Chloro atom decreases aggregation due to which fluorescence increases. Polymers and its copolymer emit different color fluorescence in different color laser light. The polymers, copolymer and its composites may serve as potential application in biological cell imaging.

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