

## Poly- thiophene-co-pyrrole with varying monomer concentrations: Synthesis, characterization and Photophysical Property Analysis

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### Abstract

Synthesis, characterization and photophysical property of the poly (thiophene-co-pyrrole) has been reported in this article. The objective was to make deep blue emitter of low cost to meet the high demand. The copolymer was synthesized using a modified Cationic Surfactant Assisted Polymerization technique (CSAP). A head to tail (HT) configuration was dominantly obtained as confirmed from <sup>1</sup>H NMR study. The crystallinity varied with the content of pyrrole-high pyrrole content induced higher crystallinity. For the pyrrole containing copolymer, the percent crystallinity was 33.1 % as determined from X-ray diffraction study. A distinct variation in molecular size and size distribution was also noted among the copolymers. Photophysical study showed that highest proportion of pyrrole induced deep blue emission thus it can act as a potential source for deep blue emitter in future.

### Keywords:

Poly- thiophene-co-pyrrole;  
Crystallinity;  
Deep blue emission.

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### 1. Introduction

High energy consumption and low efficiency is the major problem of the conventional lighting system [1-3]. Efficiency of incandescent bulb is only 5% [4-5] and that of fluorescent bulb is 20% [6]. During the last decade, or so a radical change has come in the field of display technology though the innovation of organic and polymeric light emitting diodes, abbreviated as OLED and PLED respectively [7-8]. A LED is 50% more efficient than a fluorescent lamp [9-10]. However, its poor lifetime and high cost of production hinders its

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wide scale commercialisation. Among the three primary colours PLEDs with red and green emission possesses sufficient efficiency and lifetime for wide scale commercialisation while an efficient blue emitter is still to be developed on commercial scale. Recently 9, 9-disubstituted polyfluorene have drawn much attention as an efficient blue emitter [11-12], however, it is still to be investigated in much detail before it can be reckoned as an important blue emitter for commercial use.

Polythiophene has been a blue emitter known for long but because of its low quantum yield, it has never been discussed with much importance. Instead various derivatives of polythiophene has gained importance due to a substantial improvement in fluorescent quantum yield [13]. By changing the substantial pattern both colour and intensity can be tuned from blue to deep red.

In this study we have synthesized copolymers of thiophene and pyrrole to develop a cost effective, efficient blue emitter compound. The copolymers were synthesized from a modified Cationic Surfactant Assisted Polymerization using different mass proportions of thiophene and pyrrole. Compared with expensive blue emitters synthesized from various expensive monomers [14-15], our product is cheaper primarily due to lower monomer cost. The copolymers were characterized and finally analyzed for photoemission property. Thiophene in conjunction with pyrrole heitherto showed deep blue emission especially when the proportion of pyrrole was increased. Detailed explanation has been provided during discussion of the results in the subsequent sections.

## 2. Experimental

### 2.1. Reagents and Solvents

Thiophene (99% pure) and pyrrole (99%) were purchased from Sigma Aldrich Chemical Company, USA. The monomer was distilled under vacuum before polymerization. Cetyltrimethyl ammonium bromide (CTAB) of molecular weight 336.4 g/mol was purchased from Lobachemie India Ltd., Mumbai, India. Triethanol amine (TEA), ammonium persulphate (APS), deionized water (DI Water) and N, N' dimethyl sulphoxide (DMSO) of standard laboratory grades were purchased from Merck, India Ltd, Mumbai, India. The reagents were used without further modification.

### 2.2. Cationic Surfactant Assisted Polymerization (CSAP) of thiophene and pyrrole:

A modified CSAP technique was used for the synthesis, as already mentioned. A three necked round bottom flask of 500 ml capacity was used as a reactor for the process. In a typical batch, 2.06 g CTAB was dissolved in 30 ml DI water and 2.5 ml thiophene and 4.68 g TEA were added successively and the whole liquid mass was sonicated for 30 minutes for homogenization. Subsequently, the reactor was heated to 60°C and 8.26 g APS (Thiophene to APS mole ratio was 1: 4), dissolved in 20 ml DI water, was added drop wise in the reactor for 15 min. Then pyrrole was added drop wise. The batch volume was close to 50 ml. The reactants were allowed to react for 12 hrs under slow stirring. The heating was stopped after 12 hrs and the reacted mass was allowed to cool under ambient condition. After 24 hrs, the black colored mass was recovered through centrifugation (Remi 8C, 5500 rpm, 30 min). The black copolymer settled down in the centrifuge tube. The residue was separated and washed three times, first with methanol (AR grade) and then with DI water and then finally dried in air oven (S. C. Dey and Company, Kolkata, India) at 60°C for 24 hrs. The whole process was repeated five times by varying the monomer concentration to check the viability. The air dried copolymer was characterized using different techniques. The photoluminescence (PL) was studied by dissolving the copolymer in DMSO [16].

### 2.3. Characterization of PT

Microstructure of the copolymer was studied using a Fourier Transform Infrared spectrophotometer (FTIR, Shimadzu IR Affinity-I 8000) and <sup>1</sup>H Nuclear Magnetic Resonance (NMR) (Bruker, Germany) respectively. Infra red spectroscopic analysis was done between 400 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. An average of 120 scans was represented for analysis. The <sup>1</sup>H NMR spectroscopy was done using deuterated DMSO as solvent with an external field strength of 500 MHz. The electronic transition in the copolymer was determined using an ultraviolet (UV) spectrophotometer, model Lambda 25, procured from Perkin Elmer, USA. The sample was analyzed using DMSO as the solvent. The hydrodynamic size (diameter) of the copolymer was measured from a dynamic light scattering (DLS) instrument, supplied by Malvern, USA. The analysis was done after dispersing the samples in DMSO as well. The net crystallinity of the copolymer was studied in powder form in a wide angle X-ray diffractometer (Xperto-PANAnalytical, USA) between the crystal reflection angle of 0 to 40°. The crystallinity (%) was calculated from the diffractogram using Equation 1.

$$\text{Crystallinity (\%)} = \frac{I_c}{I_a + I_c} * 100 \text{-----(1)}$$

Where,  $I_c$  denoted the intensity of the crystalline peak and  $I_a$  denoted the intensity of the amorphous halo. Analysis was done using a CuK $\alpha$  X- ray source ( $\lambda = 1.54\text{\AA}$ ) and scanning was conducted at a speed of 1°/min.

### 2.4. Studies on photoluminescence (PL) characteristics

The steady state PL measurement was carried out by using a spectrophotometer (Edinburg FLS 980) with xenon lamp fitted as the source of photon for excitation. The emission spectra were recorded by dissolving

the copolymer in DMSO at an excitation frequency of 377 nm. The fluorescent quantum yield was calculated from Equation 2 [17].

$$\Phi_f = \frac{\int_{\lambda_{em1}}^{\lambda_{em2}} \frac{[I_x(\lambda_{em}) - I_b(\lambda_{em})]}{s(\lambda_{em})} \lambda_{em} d\lambda_{em}}{\int_{\lambda_{ex}-\Delta\lambda}^{\lambda_{ex}+\Delta\lambda} \frac{[I_b(\lambda_{ex}) - I_x(\lambda_{ex})]}{s(\lambda_{ex})} \lambda_{ex} d\lambda_{ex}} = \frac{N_{em}}{N_{abs}} \quad (2)$$

Where,  $N_{em}$  is the total number of emitted photons which was obtained upon an integration of the blank-corrected ( $I_b(\lambda_{em})$ ) and the spectrally corrected ( $I_x(\lambda_{em})$ ) emission spectrum of the copolymer.  $N_{abs}$  is the number of absorbed photons which followed from the integrated difference between the excitation light resulting from measurements with the blank ( $I_b(\lambda_{ex})$ ) and the sample ( $I_x(\lambda_{ex})$ ).

### 3. Results and Discussion

#### 3.1. Calculation of yield:

Three different compositions with varying monomer mass compositions were synthesized. Composition of each batch is reported in Table 1 using Equation 3 [18].

$$\text{Yield (\%)} = \frac{\text{Mass of the product}}{\text{Total mass of the reactant}} * 100 \quad (3)$$

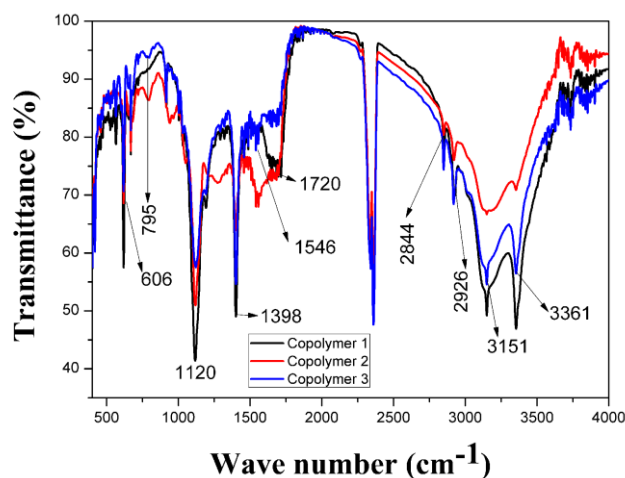
In each case, the yield was found to be different. It was seen that with increasing concentration of pyrrole the yield gradually went down. It was probably due to slower reactivity of pyrrole than thiophene in the system.

**Table 1: Copolymer yield and their percent crystallinity**

Composition	Thiophene (Mass %)	Pyrrole (Mass %)	Yield (%)	Crystallinity (%)
1	80	20	88	26.6
2	50	50	84	28
3	20	80	86	33.1

#### 3.2. Analysis of microstructure and morphology

FTIR spectra of all the copolymers are shown in Figure 1. For copolymer-1 the stretching vibration of alkyl C-H was observed at 2926 and 2844  $\text{cm}^{-1}$  while the bending (in plane) vibration was observed at 1120  $\text{cm}^{-1}$  respectively, for the five membered rings of both thiophene and pyrrole. The stretching vibration of the aromatic C=C was observed between 1397 and 1720  $\text{cm}^{-1}$ . The sharp peak at 795  $\text{cm}^{-1}$  denoted the C-S stretching of the thiophene. The copolymers existed as polarons and bipolarons. A sharp peak at 951  $\text{cm}^{-1}$  denoted the charge transfer effect between those two entities [19]. The other sharp peak at 3354  $\text{cm}^{-1}$  denoted stretching vibration of N-H in pyrrole. Peaks between 611 and 951  $\text{cm}^{-1}$  denoted the C-H in plane and out of plane deformations in pyrrole. Peak at 3151  $\text{cm}^{-1}$  denoted C-H symmetric stretching vibration in  $-\text{CH}_2$  aliphatic unit. It was also merged with the stretching vibration of N-H in pyrrole. A sharp peak at 2356  $\text{cm}^{-1}$  was due to the stretching vibration of  $\text{C}\equiv\text{N}$ . In case of copolymer-2 most of the peaks slightly changed their position due to the variation of monomer concentrations.



**Figure 1: FTIR spectrum of the copolymers**

The stretching vibration of alkyl C-H bonds was slightly shifted to 2923 and 2849  $\text{cm}^{-1}$  while the bending (in plane) vibration was observed at 1115  $\text{cm}^{-1}$  respectively. The ring stretching vibration of the aromatic C=C was observed between 1390 and 1720  $\text{cm}^{-1}$ . The peak at 3326  $\text{cm}^{-1}$  denoted N-H stretching vibration in pyrrole unit. The peak of C $\equiv$ N stretching was found to be at 2349  $\text{cm}^{-1}$ . Peaks between 616 and 912  $\text{cm}^{-1}$  denoted C-H in plane and out of plane deformations in pyrrole unit.

On the otherhand, in copolymer-3 due to maximum content of pyrrole, most of the peaks were closer to that of the pyrrole unit [20]. The N-H stretching was shifted to 2956  $\text{cm}^{-1}$  and the C $\equiv$ N stretching was observed at 2346  $\text{cm}^{-1}$ . Peaks between 616 and 1107  $\text{cm}^{-1}$  now denoted the C-H in plane and out of plane deformations in pyrrole unit. The stretching vibration of the aromatic C=C was observed between 1406 to 1697  $\text{cm}^{-1}$ . The peak at 1107  $\text{cm}^{-1}$  denoted the C-H bending vibration of thiophene. Presence of both the monomers along with their concentration changes were all well delineated in the FTIR spectrum.

NMR study of copolymer-3 was carried out to confirm the microstructure. The spectrum is showed in Figure 2. The aromatic proton of the pyrrole unit was observed at 6.920 ppm while the signals between 5.5-5.6 ppm denoted the N-H node. The signal at 7.25 ppm was for the proton present in thiophene unit. There were several peaks between 1.124 ppm and 1.782 ppm which were due to HH interaction while the peaks between 3.405 and 3.582 ppm was due to HT interaction. Relatively higher intensity of the former indicates presence of more HT bending then HH bending. The spectrum thus revealed presence of both the configuration in the copolymer (in different proportion though) due to random yet slow reaction [21].

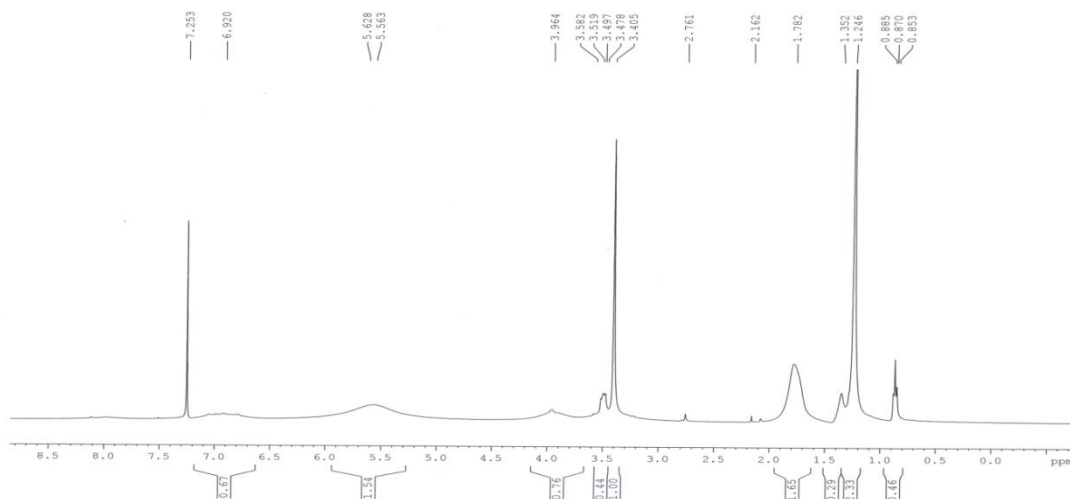


Figure 2: NMR spectrum of copolymer-3

The UV spectrum of copolymer-3 in Figure showed 3 a blue shift with two absorption maxima. Two transitions were expected  $\pi$ - $\pi^*$  and n- $\pi^*$ , respectively.

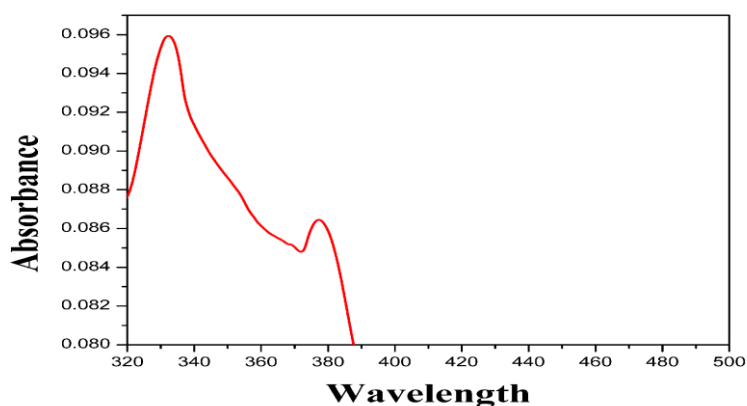


Figure 3: UV absorption spectrum of copolymer-3

The blue shift was due to electromeric effect of the compound and interaction with pyrrole while the second transition was due to  $\pi-\pi^*$  in the thiophene. The wide angle X-ray diffractogram of the model copolymer, copolymer-3 is shown in Figure 4. The net crystallinity was calculated and found to be 33.1 %. For other grades, the crystallinity data are reported in Table 1. The percent crystallinity was found to be proportional with the content of pyrrole-higher proportion led to higher crystallinity and vice-versa.

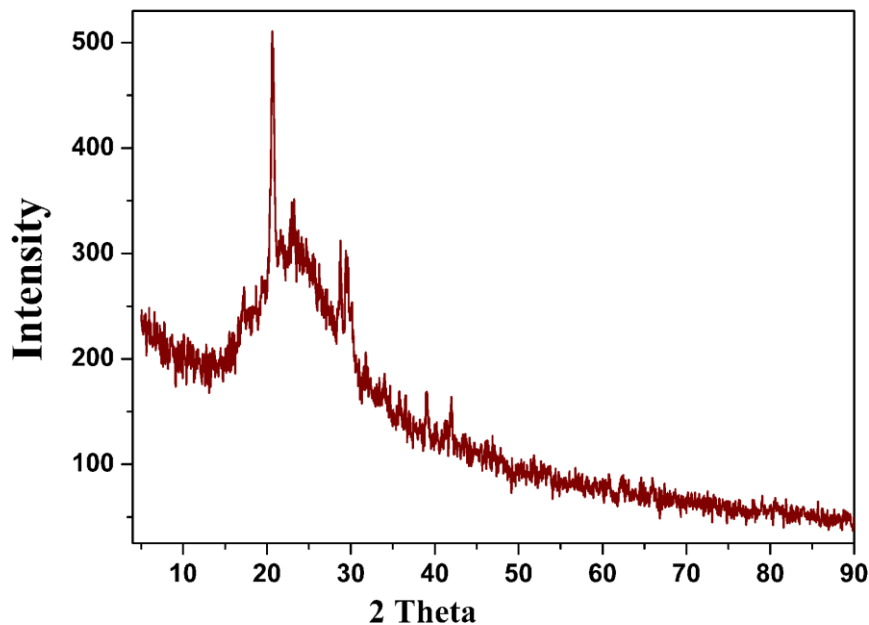


Figure 4: XRD spectrum of copolymer-3

### 3.3. DLS Study:

The particle size distribution of the copolymer 1, 2 and 3 are displayed in Figure 5. Copolymer-3 showed the narrowest distribution with an average size of 394 nm while copolymer-2 the widest one with an average size of 697 nm. It seemed like copolymer-3 was more folded while copolymer-2 was least. Copolymer-1 showed an intermediate size of the folds.

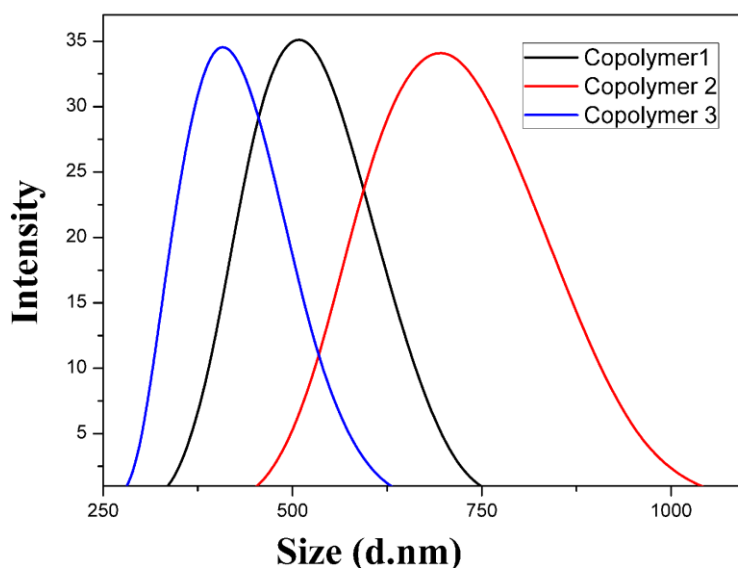
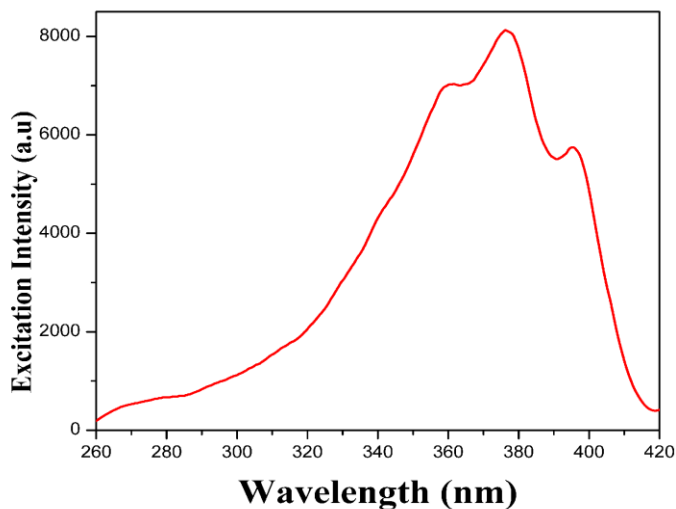


Figure 5: DLS spectrum of copolymer-3

### 3.4. PL property of the copolymer:

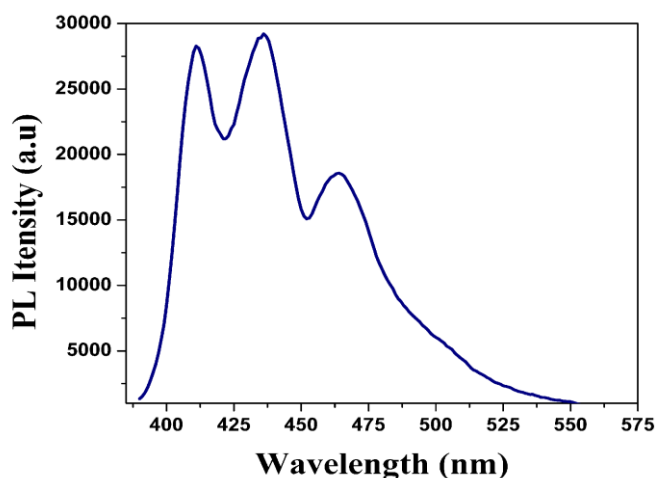
The absolute PL efficiency measured in an integrating sphere at room temperature was found to be at 377 nm of copolymer-3. Thus, the excitation was uniformly set at 377 nm for analysing the emission behaviour of the

copolymer. The excitation spectrum is shown in Figure 6. The emission spectrum is shown in Figure 7. Emission spectrum of only copolymer-3 was plotted for analysis.



**Figure 6: Excitation spectrum of copolymer-3**

It (copolymer-3) showed three different peaks at 412, 436 nm and 464 nm respectively, all were in the blue region with a well vibronic feature. On irradiation with UV A (381 nm) it displayed a deep blue colour. An increase in pyrrole concentration in the copolymer, the blue color gradually tuned into deep blue. Out of the three emission bands, the first two lied well inside the blue region while the third one was mere at the threshold. The emission peak at higher region was due to  $n-\pi^*$  and  $\pi^*-\pi$  transitions and for that are in the threshold was due to charge transfer action between the solvent DMSO and the copolymer [22].



**Figure 7: Emission spectrum of copolymer-3**

In solid state there were intra as well as interchain interaction between the copolymer molecules and they remained in different configurations (different crystallinity) while in solution/dispersion. The same compounds were twisted and possibly existed in the most stabilized state because of the free rotation of the C-C bonds. Among the three emission peaks the weaker one was due to some structural defects such as presence isolated polarons. The tendency towards a blue shift in DMSO was because of a dipolar interaction between the DMSO molecule and aromatic ring of both thiophene and pyrrole. Being a polar solvent, DMSO easily percolated through its layer structure. With time the layer structure was broken and gained a strong attraction with the polymer chain. Thus the value does not change significantly even the monomer concentration was changed. The emission peak intensity was almost same in different copolymers because of almost similar energy level. Yet there was a huge difference in peak area under the curve at each composition. Due to the difference in peak area the colour changed with the copolymer composition. The parameter generally used to characterize the quality of the blue light is Commission International d'

Eclairage or CIE chromaticity diagram (Figure 8) [23]. The X, Y coordinate locates the intensity of the emission color in the diagram. According to the CIE diagram, the intensity coordinate was (0.16505, 0.10902) for copolymer-1 (Figure 8a), (0.15461, 0.06924) for copolymer-2 (Figure 8b) and (0.15397, 0.076628) for copolymer-3 (Figure 8c) respectively. The fluorescent quantum yield was very low i.e. around 8 %. It was clear from the focus that copolymer-3 was the strongest emitter of deep blue colour than the rest of the two compositions; primarily due to high crystallinity and narrow size distribution. The providing long path for electron hopping (more HT connectivity) along the molecular chain.

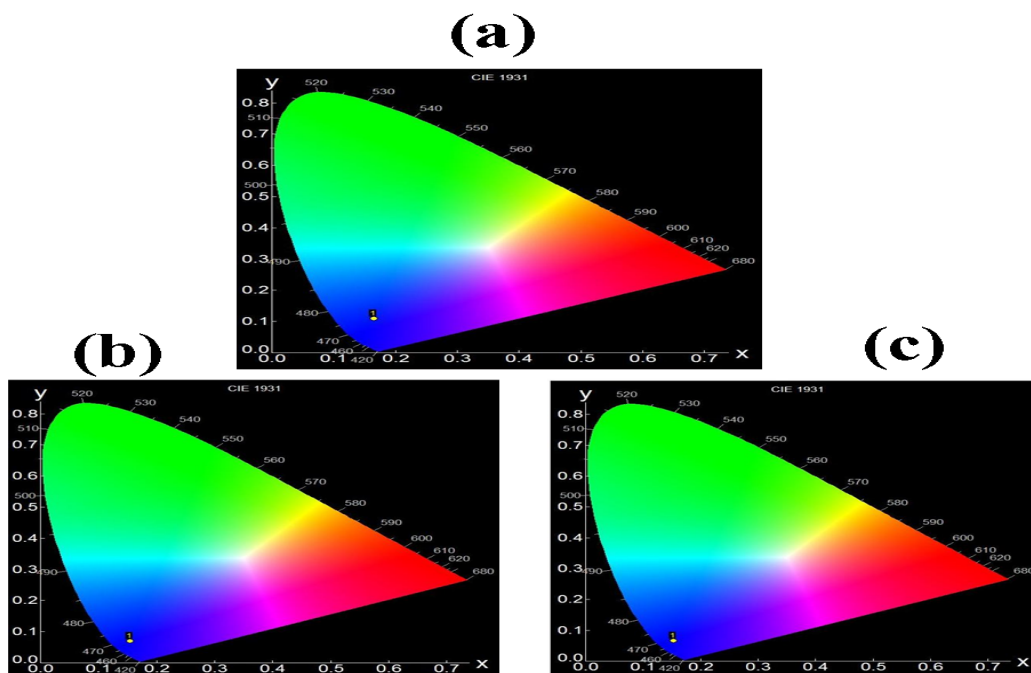


Figure 8: CIE diagram of the copolymers: (a) copolymer-1, (b) copolymer-2 and (c) copolymer-3.

#### 4. Conclusion:

In conclusion it can be said the modified CSAP was a handy process to synthesize cheap copolymers from thiophene and pyrrole for display application. Once formed, the molecular structure and the orientation were found to be dependent on the pyrrole concentration. Higher concentration of pyrrole in the copolymer was the key to produce a deep blue emission. The copolymer with high pyrrole content could be a cheap deep blue emitter and thus a scale up trial would be very interesting to have in near future.

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