

OPTO-ELECTRONIC PROPERTIES OF POLY (P-PHENYLENE VINYLENE) (PPV) INTERCALATED IN CdPS₃

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In this study Poly (p-phenylene vinylene) was successfully prepared and intercalated between the layers of Cadmium hexathiohypodiphosphates. Thermal analysis and Photoluminescence data confirmed that this polymer precursor intercalated in Cadmium hexathiohypodiphosphates were completely converted to poly (p-phenylenevinylene) upon heating. Intercalation of Potassium ion K⁺, Europium ion Eu⁺ and then poly (p-phenylenevinylene) into the layers of Cadmium hexathiohypodiphosphates was confirmed by X-rays diffraction pattern. The TGA results showed that Poly (p-phenylene vinylene) intercalated in Cadmium hexathiohypodiphosphates heated at 120°C (CPPV120) has more thermal stability as compared to pristine Poly (p-phenylene vinylene). To impart electrical conductivity to the insulating Poly (p-phenylene vinylene) , vapor doping technique was used. The samples showed the maximum conductivity of 1.81×10^{-4} S/cm for the Poly (p-phenylene vinylene) intercalated in Cadmium hexathiohypodiphosphates and heated at 120°C. The conductivity of completely converted PPV was observed in order of 10^{-7} S/cm which was increased by two orders of magnitude by doping. When the Poly (p-phenylene vinylene PPV is heated at different temperature its band gap decreases which in turn increases the conductivity. Appreciably high Photoluminescence in Poly (p-phenylene vinylene intercalated in Cadmium hexathiohypodiphosphates despite very small amount of Poly (p-phenylene vinylene in the composite along with high conductivity and enhanced thermal stability suggest that these materials are promising candidates for Light emitting diodes and other opto-electronic devices.

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1. Introduction

Poly(p-phenylene vinylene) PPV is a conjugated polymer, which become conductive by addition of electron donors or acceptors. [1, 2] There are several methods for the synthesis of PPV [3-5] but chemical synthesis is one of the easiest method. Photoluminescence (PL) from PPV and its derivative has been extensively studied due to their potential applications in Light emitting diode LEDs. As regards the applied aspects of PPV [6, 7, 8, and 9] has been developed for use in large-area luminous displays and back-lights for mobile phones, etc, the stability of PPV trapped in nanocomposite form is enhanced, and the microstructure offers the opportunity for stabilised biosensor electrode fabrication. In some nanocomposites containing inorganics and a conducting polymer, the units behave like nano-scale electrical components (p-n junctions) with the ability to convert solar energy into electricity [10, 11]. Another consequence of the molecular organisation in these materials is that the fluorescence efficiency of the conducting polymer appears to increase significantly [11].

Cadmium hexathiohypodiphosphates here termed as CdPS₃ have attracted much attention over the last 30 years because of their ability to form intercalation compounds with various inorganic and organic species [12].

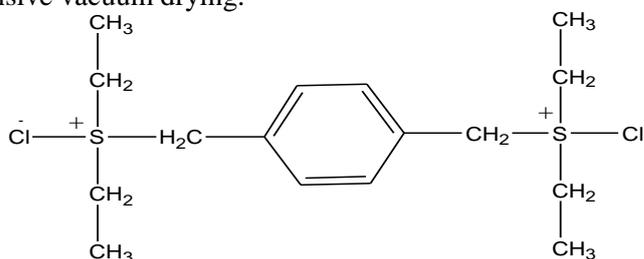
Insertion of ICPs in layered host materials results in a dramatic modification of the physical properties, which has led to various applications as nonlinear optical materials [13, 14] as magnetic materials [15, 16] as catalysts and as cathode materials in battery applications [17, 18]

Different synthetic approaches [19, 20] combining a variety of host [21] and guest molecules [22–25] have been developed. Ordering of guest molecules has been shown to occur in several cases [26, 27] Finding proof for vacancy ordering is much more difficult since vacancies can be traced spectroscopically only by indirect evidence [28] The insertion of specifically functionalized molecules may add some specific properties to some CdPS₃ host lattices. [29]

This manuscript describes work done to achieve high PL efficiencies by optimising the conversion of the prepolymer to the conjugated polymer PPV, in order to get the best conditions for the elimination process after intercalation into the layers of CdPS₃.

2. Experimental:

Synthesis of the monomer *p*-xylene-bis (diethyl-sulphonium chloride) is achieved by reacting α,α,α' -dichloro-*p*-xylene at a concentration of 0.75M with excess diethyl sulphide (2.25M) at 50°C in a methanol water (80:20) solution for 20h [30] This monomer (fig. 1) is purified by concentrating the reaction solution and precipitating the product in cold acetone (0°C), followed by filtration and extensive vacuum drying.



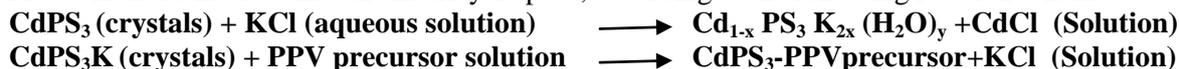
P-Xylene-bis(diethyl sulphonium chloride) monomer

Fig. 1. PPV monomer

There are several points concerning the quality of the polymer. For a ‘good’ polymer and consequently a stable device not only optimization of the conversion conditions is essential but also the purity of the prepolymer and the film formation process are crucial [31]. Other researchers have commented that oxygen might have a significant influence on the electrical and optical properties of PPV. One expects that oxygen might lead to carbonyl defects on the polymer chain, thus interrupting the conjugation. These defects can either be created via the synthesis of the prepolymer or during the conversion process. Several attempts have been made to reduce these problems. Hudson et al [32] reported results of detailed investigations of the conversion process where the prepolymer films had been converted under different gases. The best results were obtained with forming gas (85% N₂, 15% H₂): however, even under these extremely pure conditions, they observed a significantly carbonyl stretch band at 1690 cm⁻¹. This carbonyl acts as a quenching site for PL and strongly affects the photoluminescence life time.

An attempt has been made to intercalate PPV into the layers of CdPS₃ to study the PL efficiency and further evaluated by XRD, FT-IR, UV, spectroscopy and TGA techniques.

During the process of intercalation Cd⁺² ions are removed from the layers, leaving vacancies behind. The local charge of these vacancies is compensated by ionic guest species K⁺, Eu, and PPV which are inserted into the interlayer space, according to the following reaction scheme.



The samples are named as

1. As prepared Cd(PS₃)₂ (CdPS₃)
2. Cd_{1-x}PS₃K_x(H₂O)_y (CdPS₃K)
3. Cd_{1-x}PS₃Eu_x(H₂O)_y (CdPS₃Eu)
4. Cd_{1-x}PS₃PPV_xprecursor (H₂O)_y (CPPV)
5. Cd_{1-x}PS₃PPV_xprecursor (H₂O)_y heated at 80°C (CPPV 80)
6. Cd_{1-x}PS₃PPV_xprecursor (H₂O)_y crystals heated at 120°C for 8h (CPPV 120)

3. Results and discussion

XRD pattern of $\text{CdPS}_3\text{A}(\text{H}_2\text{O})_y$ [$\text{A}=\text{K}^+$, Eu^+ ions and PPV] is shown in Fig.2, the same space group as that of the host CdPS_3 is observed with the only change from the parent CdPS_3 structure being the expansion in the c-axis in K^+ , Eu^+ and PPV (Fig 2 b, c, d) intercalated CdPS_3 , along with the appearance of the broad peak showing amorphous nature of PPV in CPPV 120 compound (Fig 2 d). The lattice parameters a and b remains unchanged. The calculated and observed lattice parameters along with the d spacing are given in the table 1.

Complete intercalation ascertained by the shifting of $00l$ reflection to lower angle. Preparation of $\text{Cd}_{1-x}\text{PS}_3$ PPV is very slow. The more facile route was used by exchanging K^+ ions. Then ions of K^+ in $\text{Cd}_{1-x}\text{PS}_3 \text{K}_{2x}(\text{H}_2\text{O})_y$ were further exchanged by Eu and PPV subsequently causes to increase lattice spacing from 0.867 nm to 0.883 nm and 0.921 nm respectively.

Table 1 d spacing and conductivity of all samples

| Sample | | d.spacing (nm) | Conductivity (S/cm) |
|--|--------------------------|----------------|-----------------------|
| CdPS_3 | CdPS_3 | 0.622 | $\sim 10^{-10}$ |
| $\text{Cd}_{1-x}\text{PS}_3 \text{K}_{2x}(\text{H}_2\text{O})_y$ | CdPS_3K | 0.867 | $\sim 10^{-8}$ |
| $\text{Cd}_{1-x}\text{PS}_3 \text{Eu}(\text{H}_2\text{O})_y$ | CdPS_3Eu | 0.883 | $\sim 10^{-9}$ |
| $\text{Cd}_{1-x}\text{PS}_3 \text{PPV}(\text{H}_2\text{O})_y$ | CPPV precursor | 0.921 | 2.47×10^{-7} |
| PPV doped with I_2 | PPV I_2 | - | 3.4×10^{-5} |
| $\text{Cd}_{1-x}\text{PS}_3$ -PPV doped with I_2 | CPPV 120- I_2 | 0.911 | 1.81×10^{-4} |

PPV belongs to a class of conjugated polymers that become electrically conductive upon the addition of electron donors and acceptors. The electrical conductivity of PPV and CdPS_3 intercalated PPV (CPPV 120) was investigated by using a doping agent I_2 . The conductivity was measured by conventional 2probe method and was found to be enhanced by doping single crystal CdPS_3 intercalated with PPV by Iodine after heating it at 120°C for 8h. The crystals were immersed in a box having iodine for half an hour and than the conductivity were measured. The conductivities obtained for each sample are given in Table 1. Higher conductivity in Iodine doped intercalated PPV may be due to straightening of PPV chains and causing diffusion of dopant may be due to the easier diffusion of the dopant into the polymer matrix. The samples showed the maximum conductivity of $\sim 10^{-4}$ S/cm.

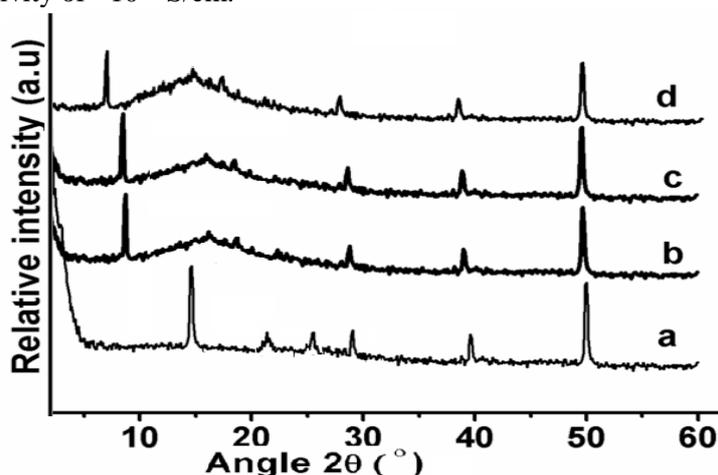


Fig. 2. XRD pattern of (a) CdPS_3 , (b) K intercalated, (c) Eu intercalated CdPS_3 and (d) PPV intercalated CdPS_3

The IR spectra of $\text{CdPS}_3\text{A}(\text{H}_2\text{O})_y$ [$\text{A}=\text{K}$, Eu and PPV] is shown in Fig.3 the spectra of intercalated compound show that the $\nu(\text{PS}_3)$ asymmetric stretching band which occurs at 570 cm^{-1} in pure CdPS_3 (Fig.3 a) is split into two components at 559 and 608 cm^{-1} . This splitting has been

observed in most intercalated compounds of metal thiophosphates and has been ascribed to the presence of interlamellar vacancies. [33] The intercalated compounds also show bands due to intercalated water at 3430 and 1617 cm^{-1} . The band at 3430 cm^{-1} is ascribed to the stretching vibration of OH group ν (OH) and the band near 1617 cm^{-1} to bending vibration of this group. The asymmetric stretching and bending vibrational frequencies observed are similar to that observed in ice [34] and for interlamellar water in mica type silicate clays [35]

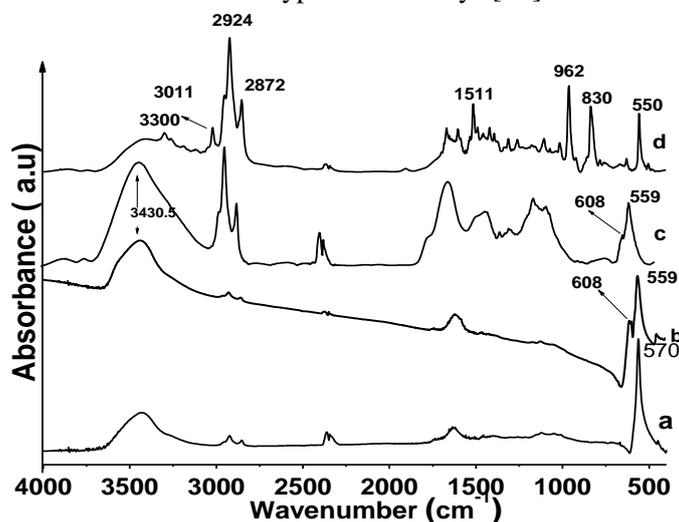


Fig. 3. FT-IR spectra of (a) CdPS₃, (b) K intercalated CdPS₃; (c) CdPS₃ intercalated with PPV precursor and (d) CdPS₃-PPV120.

UV-visible spectra were obtained for the pure polyelectrolyte films and partially eliminated films at different temperatures. The UV spectra for the clear, saturated film (fig.4) displayed three absorption bands with overlapping maxima associated with the phenyl group $\lambda=198$ and 229nm and the sulphonium group $\lambda= 265, 270$ and 276 nm³. As the sulphide was thermally eliminated, the absorption bands broadened and the new bands appeared at longer wavelengths at which point the UV spectrum showed a continuous absorption with an edge centred at 500 nm, indicative of a highly conjugated system (fig.4)

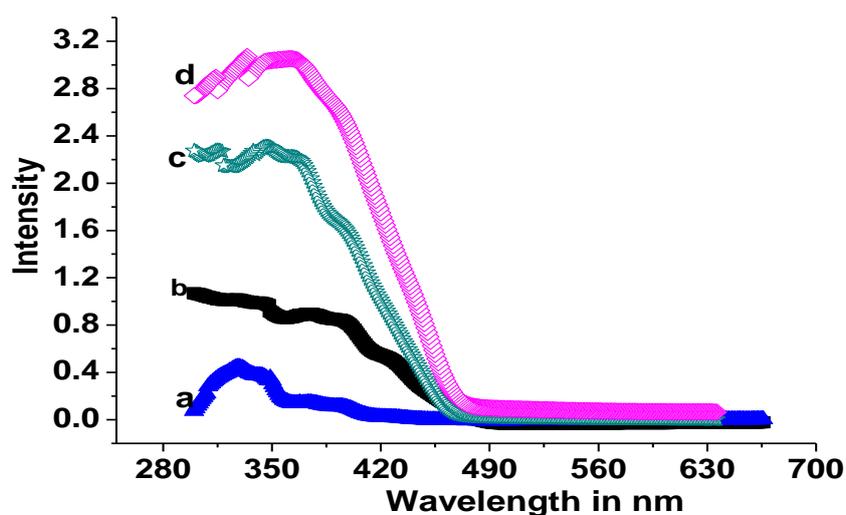


Fig. 4. UV-Visible spectra of PPV after pyrolysis of the precursor polymer at (a) 40°C, (b) 80°C, (c) 160°C and (d) 180°C.

Energy gap was calculated by manipulating absorption edge to zero absorption value and corresponding wavelength λ was estimated and by using formula $E = hc/\lambda$, where h is planks constant c is speed of light and λ is wavelength at zero absorption. As the temperature and time of the elimination increased, the energy gap decreased as shown in Table. 2

Table 2 Energy gap obtained from UV-Visible absorption spectra of PPV at different elimination conditions.

| Sample | Energy gap |
|---------------------------|------------|
| Free standing film of PPV | 3.1eV |
| PPV at 120°C | 2.82 eV |
| PPV at 180°C | 2.75 eV |
| PPV at 200°C | 2.43 eV |
| CPPV 120 | 2.85 eV |

UV-vis spectrum of CdPS₃ intercalated with PPV layers converted in vacuum at 120 °C is shown in figure 5 a. The absorption bands broadened and the new bands appeared at longer wavelengths at which point the UV spectrum showed a continuous absorption with an edge centred at 500 nm, as has been observed in pristine PPV heated at 120 °C which is as indicative of a highly conjugated system (fig.5 b). This result also confirmed that PPV is present in the layers of CdPS₃ in its original form and fully eliminated.

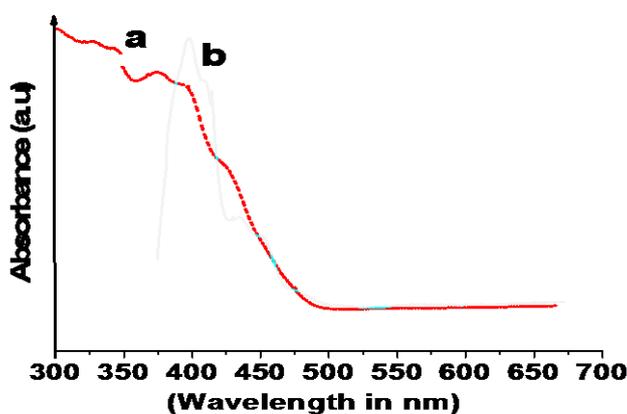


Fig. 5. UV-Vis spectra of (a) PPV heated at 120 and (b) CPPV120

Single crystals CdPS₃ intercalated with PPV were placed on quartz plates. The UV-visible absorption and photoluminescence spectra are shown in Figure 5 and 6 respectively. The main emission spectrum of PPV is located at 505 nm. The main band of PPV is shifted from 505 nm to 550 nm wavelength. Shoulder peak at 515 nm is also observed in CPPV 120 sample. This band has also been observed in many PPV/nanoparticles composites previously [36]. Two possible explanations can be proposed for this observation. First, energy of 515 nm may indicate that the short segment of PPV is involved in emission process. This explanation is agreement with UV and Raman results. The second process to be considered is the reduction of film thickness, which also given the emission at 515 nm [19], however this does not explain the shifts observed in UV-Vis and Raman spectra.

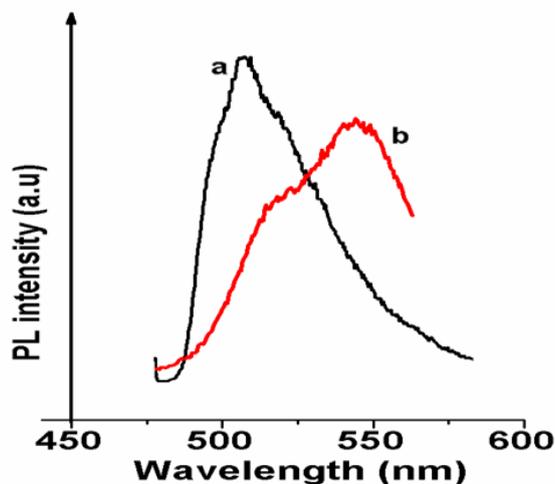


Fig. 6. PL spectra of (a) PPV heated at 120 and (b) CPPV120

The thermogravimetric analysis (TGA) of PPV (120°C, 8h) obtained three transitions at 233°C, 280°C and 440°C. The first transition at 243°C is related to the thermal elimination of diethyl sulphide and HCl and the second is due to the elimination of ethyl sulphide. The third thermal transition, seen at 440°C, is the result of the degradation reaction of PPV

TGA mainly serves as an analytical technique to quantify the amount of volatile or degradable organic matter (e.g. PPV in this study). In the PPV and CPPV120 samples, weight loss events were observed in the temperature range 32 to 500 °C. It is obvious from Fig.7 (a, b). The TGA results confirmed that organic sulfides and solvents were approximately eliminated and both PPV and CPPV120 were almost completely converted to the PPV. The TGA results also showed that CPPV120 has higher thermal stability, because after the thermal treatment the amount of residue for CPPV120 is higher than that of pristine PPV. These results show that PPV precursor intercalated into the layers of CdPS₃ is not only completely converted to PPV but its thermal stability is also enhanced. The decomposition for pure PPV film started from 233 °C and 80% of the polymer is lost at 550 °C, whereas the decomposition of CPPV120 started from 265 °C and only 40% of the polymer is lost upto 500°C.

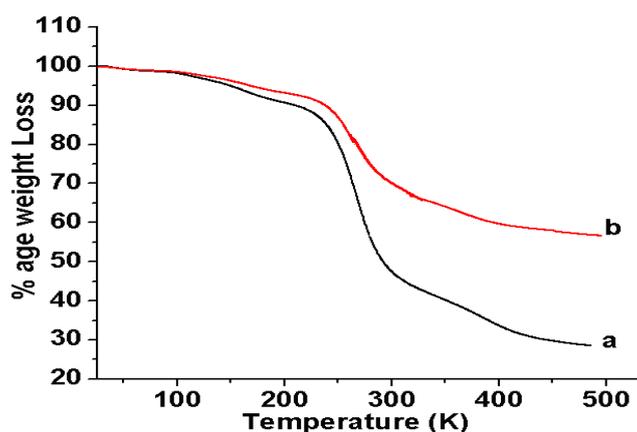


Fig. 7. TGA of (a) PPV heated at 120 °C under vacuum and (b) CdPS₃-PPV at 120°C under vacuum (CPPV120)

4. Conclusions

In this study PPV was successfully prepared and intercalated between the layers of CdPS₃. PPV was synthesized by chemical polymerization method. By this method, water soluble PPV precursor was obtained. These samples were investigated by using XRD, FT-IR, UV, PL and TGA techniques. Thermal analysis and FTIR data confirmed that polymer precursor intercalated in CdPS₃ were completely converted to poly (p-phenylenevinylene) PPV upon heating. Intercalation of K⁺, Eu⁺ and then PPV into the layers of CdPS₃ was confirmed by XRD. The TGA results showed that PPV intercalated in CdPS₃ heated at 120°C (CPPV120) was more thermal stability as compared to pristine PPV. FTIR spectra indicated that the intensity of the absorption band near 960 cm⁻¹ increases as the heat treatment temperature rises, which is due to the formation of the trans-vinylene unit on the polymer backbone.

The same trend was observed for PPV intercalated in CdPS₃ and heated at 120°C (CPPV120) sample which confirm the trans-vinylene unit in the intercalated PPV as well. To impart electrical conductivity to the insulating PPV, vapor doping technique was used. The samples showed the maximum conductivity of 1.81 X 10⁻⁴ S/cm for the PPV intercalated in CdPS₃ and heated at 120°C. The conductivity of completely converted PPV was observed in order of 10⁻⁷ S/cm which was increased by two orders of magnitude by doping. When the PPV is heated at different temperature its band gap decreases which in turn increases the conductivity. Appreciably high PL in PPV intercalated in CdPS₃ despite very small amount of PPV in the composite along with high conductivity and enhanced thermal stability suggest that these materials are promising candidates for LEDs and other opto-electronic devices.

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